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Green Technologies for Sustainable Water Management

Edited by

Huu Hao Ngo, Wenshan Guo,
Rao Y. Surampalli, and
Tian C. Zhang

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Green Technologies for Sustainable Water Management

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Sponsored by the
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Preface

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The consumption and degradation of our limited water resources has not only brought numerous challenges to our safe water supply but also various adverse impacts on the environment. These challenges and environmental problems are the main impetus for promoting green technologies to ensure our own well-being in the future as well as preserve the environment for a better tomorrow. Thus, in terms of sustainable water management, the main strategies are directed toward developing environmental-friendly, economically viable and energy effective treatment processes, which have higher removal efficiency of pollutants and possible nutrient recovery while enabling to reduce carbon footprint, minimize waste production and protect human and environmental health.

According to United Nations Environment Programme, "Green technology covers a broad area of production and consumption technologies. The adoption and use of green technologies involves the use of environmental technologies for monitoring and assessment, pollution prevention and control, resource and energy recovery, mitigation of climate change, and remediation and restoration."

Nowadays, increasing environmental awareness has driven new insights into the competing factors for water and wastewater treatment technology such as energy consumption, use of hazardous chemicals, health impacts, waste generation, sludge handling and disposal. The purpose of this book is to elucidate basic scientific principles and technological advances of current green technologies for sustainable water management. Solutions to pressing all concerned problems associated with energy optimization during wastewater treatment, the possibility of wastewater as a possible resource, health impacts of treatment technology due to the release of trace organic contaminants and prevention of surface water pollution, are presented in this book.

This 28-chapter book consists of three themes: 1) green technologies for water and wastewater management; 2) green technologies for pollution prevention/control and remediation/restoration; and 3) green technologies toward sustainable society. These three themes are linked by the central thread of sustainable water and wastewater management.

We hope that this book will be of interest to researchers, students, scientists, engineers, government officers, process managers and practicing professionals. As an excellent state-of-the-art reference material, the book will contain rich knowledge on the principles and provide them in-depth understanding and comprehensive information of current green technologies, their different environmental applications, recent advantages and disadvantages, critical analysis and modeling of the processes, and future perspective toward research directions and development.

The editors gratefully acknowledge the hard work and patience of all the authors who have contributed to this book. The views or opinions expressed in each chapter of this book are those of the authors and should not be construed as opinions of the organizations they work for.

Huu Hao Ngo, Wenshan Guo, Rao Y. Surampalli,
and Tian C. Zhang

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About the Editors

Dr. Huu Hao Ngo is a Professor in School of Civil and Environmental Engineering at the University of Technology Sydney (UTS), Australia. He received his Ph.D. in Environmental Engineering from UTS in 1995. His research involves wastewater treatment and reuse technologies, especially advanced biological waste treatment technologies (membrane bioreactor, specific attached and/or suspended growth bioreactors, biomass and biosorption), membrane technologies and physical-chemical separation technologies as pretreatment or post-treatment. His expertise and practical experience also covers solid waste management and desalination. Currently, his activities more focus on developing specific green technologies: water-waste-bioenergy nexus and greenhouse gas emission control. He is also an Honorary Professor/Adjunct Professor and International Chair Professor of numerous universities in China, Taiwan and Vietnam. He was awarded the fellowship of Australian Academy of Science (AAS) - Korean Science and Engineering Foundation, AAS - Science and Japan Society for the Promotion of Science, and AAS - French Embassy. He is a one of the founders of the Joint Membrane Bioreactor Centre (UTS, Tongji University and Tianjin Polytechnic University). Being a member of global professional societies (ACS, IWA, AWA, EDS), he is also a Council Member of International Forum on Industrial Bioprocess, Managing Committee Member of IWA Working Group on Alternative Water Resources (China), key member of the International Science & Technology Cooperation Center for Urban Alternative Water Resources Development, XAUAT and Advisory Committee Member of Tianjin Engineering Center of Biomass-derived Gas/Oil Technology. Ngo has published more than 300 peer-reviewed journal articles, 2 books and 19 book chapters. He is an Editor of *Bioresourse Technology, Elsevier* and also a founder and Editor in Chief of *Journal of Water Sustainability* while being editorial board member of numerous international journals such as *Science of the Total Environment*, Elsevier, *Environmental Nanotechnology, Monitoring and Management, Elsevier, Journal of Energy and Environmental Sustainability*, ISES etc.

Dr. Wenshen Guo is a Senior Lecturer in the Faculty of Engineering and Information Technology at University of Technology, Sydney (UTS). She received her Ph.D. in Environmental Engineering from UTS in 2005. After the completion of her 3-year UTS Chancellor's Postdoctoral Research Fellowship, she has been working at UTS since 2010. Dr. Guo teaches one postgraduate subject (Green technologies: Water-Waste-Energy Nexus) and two undergraduate subjects (Environmental and Sanitation Engineering and Pollution Control and Waste Management). Her research focuses on the innovative water and wastewater

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treatment and reuse technologies. Her expertise and practical experience cover the areas of water and wastewater engineering such as membrane technologies, advanced biological wastewater treatment technologies as well as environmental assessment and solid waste management. She is a one of the founders of the Joint Membrane Bioreactor Centre (UTS, Tongji University and Tianjin Polytechnic University). She is also the Life Membrane of International Forum on Industrial Bioprocesses (IFIBiop). Dr. Guo has published 155 journal papers and 10 book chapters since 2004. She has been the Guest Editor for *Bioresource Technology, Journal of Hazardous, Toxic and Radioactive Waste* and *Membrane Water Treatment*. She is currently serving as an Editor for *Journal of Water Sustainability* and Editorial Board Member of *Journal of Chemistry*.

Dr. Rao Y. Surampalli, P.E., Dist.M.ASCE, is President and Chief Executive Officer of the Global Institute for Energy, Environment and Sustainability. He was with the U.S. Environmental Protection Agency (USEPA) for 29 years and retired as an Engineer Director in October, 2014. He received his M.S. and Ph.D. degrees in Environmental Engineering from Oklahoma State University and Iowa State University, respectively. He is a Registered Professional Engineer in the branches of Civil and Environmental Engineering, and also a Board Certified Environmental Engineer (BCEE) of the American Academy of Environmental Engineers (AAEE) and a Diplomate of the American Academy of Water Resources Engineers (DWRE). He is an Adjunct Professor in seven universities and distinguished/honorary visiting professor in six universities. Currently, he serves, or has served on 66 national and international committees, review panels, or advisory boards including the ASCE National Committee on Energy, Environment and Water Policy. He also served as President of Civil Engineering Certification (CEC), Inc., that was started by ASCE for Board Certification of various specialties within civil engineering. He is a Distinguished Engineering Alumnus of both the Oklahoma State and Iowa State Universities, and is an elected Fellow of the American Association for the Advancement of Science, an elected Member of the European Academy of Sciences and Arts, an elected Member of the Russian Academy of Engineering, an elected Fellow of the Water Environment Federation and International Water Association, and a Distinguished Member of the American Society of Civil Engineers. He also is Editor-in-Chief of the ASCE Journal of Hazardous, Toxic and Radioactive Waste, past Vice-Chair of Editorial Board of Water Environment Research Journal, and serves on the editorial boards of 8 other refereed environmental journals. He has authored over 600 technical publications in journals and conference proceedings, including 15 patents, 16 books, 115 book chapters, 270 refereed journal articles, over 230 refereed national and international conference proceedings, and presented over 115 plenary/keynote or invited presentations worldwide.

Dr. Tian C. Zhang, P.E., D.WRE, BCEE, F.ASCE, A.EASA, F.AAAS is a Professor in the department of Civil Engineering at the University of Nebraska-Lincoln (UNL), USA. He received his Ph.D. in environmental engineering from the University of Cincinnati in 1994. He joined the UNL faculty in

August 1994. Professor Zhang teaches courses related to water/wastewater treatment, remediation of hazardous wastes, and non-point pollution control. Professor Zhang's research involves fundamentals and applications of nanotechnology and conventional technology for water, wastewater, and stormwater treatment and management, remediation of contaminated environments, and detection/control of emerging contaminants in the environment. Professor Zhang has published more than 95 peer-reviewed journal papers, 62 book chapters and 10 books since 1994. Professor Zhang is a member of the Water Environmental Federation (WEF), and the Association of Environmental Engineering and Science Professors (AEESP). Professor Zhang is a Diplomate of Water Resources Engineer (D.WRE) of the American Academy of Water Resources Engineers, and Board Certified Environmental Engineers (BCEE) of the American Academy of Environmental Engineers, Fellow of American Society of Civil Engineers (F. ASCE), Academician of European Academy of Sciences and Arts, and Fellow of American Association for the Advancement of Science (F.AAAS). Professor Zhang is the Associate Editor of *Journal of Environmental Engineering* (since 2007), *Journal of Hazardous, Toxic, and Radioactive Waste* (since 2006), and *Water Environment Research* (since 2008). He has been a registered professional engineer in Nebraska, USA since 2000.

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CHAPTER 1

Green Technologies for Sustainable Water Management: Introduction and Overview

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Wenshan Guo[2]
Zhuo Chen[3]
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Tian C. Zhang[5]

1.1 INTRODUCTION

Climate change, rapid development and population growth of many nations and the consequent rapid rise in levels of water consumption and contamination have raised concerns about the unsustainability of current water use patterns and supply systems. Specifically, the world population continues to expand with a growth rate of 1.2% each year, resulting in increased pressure on water quality, safety and health. Although the global amount of water is generally considered to be sufficient for the current population from the perspective of the total hydrologic cycle, world water resources are concentrated in certain areas, and severe water shortages are emerging in other places (Pimentel and Pimentel 2008). In addition to water deficits, improperly managed freshwater resource systems have triggered considerable water pollution. The problems are even worse in developing countries as they discharge approximately 90–95% of their untreated urban sewage directly into surface waters without rigorous water regulations (Pimentel et al. 2012). Therefore, to alleviate these existing situations, the awareness of environmental responsibilities should be strengthened (Tseng et al. 2013).

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The concept of sustainable water management generally involves the improvement of the health of surface water and groundwater systems, avoidance of over-extraction of freshwater supplies, identification of alternative water resources (e.g., rainwater, stormwater, desalinated water and recycled water), and implementation of environmental related policies and educational campaigns (NWC 2011). Faced with many challenges, the use of green technologies that encourage efficient forms of recycling and reuse is encouraged in the water industry. These include various innovations on water collection, treatment, distribution and drainage systems as well as enhanced approaches to management, assessment strategies, policies and regulations. After being successfully implemented, they can play crucial roles in enhancing sustainability, driving green growth and achieving a balance between economic, social and environmental factors while maintaining productivity, prosperity and efficiency (ATSE 2012).

This chapter presents the background, current development and future opportunities of green technologies and issues to facilitate the strategic planning of sustainable water management systems. The chapter is structured as follows: the first and second sections introduce the background and deal with fundamental concepts and demand analysis; the third section describes in detail the current and future applications of green technologies for sustainability improvement in water management; and the fourth section overviews the core ideas and key findings from each book chapter. The chapter concludes by discussing the appropriate approaches and policies in achieving sustainability objectives and promoting green design and supplies for water utilization.

1.2 FUNDAMENTALS

1.2.1 Concepts and Need Analysis of Sustainable Water Management

Achieving sustainable solutions to today's environmental problems requires long-term planning and actions. Sustainable management generally incorporates environmental, economic, social, and energy and resource sustainability (Dincer and Rosen 2005). Fig. 1.1 outlined these four essential factors impacting sustainable development and their interdependencies. Resource issues are particularly prevalent at present, and water management appears to provide one component of an effective sustainable solution. Specifically, the sustainable water management approach is to view all water systems as a whole, including drinking water, wastewater, rainwater, and stormwater drainage as a collective system that should be managed together to be truly efficient and sustainable, namely, integrated water management. In this approach, all water systems are looked upon as a positive resource in the environment with multiple supplies for use in many cases (Struck 2012).

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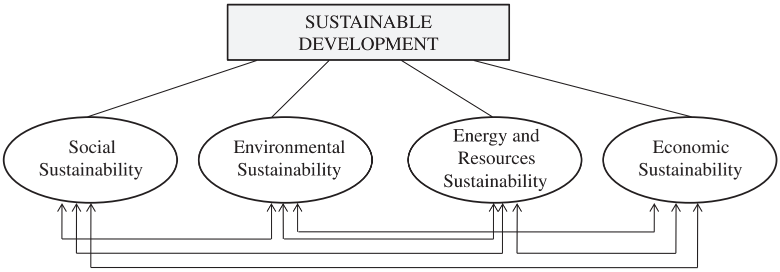

Figure 1.1. Factors affecting sustainable development and their interdependences
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Sustainable water management approaches have been increasingly applied to explore and analyze existing and future water-related issues, as well as to support water managers and decision-makers to put forward solutions for potential problems. They are of great necessity and importance as mismanagement is likely to impose significant constraints on exploitation and development and to affect the performance of water resource systems, including their effects on future water availability, water demand and water management strategies (Dong et al. 2013). The specific advantages of sustainable water management are presented as follows:

- **Solving problems.** Some water-related problems such as drought, flooding, groundwater over-extraction, water-borne diseases, land and water degradation, insufficient wastewater treatment, on-going damage to ecosystems, and escalating water conflicts in rural areas that might be intractable to conventional, single-sector approaches can be addressed by sustainable water management approaches. As such, issues could be identified holistically and solved effectively from multiple sectors without creating other troubles and complications.
- **Avoiding poor investments and expensive mistakes.** Decision-making based on short-term, segmented view would be rarely effective in the long-haul and can trigger unsustainable gains, unforeseen consequences and lost opportunities. Worse still, it is often the environment that has been sacrificed, together with negative consequences for both social and economic development. Comparatively, sustainable water management promotes the consideration of economic implications of infrastructure maintenance, water services and potential for cost-recovery, and both short- and long-term environmental impacts. This can avoid the losses and high costs associated with unsustainable development and irreparable harms.
- **Getting the most value from investments in infrastructure.** Sustainable water management can ensure maximum returns on investments from infrastructure planning, design and management both socially and economically. It facilitates the different investments working synergistically

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and producing greater returns than possible through a single-sector approach.

- **Allocating water strategically.** Sustainable water management can provide strong links among allocation decisions, national development and economic planning processes, using tools such as water pricing and tariffs, appropriate incentives and subsidies, and the removal of ill-considered incentives and subsidies both inside and outside the water sector. This could significantly contribute to the improvement of water use efficiency (GWP 2004).

To achieve sustainability, it involves the continuous reconciliation of water demand by the human environment with water supply by the natural system. Thus, depending on specific problems, it may also requires the consideration of land and water management, evapotranspiration, water quality and quantity, upstream and downstream water uses, and all stakeholders in the planning and management processes (GWP 2000). The uncertainties associated with climate, demographic, economic, social, technical and political conditions also need to consider. However, instead of trying to be comprehensive, the optimal water management should mainly focus on the key components and relationships accounting for the greatest variability in the system behavior. This would allow decision makers and water authorities to consider multiple factors and to deal with the complexity and interconnections within and between natural and human environments (Liu et al. 2008).

1.2.2 Concepts and Need Analysis of Green Technologies

Green technologies are technologies creating products and facilities that can improve economic productivity, conserve natural resources and limit adverse impacts on the environment and social wellbeing (Environmental Leader 2013). The concept of green technologies can be applied to the water management field to support the growth of new industries (e.g., new end uses of recycled water), bring technological innovations (e.g., state-of-the-art water treatment approaches) to water market and position the country to capture green growth opportunities. While the application of green technology could greatly harness economic opportunities by promoting productivity, prosperity and living standards, the strategies and innovations can also balance the other environmental, social and technical aspects, which would underpin sustainable water management into the future (ATSE 2012).

There is an urgent need to exploit and develop appropriate green technologies that promote design, production and supply chain because the major cause of water shortage and continued deterioration of the global environment is the unsustainable and unregulated pattern of consumption and production (Tseng et al. 2013). The limitations on the amount of freshwater consumption that can be taken from natural sources such as groundwater and surface water have forced the industry to expand the supplementary sources of water such as rainwater, stormwater, desalinated water and/or recycled water, which in most cases need

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extensive treatment before usage for health and environmental safety reasons. Apart from environmental drivers associated with water scarcity issues, to control water quality, many governments promote effluent discharge regulations and encourage the use of best available technologies to limit the allowable concentrations of certain contaminants in waste streams. Additionally, highly purified water is increasingly needed in industries (e.g., energy industry) that require technological solutions to fulfill their water needs (Frost and Sullivan 2010). For instance, the recycled water used as boiler's make-up water should be of very high quality, especially when the boiler is operated under high pressure. As wastewater containing impurities may lead to boiler corrosion, deposits, sludge formation, scaling, fouling and foaming, advanced treatment processes such as ultrafiltration (UF), reverse osmosis (RO), or ion exchange are often required. Likewise, only high-quality water can be adopted in electronics, food processing, chemical and pharmaceutical industries (U.S. EPA 2004; Chen et al. 2013).

To develop green technologies strategically, a comprehensive framework for managing water resources and prioritizing investment decisions is needed. Figure 1.2 shows the procedures and major considerations involved in the establishment of a full assessment framework. It consists of four phases, where phase 1 is the primary screening step to identify the prospects of new green technologies. To verify the feasibility of proposed technologies, Phase 2 starts with the consideration of particular evaluation criteria from five identified categories, including environmental, social, technical, economic and commercial aspects, and then applies the qualitative or quantitative approach for making a trade-off among different factors. Furthermore, phase 3 is to implement fit-for-purpose policies on green growth principles and shared responsibilities according to the analysis

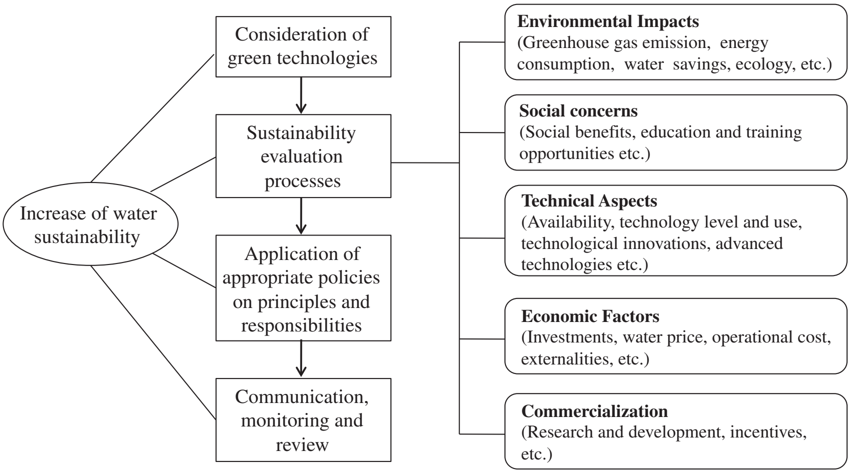

Figure 1.2. The comprehensive framework in the development of green technologies for sustainable water management

Source: Adapted from Dincer and Rosen (2005); reproduced with permission from Elsevier results. Finally, phase 4 is the management step that includes the communication, review and reporting so as to achieve community-wide acceptance and satisfying outcomes for water sustainability.

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1.3 CURRENT STATUS AND FUTURE PERSPECTIVES

1.3.1 Current Status, Key Drivers and Restraints

With respect to water collection and supply systems, water balance analysis becomes essential, as it determines the relationship between storage capacity, reuse demand, and reliability of supply. Particularly, the designs should be effective not only at the full capacity level, but also in reduced-service scenarios such as under non-optimal, supply-limited and unforeseen conditions. However, the over-reliance of supply-driven urban water supplies has been increasingly discovered and criticized, which are regarded as wasteful and expensive supply-side solutions. Thus, demand management should be implemented with a focus on measures that make better and efficient use of limited supplies. The specific definition of demand management is the adaptation and implementation of a strategy (policies and initiatives) by a water institution influencing water demand and water usage to meet objectives (such as economic efficiency, social development, social equity, environmental protection and political acceptability) so as to achieve sustainability of water supply and services (Vairavamoorthy et al. 2008). Table 1.1 lists a series of green technology opportunities proposed for different water resources under the demand management methodology. They are assessed across multiple green-growth and sustainability indicators covering environmental, economic and social impacts via a qualitative approach. Notably, a rigorous quantitative approach (e.g., cost-effectiveness analysis, triple-bottom-line analysis or multi-criteria analysis) should be utilized for a complete evaluation (ATSE 2012).

In terms of water treatment, as each source of water has its own characteristics and constituents, it requires different treatment levels and technologies for certain use purposes. For example, high pathogenic levels in water are likely to trigger health and environmental risks while chemical composition (e.g., ammonia, calcium, magnesium, silica and iron) may cause corrosion of pipes and machinery, scale formation, foaming, etc. Besides, physical parameters such as suspended solids, sand and grit can lead to solids deposition, fouling and blockages, whereas excessive nutrients may result in slime formation and microbial growth (DEC 2006). Thus, it is indispensable to understand all kinds of water sources and their characteristics for fit-for-purpose treatment and applications. A detailed discussion on specific green technologies for different water resources is presented as follows. As readily-available surface, ground and rain water require only minimal treatment, they are not discussed in detail.

Rainwater/stormwater. Rainwater generally has very good water quality even though it does contain some particulate matter from dust particles from the air.

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Table 1.1. Green technology opportunities for different water resources collection and supply

Water resources collection and supply	*Green technology opportunities*	*Water sustainability indicator*				
		Lower energy & resource demand	*Reduce waste & pollutant*	*Increase economic efficiency*	*Conserve natural assets*	*Promote social cohesion*
Surface water	• Improve understanding of surface water-groundwater connectivity and hydrological modeling	√			√	
	• Measure soil moisture in real-time for efficient water application in irrigation	√	√	√	√	
	• Control water conveyance systems in real time	√	√	√		
	• Intermittent water supply by physically cutting off the supply and limiting the consumers' ability	√	√		√	
Groundwater	• Ensure extraction is sustainable over time	√		√	√	
	• Expand managed aquifer recharge, storage and reuse		√	√	√	
	• Install low-energy high-efficiency pumping	√		√		

(Continued)

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Table 1.1. Green technology opportunities for different water resources collection and supply (Continued)

Water resources collection and supply	*Green technology opportunities*	*Water sustainability indicator*				
		Lower energy & resource demand	*Reduce waste & pollutant*	*Increase economic efficiency*	*Conserve natural assets*	*Promote social cohesion*
	• Recover energy through mini- and micro-hydroelectric generation	√		√		
Rainwater	• Install tanks in areas with suitable rainfall patterns				√	
	• Consider monolayer-based evaporation mitigation systems for reservoirs			√		
	• Improve climate and rainfall predictions and projections over multiple time scales			√		√
Stormwater	• Harvest stormwater (online or offline)		√		√	√
	• Reduce leakage from water assets	√	√	√		
Recycled water	• Recycle wastewater when there is a positive business care		√	√		
	• Deploy satellite and airborne sensors for early detection of water pollution		√			

Source: ATSE (2012); reproduced with permission from the Australian Academy of Technological Science and Engineering

Table 1.2. Water quality of harvested rainwater from various surfaces

Sample	*pH*	*Turbidity (NTU)*	*Conductivity (µSiemens)*	*Hardness (ppm CaCO$_3$)*	*TSS (ppm)*	*Coliform (CFU/mL)*
Metal Roof	5.97	1.3	12.4	0.5	3	100
Plumbing	6.89	0.5	17.1	6	6	>500
Cistern	8.91	2.4	735	10	9	3
Tap Water	7.32	0.3	77.1	24	2	0
Shingle Roof	5.94	8.3	455	41	6	>500
EWEB Range	7.5–7.8	0.02–0.04	45–65	18-25	<0.5	0

Source: Matt and Cohen (2001)

The level of total dissolved solids varies from region to region but is typically between 2 and 20 mg⁄l (Brown et al. 2005). The water quality of collected rainwater depends significantly on the surface from which the water is collected (Table 1.2). Stormwater typically contains material mobilized in its path of flow including litter, dust and soil, fertilizers and other nutrients, chemicals and pesticides, micro-organisms, metals, oils and grease, and thus, needs better management for non-point source pollution. However, management practices are different in different countries. For example, in the U.S., regulations for Municipal Separate Storm Sewer System (MS4) belongs to the Clean Water Act. A sector (e.g., a state's department of transportation) is required to manage its runoff pollution within its MS4 boundaries, such as 1) capture/treat the first 0.5 inches Water Quality Volume (WQV) that runs off of any new/redeveloped impervious area; and 2) implement 6 minimum Best Management Practices (BMPs) to reduce stormwater pollutant effluents to the Maximum Extent Practicable (MEP). However, so far, there is no water quality criterion linked with numeric limits.

- However, a treatment system for rainwater/stormwater harvesting and reuse needs to consider both stormwater quality criteria and treatment techniques to meet the end-use requirements and minimize public health and environmental risks. According to Table 1.3, the main aspects of water quality relevant to public health considerations specified in Australian guidelines are *Escherichia* coli concentration, turbidity, pH and chlorine residual. *Escherichia* coli is an important microbial quality indicator whereas turbidity and pH are important chemical indicators that may affect the efficiency of chlorine disinfection. However, specific stormwater quality criteria should be applied when considering the site-specific conditions of catchment areas (e.g., catchments with industrial land uses or significant sewer overflows) and different end-uses (e.g., residential uses, irrigation, industrial uses and aquifer storage and recovery) (DEC 2006; Asano et al. 2007).

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Table 1.3. Stormwater quality criteria for public health risk management in Australia

	Water quality criteria[1]		
Water indicators	*Level 1*	*Level 2*	*Level 3*
E. coli	<1 cfu/100 mL	<10 cfu/100 mL	<1000 cfu/100 mL
Turbidity	≤2 NTU	≤2 NTU	—
pH	6.5–8.5	6.5–8.5	6.5–8.5
Cl_2 residual	1 mg/L after 30 mins or equivalent level of pathogen reduction	1 mg/L after 30 mins or equivalent level of pathogen reduction	—
Applications	Reticulated non-potable residential uses (e.g., garden watering, toilet flushing and car washing)	Spray or drip irrigation of open spaces, parks and sports grounds (no access controls)	Spray or drip irrigation (controlled access) or subsurface irrigation of open spaces, parks and sports grounds
		Industrial uses: dust suppression, construction, site use (human exposure possible)	Industrial uses: dust suppression, construction, site use, process water (no human exposure)
		Ornamental water bodies (no access controls)	Ornamental water bodies (access controls)
		Fire-fighting	
Specific concerns for applications	Salt, nutrients, heavy metals, pesticides	Suspended solids, nutrient level: TP[2] (mg/L): 0.05 (long term); 0.8–12 (short term); TN[3] (mg/L): 5 (long term); 25–125 (short term)	

[1] Values are median for *Escherichia* coli, 24-hour median for turbidity and 90th percentile for pH; [2] Total phosphorus; [3] Total nitrogen

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As can be seen in Table 1.4, stormwater treatment measures can be generally grouped into three categories: primary, secondary and tertiary (CSIRO 2006; Begum et al. 2008; Blecken et al. 2010). The physical screening or rapid sedimentation techniques in the primary stage are mainly to retain gross pollutants and coarse sediments. Comparatively, secondary treatment involves applications of finer particle sedimentation and filtration techniques to remove fine particles and attached pollutants. Additionally, tertiary treatment aims to mitigate nutrients and heavy metal concentrations (Begum et al. 2008). For some schemes that require further pathogen removal, disinfection (e.g., UV light, chlorination or ozonation) and/or advanced treatment techniques (e.g., membrane filtration) should be employed at the end of the treatment train. While technologies designed for general stormwater pollution control are frequently utilized, more innovative technologies designed specifically for stormwater recycling together with new assessment technologies should be exploited to guarantee the necessary reliability of treatment and reuse. Several studies have retrofitted the conventional biofilters by introducing a submerged (partly anoxic) zone with an embedded carbon source. With this advanced technique, total nitrogen removal has been enhanced significantly due to improved denitrification (Dietz and Clausen 2006; Zinger et al. 2013). Li et al. (2012) further indicated that this approach could eliminate adverse effects of drying weather conditions on E. coli removal and achieve the recommended water quality for secondary contact recreational water use in relation to E. coli. Blecken et al. (2009) showed that the modified biofilter also exhibited positive impact on metal treatment, especially on the copper (Cu) removal. The presence of submerged zone and carbon source allows the outflow Cu concentrations to meet Swedish and Australian water quality guidelines.

Desalinated water. Desalinated water is relatively expensive to produce. Therefore, its efficient management from the inception of the water cycle at treatment plants to the reuse of treated effluent is of paramount importance. Figure 1.3 depicts management approaches to develop in terms of operational, technological and research aspects of desalinated water treatment and reuse. The RO membrane system is by far the dominant technology used primarily due to its lower cost in comparison to other technologies. To further reduce the cost of RO technology, modifications of the traditional RO process are being increasingly considered and employed, including i) the blending of existing technologies (e.g., multiple-effect distillation, multi-stage flash, and vapor compression) or innovative technologies (e.g., forward osmosis, membrane distillation, adsorption desalination, and microbial desalination cells), and ii) process optimization (e.g., more efficient pretrement, longer lasting membranes, more energy efficient pumps) (Zhang et al. 2012). The key drivers and prospective green technological developments in desalination plant treatment processes include:

1. Distillation processes, which cover: i) Scaling prevention techniques for film evaporation. Some existing technologies on the reduction of scaling on the

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Table 1.4. Stormwater treatment approaches and corresponding performances

Stormwater treatment techniques	*Catch. area (ha)*	*Pollutant trapping efficiency*						*Cleaning frequencies*	*Head needs*	*Initial costs*	*O & M costs*
		Gross	*Coarse sed.*	*Med. sed.*	*Fine sed.*	*Att.*	*Diss.*				
Primary treatment approaches											
Baffled pits	0.1–2	L	M	L/M	L	N	N	monthly	L	L/M	L/M
Circular settling tanks	1–20	L/M	H	M/H	M	L/M	N	monthly	L	H	M
Circular screens	5–150	VH	H	M	L/M	L	N	quarterly	L	H	M
Sediment settling basins	10–500	N	M/H	M	L	N/L	N	half-yearly	L	L/M	L/M
Green gully	—	H	L	L	L	N	N	monthly	L	L	L
Secondary treatment approaches											
Grass swales	0.1–5	L	M/H	M	L/M	L/M	L	—	L	L	L
Infiltration trenches	0.1–5	L	M/H	M	L/M	L/M	L	—	L	L	M/H
Infiltration basin	10–100	N	M/H	M	M	M	L	—	L	L/M	H
Extended detention basins	10–500	L	M/H	M	L/M	L/M	L	—	L	L/M	M/H
Sand filters	1–50	L	M/H	M/H	M	M	L	—	H	M/H	M/H
Tertiary treatment approaches											
Constructed wetlands	>10	L/M	H	M/H	L/M	M/H	L/M	10–13 yrs	L/M	H	M
Biofilters	—	L/M	H	M/H	M/H	M/H	M/H	—	L/M	H	M

Catch. = Catchment; Med. = Medium; Sed. = Sediment; Att. = Attached; Diss. = Dissolved; N-negligible; L-low; M-moderate; H-high; VH-very high
Source: CSIRO (2006); reproduced with permission from CSIRO

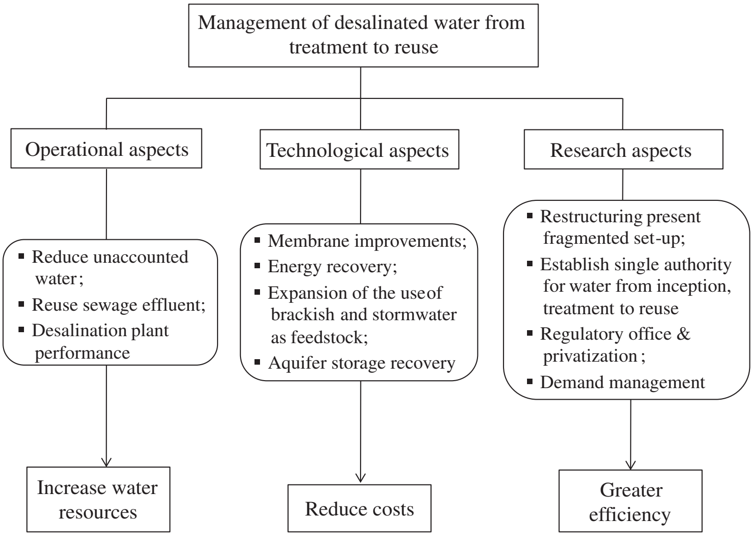

Figure 1.3. Elements of desalinated water management from treatment to reuse
Source: Adapted from Dabbagh (2001); reproduced with permission from Elsevier

Multistage Flash System (MSF) tube surfaces seem to lead to scale deposition being transferred into the flash chambers and causing blockage of the demisters. Apart from MSF, other thermal desalination technologies, such as multiple effect distillation (MED) with thermal vapor compression (TVC) and mechanical vapor compression (MVC) should be taken into account as well. They have become the most efficient distillation processes available in the market today in terms of energy consumption and water recovery ratio. As the systems are electrically driven, they are considered as clean and green processes with high reliability and simplicity for operation and maintenance. ii) Corrosion reduction. There is a need to develop alloys and other materials for moving and non-moving parts with corrosion resistance similar to those that have been recently developed but at more economical prices. iii) Computer modeling and capacity increase. The increase of plant capacity and utilization of modeling techniques to optimize the design, simulation, and operating conditions can provide desalinated water at a lower cost. iv) Heat transfer improvement. New alloys with higher heat transferability than those presently available could improve the efficiency of MSF drastically (Dabbagh 2001; DEP 2010).

2. Membrane processes, which cover: i) Membrane improvement. Disinfection of feed water prior to RO is essential to prevent biofouling of the membrane surfaces, which can inevitably lead to additional energy consumption and a loss of performance. Chlorine is by far one of the most cost-effective disinfection approaches for water treatment. However, since modern RO membranes are generally susceptible to chlorine damage, there is a demand

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for membrane improvement so as to tolerate biocidal concentrations of chlorine in continuous operation over several years. Graham-Rowe (2008) and Gunderson (2008) reported on newly developed nanocomposite membranes, which are thin-film composite membranes with the nano-structured material. When being applied, the benefits such as improved efficiency of extraction, reduced biofouling and maintenance costs by repelling impurities, reduced energy needs, and longer membrane life can be obtained. Alternatively, other biocides such as ozone may be advantageous in RO systems but have not been adequately studied. ii) Fouling and scaling mechanisms and control measures. A more fundamental understanding of fouling and scaling mechanisms and implementation of green control measures can result in lower operational cost and extended membrane life. The control measures include: fouling control by operating these membrane systems below critical flux, pretreatment of the feedwater, membrane backwashing and cleaning, and addition of carriers (e.g., zeolite, powdered activated carbon and sponge) (Ngo et al. 2013). iii) Seawater coagulation and filtration techniques. The removal of most organic suspended and colloidal matter in large seawater RO plants is usually carried out using conventional coagulation and filtration techniques. Thus, research into broader spectrum green coagulants might be of benefit and should be given more consideration. iv) Energy recovery devices. Improved efficiency in energy utilization could contribute to the reduction of desalination cost. Additionally, the use of alternative energy sources like waste heat, solar and/or geothermal can reduce the need for fossil fuel-based energy. For instance, energy-efficient pumps such as axial piston pressure exchanger pump and rotary-type energy-recovery device could not only lessen the costs but also improve the consistency of pressure (Gunderson 2008). v) Expansion of the use of brackish and stormwater as feedstock. Although seawater is the primary feedstock, brackish water and stormwater are potential starting materials for inland communities. vi) Aquifer storage recovery. The system involves the use of injection wells for underground storage of desalinated water in a suitable aquifer when the capacity of water supply facilities exceeds the demand, and its subsequent recovery from the same well to meet seasonal, peak, emergency or long-term demand. As this approach is low-cost, it can be developed to improve the use of water supply and water treatment facilities (Dabbagh 2001).

Table 1.5 presents some other recent innovations in desalination technologies. They are regarded as green approaches due to the reduced costs and lower adverse impacts to the environment. Additionally, co-location of desalination facilities at or near existing power plants or large municipal wastewater treatment plant (WWTP) can also substantially reduce the carbon footprints, environmental impacts and capital and/or operational costs through the use of existing intake and outfall structures and the blending of desalination brine and power plant heated effluents (DEP 2010).

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Table 1.5. Recent green innovations in desalination technologies

Desalination technology	*Key principles*	*Recent innovations*	*Advantages*
Forward osmosis	1. Use a high concentration of a chemical to draw the water molecules through the membrane, leaving salts behind; 2. Separate the chemical from water by heating; 3. Reuse the chemical in process	1. New chemical compounds to drive process; 2. New membrane; 3. Use waste heat to drive the separation	1. Lower energy usage; 2. High feed water recovery; 3. Reduced brine discharge
Clathrate desalination	1. Trap water molecules in carbon dioxide molecules; 2. Pressure water molecules into a Clathrate crystal; 3. Break down the crystal to release the water molecules	1. Increase the size of the crystal; 2. Reduce the energy demand	1. Operates at low pressures; 2. Suitable for all qualities of water sources
Dewvaporation	1. Humidify a stream of heated air by running a stream of saline water on a heated surface; 2. Collect the condensate as product water when the saturated air is moved along condensing heat transfer films	Newer energy sources such as waste heat and/or solar	1. Energy efficient - uses recycled energy; 2. Inexpensive to manufacture; 3. Passive-lower O&M; 4. Suitable for all qualities of water sources
Freeze desalination	1. Use the phase shift of water from liquid to solid to exclude the salt from the ice crystals; 2. Melt the crystals to produce freshwater	1. Washing of salts; 2. Use of density gradients	1. Improved energy efficiency compared to distillation processes; 2. Minimal potential for corrosion; 3. Little scaling or precipitation

Source: CSIRO (2006); reproduced with permission from CSIRO

Recycled water. To ensure safe and reliable water reuse, green technologies that require less non-renewable energy sources, higher level of energy and nutrient recovery, reduced consumption of hazardous chemicals and enhanced removal of contaminants should be given more attention in the WWTP design and operation (Lofrano 2012).

1. Fit-for-purpose treatment. The adoption of fit-for-purpose treatment methods allows the prioritized identification of hazards and enables the targeted pollutants to be removed efficiently and cost-effectively. As for greywater, it includes water from household kitchen sinks, dishwashers, showers, baths, hand basins, and laundry, but excludes any input from toilets. Hence, compared with municipal and industrial sources, it is less polluted and low in contaminating pathogens, nitrogen, suspended solids and turbidity. Regarding the current treatment methods, physical (e.g., coarse sand, soil filtration, microfiltration (MF), and UF) and chemical (e.g., coagulation, photocatalytic oxidation, ion exchange and granular activated carbon) treatments are suitable to treat low strength greywater (e.g., laundry and showering wastewaters) for either restricted or unrestricted non-potable uses under safe conditions. These treatment technologies are widely used in small-scale residences, which are able to reduce 30–35% of freshwater consumption. While for medium and high-strength greywater (e.g., kitchen wastewater), additional biological treatment processes such as sequencing batch reactor (SBR), constructed wetland (CW), or membrane bioreactor (MBR) are often used to remove biodegradable organic substances (Chen et al. 2013). The applications of treated greywater include toilet flushing, garden irrigation, recreational impoundments watering and clothes washing (Zhang et al. 2012).

Municipal wastewater often contains a broad spectrum of contaminants such as organic matters, pathogens and inorganic particles, which can be potential risks to human health and the environment. Particularly, some inorganic chemical pollutants (e.g., sodium, potassium, calcium, chloride, bromide, and trace heavy metals) are of concern in agricultural and landscape irrigation, as highly saline irrigation water can severely degrade the soil and the accumulation of heavy metals in soil can pose threats to the food chain. Furthermore, when considering the recycled water for potable reuse schemes, the trace organic pollutants such as pharmaceutical active compounds (PhACs) and endocrine disrupting compounds (EDCs) are important parameters that are likely to trigger adverse biological effects to health at part per trillion concentrations (Weber et al. 2006; Bhandari et al. 2009). Besides, from microbiological aspects, the main pollution groups are excreted organisms and pathogens from human and animal origins, where enteric viruses and protozoan pathogens are significantly more infectious than other bacterial pathogens. In terms of treatment approaches, membrane filtration has received considerable attention as it is capable of removing not only suspended solids and organic compounds but also inorganic contaminants such as heavy metals in wastewater through physical means. Depending on the pore size of the

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semi-permeable membrane, membrane technologies include MF, UF, nanofiltration (NF), and RO. MF membranes have the largest pore size (0.05–2 μm) and typically reject suspended particles, colloids, and bacteria. UF (<0.1 μm) and NF (2 nm) membranes have smaller pores, which can remove natural organic matter/ soluble macromolecules and dissociated acids/sugars/pharmaceuticals/divalent ions, respectively. RO membranes (0.1 nm) are effectively nonporous and retain even many low molar mass solutes as water permeates through the membrane (ASTM 2010).

Comparatively, the composition of industrial wastewater varies considerably owing to different industrial activities. Even within a single type of industry, specific processes and chemicals used to produce similar products can differ, which leads to significant changes in wastewater characteristics over time. Generally, wastewaters from food processing industries (e.g., potato, olive oil, and meat processing) are contaminated with high levels of biological oxygen demand (BOD), chemical oxygen demand (COD), oil and grease, total suspended solids (TSS), nitrogen, and phosphorous. By contrast, industrial wastewaters (e.g., chemical and pharmaceutical producing, paper, textile, tannery, and metal working and refinery wastewaters) might be rich in heavy metals (e.g., Cd, Cr, Cu, Ni, As, Pb, and Zn) and other toxic substances. As for the existing treatment methods, MBR is proved to be effective, especially in removing low biodegradable pharmaceutical compounds whereas CW can be considered as a relatively low-cost option but requires large space for treatment. Apart from membrane filtration technologies, Barakat (2010) reported the effectiveness of employing new adsorbents in treating heavy metal-contaminated wastewater. Especially, the use of biological material (e.g., bacteria, algae, yeasts, fungi or natural agricultural by-products) as biosorbent has received a great deal of interest because of the higher removal efficiency and relatively lower cost, compared to conventional methods such as precipitation and ion exchange (Wang and Chen 2009).

2. Capture of treatment side- or by-products. Green technologies that collect treatment byproducts (e.g., biogas, heat, steam and biosolids) and convert them into resources for local use would be an essential part of wastewater treatment systems (Tyagi et al. 2009; Khanal et al. 2010; Struck 2012). Presently, some wastewater treatment facilities have already incorporated anaerobic digesters, where energy-rich waste materials and biosolids (e.g., fats, oils, grease, food scraps, yard trimmings, applicable construction and/or destruction debris) can be converted into biogas, a methane-rich byproduct that is usable for energy generation. If additional organic waste streams are diverted to these facilities (e.g., food waste from landfills), even greater efficiencies and energy potential can be attained. Co-digestion technology has at least three times the methane production potential (e.g., biogas) of biosolids and manure. Remarkably, anaerobic digesters lead to environmental benefits from methane capture, greenhouse gas reduction, renewable energy generation, and organic waste volume reduction (Khanal et al. 2010). Other benefits include reduced operational costs associated with

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energy consumption, waste disposal, and existing infrastructure and expertise savings as well as economic benefits and opportunities from processing additional waste streams. To harness the energy contained in biogas, the gas can be cleaned, compressed and burned in a boiler, generating heat for maintaining digester temperatures and onsite heating. The produced biogas can also be used as a source of energy similar to natural gas and applied to maintain facility temperatures, pumps, electrical systems, and other energy needs. The excess methane can be captured and supplied to local power companies for external purposes. In California, US, there are almost 140 wastewater treatment facilities that utilize anaerobic digesters, with an estimated excess capacity of 15–30% (U.S. EPA 2013). Besides, Lofrano (2012) pointed out the application of chemically assisted primary sedimentation, which consists of adding chemicals such as chitosan and other organic coagulants to increase the coagulation, flocculation and sedimentation of raw wastewater. This can contribute to increased sludge and biogas production and then reduced energy consumption.

Additionally, combined heat and power (CHP) systems, of which the concept is to use a single fuel for the production of electricity and heat and recover the waste heat from electricity generation for productive use, have received considerable attention. The five typically-considered CHP types are: gas turbines, microturbines, steam turbines, reciprocating engines and fuel cells, each with different benefits and challenges (Wong et al. 2015). CHP system can be operated in conjunction with anaerobic digesters to accomplish optimal performance. Moreover, if incineration is used, insulators and heat collectors could also be employed to capture heat/stream to convert to energy (Wong 2011). Furthermore, nutrient recovery can be gained through the beneficial reuse of biosolids in sludge treatment processes of WWTP. When properly treated, biosolids can be rich soil conditioners that contain essential nutrients (nitrogen and phosphorous, trace minerals, carbon, etc.) and provide a significant enhancement in soil water-holding capacity. These qualities can significantly improve crop growth and yields, reduce the use of chemical fertilizers, and allow communities to balance needs for sanitation and public health protection with environmentally sound methods (WERF 2010).

3. Optimization of processes in WWTP. To arrive at a sustainable utility, it is indispensable to look for strategies where water management and energy use are assessed jointly. Hence, a number of considerations should be integrated into the design and planning processes. Several studies have evaluated competing influential factors, with a focus on environmental influences. For example, Ortiz et al. (2007) used a processed-based Life Cycle Assessment (LCA) in comparing four wastewater treatment scenarios, including Conventional Activated Sludge System (CAS), CAS-UF, external MBR and immersed MBR. The construction, operation and dismantlement phases of the plant were considered in the system boundary, and the airborne

emissions were of prime concern. The results indicated an overall lower environmental impact in CAS, followed by immersed MBR and external MBR. Additionally, when combining the treatment technologies with electricity production models, CAS with hydroelectric consumption model demonstrated the lowest impact as renewable energies are much more environmental friendly in electricity production compared with fossil fuels and nuclear resources. Furthermore, CAS produced high effluent quality, which not only allowed the water to be safely reused in irrigation but also enabled other applications such as groundwater recharge, household, and industrial uses. Thus, considering both environmental impact and water quality, immersed MBR coupled with the renewable energy consumption pattern was optimal. Nevertheless, this study did not take into account the environmental impacts on soil and water nor consider the toxic and health effects.

Moreover, Zhang et al. (2010) have adopted a hybrid LCA model to measure the life cycle benefit of treated water reuse in industrial and domestic applications as well as the corresponding life cycle energy consumption in the construction, operation and demolishment phases of the WWTP in Xi'an, China. The study quantified environmental impacts of different treatment stages as equivalent energy consumption. It indicated that energy consumption in operating tertiary treatment (2065.28×10^9 kJ) can be significantly compensated by life cycle benefit of water reuse in terms of reduced wastewater discharge (74.2×10^9 kJ) and freshwater saving (1598.4×10^9 kJ). Although this study successfully linked the life cycle energy consumption with direct benefits of recycled water reuse (e.g., wastewater reduction and freshwater saving), other indirect benefits such as ecosystem protection and water cycle improvement were not considered (Chen et al. 2012).

4. Localized and networked treatment systems. The emerging use of localized treated nodes interlinked into a network allows water to be stored and used close to its source. It also increases the community's ability to respond to changes in demand and supply, improves capital efficiency and disaster resiliency, reduces impacts on natural systems, and has the potential to complement and be enhanced by the growing use of onsite energy generation systems (Slaughter 2010).

Regarding the water distribution, consumption and disposal systems, a principle target is to improve the water efficiency while minimize unnecessary water losses. For distribution systems, measures can be good solutions in increasing economic efficiency but lowering energy and resource demand, such as: i) decentralized treatment and distribution centers; ii) extended asset life through the adoption of new technology; iii) conversion of distribution systems into intelligent networks; and iv) development of smart inexpensive monitoring of asset condition. When it comes to consumption systems, the green technological opportunities exist in the exploitation of new recycled water end uses, adoption of

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water and energy efficient appliances, adjustment of water prices and improvement of water efficiency, etc.

Particularly, to enhance the water and energy efficiency, in Australia, the state of New South Wales (NSW) has introduced the building sustainability index (BASIX) scheme for residential buildings. BASIX mandates that the amount of water consumed in most new residential dwelling should be 40% less than that of an average residential dwelling. The initial energy target for BASIX was set at a 25% reduction in greenhouse gas emissions compared to an average dwelling. In 2006, the energy target increased to 40% for most new homes. The regulations have forced the increasing considerations on dual flush toilets, water saving and flow regulation devices in shower heads, washing machines and dishwashers in many households. Similarly, in Western Australia, it is imperative to use pool covers for new pools and spas under the Smart Approved WaterMark scheme (AWA 2012). The strengths of these different aspects for water sustainability are discussed in Table 1.6 in detail.

Furthermore, since water drainage and disposal systems (e.g., open drainage corridors, wetlands and small ponds) are becoming more visible in the urban environment, the prime green development objectives are to optimize the design of sustainable drainage facilities, minimize effluent volumes transported to treatment plants and target releases as environmental flows. In addition, many of the storage systems can potentially offer locations for urban rooftop or similar gardens, creating small but centralized sources of locally grown food. These systems can be operated on a more distributed fashion, where appropriate, with small systems servicing smaller areas and centralized systems serving larger urban and suburban needs (ATSE 2012; Struck 2012).

Nonetheless, a key restraint for establishment and implementation of green technologies in water sectors is that water can no longer be viewed in isolation by one institution or any one group of professionals without explicit and simultaneous consideration of other related sectors and issues. Currently, water issues have become large, complex, and interconnected with other resources like renewable energies and natural ecosystems, with development sectors like agriculture, industry, transportation and communication, and with social sectors like education, health, and rural or regional development. They are also closely related to economic, environmental, legal and political factors at local, national and international scales. Consequently, water policies and major water-related issues should be assessed, analyzed, reviewed and resolved within an overall societal and development context. Otherwise, the main objectives of sustainable water management, such as improved standard and quality of life, poverty alleviation, regional and equitable income distribution, and environmental conservation could hardly be achieved (Biswas 2004). However, current failures in managing many water systems have pushed the local areas beyond their sustainable limits. For instance, some of the schemes sought to achieve considerable environmental savings through maximized water efficiency regardless of utility, economic feasibility and geographical conditions whereas other water activities that have

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Table 1.6. Green technology opportunities in water consumption systems

Green technology opportunities	*Water sustainability indicator*				
	Lower E&R demand	*Reduce waste & pollutant*	*Increase economic efficiency*	*Conserve natural assets*	*Promote social cohesion*
Expand use of recycled water for non-potable and potable supplies	√	√		√	
Encourage the use of water-efficient appliances (e.g., showerheads, washing machines and dishwashers)	√	√	√	√	
Install energy-efficient water appliances, especially in water heating	√		√		
Recovery and reuse waste heat	√	√	√		
Embrace new technology of cost effective metering of individual apartments	√		√		
Move to cost-reflective water pricing	√		√	√	
Include negative externalities such as pollution and environmental degradation in water pricing		√	√	√	√
Improve water efficiency in urban irrigation techniques and industrial processes	√	√	√	√	
Provide real-time feedback on water consumption to users	√		√		√

E&R = energy & resource

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political or financial underpinnings might trigger the degradation of ecological habitats in the long run (Chapagain and Orr 2009).

In addition, Lambooy (2011) pointed out that some green strategies for sustainable water management that encourage the reduction of fossil fuel consumption and greenhouse gas emissions by the deployment of white biotechnology (i.e. agricultural products) can come into conflict with other environmental targets. It was shown that the increased biomass for industrial usage and biofuel production would require the use of additional land and water. For example, the manufacture of one liter of bio-ethanol requires 4 L of process water, whereas the growth of the necessary sugar cane calls for approximately 1000 L. This could bring nature, food, industry and biofuels into competition. Therefore, special attention needs to be paid to the potential impact of the availability of water for industrial white biotechnology. To ensure the long-term regional development, a comprehensive and systematic assessment in water use planning is essential for determination of the trade-off among a variety of issues (e.g., ambient ecosystem, engineering feasibility, cost, energy consumption, water pricing, community attitudes, etc.). Moreover, water use guidelines and regulations towards specific end uses as well as considerable national or local reports on water quality and risk control should also be established. These actions would undoubtedly standardize the treatment level, improve the reliability and enhance the public acceptance (Chen et al. 2012).

1.3.2 Future Research Opportunities and Challenges

The current and the foreseeable trends indicate that water related issues will continue to become complex and will be more and more intertwined with other sectors in the future. The main trends and future research needs are described as follows:

1. Formulation of water management policies. There is an urgent need to develop and apply appropriate policies that promote green design, supply and production, worker health and safety, and consumer protection and sustainable water management should be strengthened in the direction of holistic resource governance. Table 1.7 summarizes the key aspects of the management and administrative systems for governing and delivering water sources at different levels of society (GWP 2004).
2. Integrated water management. The integrated water management has been addressed as this approach involves explicit considerations of source separation, solids treatment, waste management, liquids treatment, etc. Surrounding factors like air, amenities, energy, solid waste, transportation and urban development would also be taken into account. This allows the capture of added aesthetic, ecological, economic, energy production and conservation, recreational, social, and other benefits in ways that have never been realized before (Struck 2012).
3. Reduction of water losses. This includes the reduced evaporation losses from reservoirs, reduced leakage from distribution systems, and more

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Table 1.7. Key areas for water resource governance and delivery

Water governance	*Key aspects*
Management categories	
Water resources assessment	Understanding of different water resources and needs
Plans for integrated water management	Combination of development options, resource use and human interaction
Demand management	Use of water more efficiently
Social change instruments	Encouragement of a water-oriented civil society
Conflict resolution	Management of disputes and guarantee of sharing of water
Regulatory instruments	Allocation and water use limits
Economic instruments	Water value and prices for efficiency and equity
Information management and exchange	Improvement of knowledge for better water management
Administrative roles	
Policies and plans	Set of goals for water use, protection and conservation
Legislative framework	The rules to follow to achieve policies and goals
Organizational framework	Forms and functions
Financing and incentive structures	Allocation of financial resources to meet water needs
Institutional capacity building	Development of human resources

Reference: Gallego-Ayala and Juízo (2011); reproduced with permission from Elsevier

effective management of surface and groundwater reservoirs (Shamir and Howard 2012). The greater use of water and energy efficient products has also been highlighted. In Australia, by conducting the Water Efficiency Labeling and Standard scheme, it is estimated that by 2021, the domestic water consumption will be decreased by 100,000 megalitres each year. The total greenhouse gas output will be reduced by 400,000 tonnes each year, which is equivalent to taking 90,000 cars off the road. The major savings would come from showerheads, washing machines and toilets (AG 2013).

4. Monitoring. High-advanced monitoring technologies such as remote sensing that provide diagnostic measurements even in data sparse regions are being used to detect changes in soil moisture, water stored in snow, river and lake levels. New sensors, algorithms and improved near-real-time estimates

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will be proficient in providing more accurate and efficient for controlling systems that manage floods, predict droughts and distribute water to fields and cities (Shamir and Howard 2012).

5. Point-of-use water treatment technologies. There are opportunities to advance in point-of-use water treatment technologies in conjunction with stringent water quality guidelines. These range from simple, decentralized and cluster water treatment systems for rural and peri-urban areas to RO and UV-based systems that can be used in homes, public buildings, restaurants and mass feeding establishments (Shamir and Howard 2012).
6. Assessment tools and models to support decision-making. Another focus is to provide a comprehensive means to evaluate current resource recovery technologies and identify the next markets and value added products (WERF 2010). The assessment tool should assemble data in a manner that enables water to be managed effectively and guarantee the performance of one region to be accurately compared with other regions (Young 2013). As the descriptive results are unconvincing to some extent, there is a need for a quantitative assessment with respect to technical, economic, environmental and social considerations. The adoption of Multi-Criteria Analysis (MCA) is recommended which is to investigate the tradeoffs among the selected multiple conflicting criteria and then obtain rankings of different management alternatives under certain mathematical algorithms. From the computerized MCA simulation, the least preferred management options could be quickly eliminated whereas the superior alternatives can be further discussed. This can provide a powerful guidance for sustainable water management in the long term as it is possible to suggest how much a successful strategy could benefit the decision maker in exploitation, planning, development and expansion stages of water resources. With these highly persuasive data, the public acceptability and trust on green growth principles of water applications, as well as public shared responsibilities can also be greatly improved, which in turn further accelerate the booming of potential water markets (Chen et al. 2014). Other improved models could be developed for supply and flooding forecasting and for chemistry and biology in rivers, water bodies, groundwater, wetlands and other ecological systems (Shamir and Howard 2012).

1.4 BOOK OVERVIEW

As the primary objective of this book is to elucidate basic scientific principles and technological advances of current green technologies for sustainable water management, this 28-chapter book is divided into three themes: I) green technologies for water and wastewater management (Chapters 2–5); II) green technologies for pollution prevention/control and remediation/restoration (Chapters 6–20); and III) green technologies toward sustainable society (Chapters 21–28).

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Chapter 2 describes rainwater harvesting used to augment water supplies in urban and low populated areas in Australia. Typical water quality measurements of rainwater from various locations in terms of physical, chemical, biological and organic characteristics are explained. Potable purposes are assessed and compared against the Australian Drinking Water Guidelines (ADWG), including the influence of first flush volumes on the water quality in the rainwater tank. Moreover, treatment technology for rainwater is assessed using long term pilot scale.

Chapter 3 discusses stormwater treatment technology for water reuse, indicating stormwater for harvesting and reuse purposes should be assessed primarily for nutrients, physical properties, bacteriological properties, heavy metals, organic matter since it is more unlikely to meet these water parameters. Typical water quality measurements of stormwater from various locations in terms of physical, chemical, biological and organic characteristics are compared against reuse and drinking water standards. Conventional technology for treating stormwater is also critically reviewed in terms of its treatment ability for reuse.

As groundwater is an important component of the global water cycle and is also a resource of vital socio-economic importance, Chapter 4 summarizes the critical policy for its sustainable management in a changing climate and modern satellite technologies allowing the measurement of groundwater volumes available for water supply, irrigation and environment. The changing availability of groundwater on food security and ecosystems is examined within the framework of risk management. In addition, the risk to groundwater resources from coal mining, coal bed methane and shale gas production also poses policy challenges to sustainable resource management.

Chapter 5 discusses the concepts of district water cycle management which follows the nature's example of a hydrological water cycle. The fundamental methods for water cycle analyses are proposed based on the water budget and materials balance relationships following a series of conceptual models. For a district water cycle with a partially closed loop of reclaimed water, prevention of pollutants accumulation in the water cycle becomes the basic requirement of system design. This needs a selection of technologies for pollutants removal in wastewater treatment and reclamation, prevention of water quality deterioration during reclaimed water storage, and enhancement of natural purification in the water cycle. A real case is introduced in this chapter as an example of application of the district water cycle management principles. By reclaiming all collectable wastewaters in a university campus and use the reclaimed water for all non-potable water uses, the efficiency of water utilization is doubled.

Chapter 6 first introduces the concepts and major categories of green and sustainable natural wastewater treatment systems, and then focuses on a few selected systems, including lagoon treatment systems, wetlands and aquifer treatment systems as well as anaerobic treatment systems with suitable case studies being discussed. Mechanism of pollutant removal in each system is described in detail; prototypes of different systems used along with their potential problems in operation are listed. The chapter concludes with the strategies used to

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implement these sustainable green and nature wastewater treatment systems along with future trends and brief conclusions.

Advanced anaerobic processes integrating granular sludge are emerging technologies for efficient wastewater treatment. Chapter 7 reviews current research work encompassing salient features which include merits and limitations of anaerobic granulation. In comparison with aerobic processes, major advantages of treatment by anaerobic granular sludge systems are discussed. Energy production and assessment associated with anaerobic granulation are delineated in the perspective of water-energy nexus. Additionally, anaerobic reactor systems integrating granular sludge for waste degradation and the prospects of anaerobic granulation are also outlined.

Chapter 8 provides a thorough discussion of the recent trends in bioconversion of sludge to value added products, namely, polyhydroxyalkanoates (PHA) production, Bacillus thuringiensis (Bt) based bio-pesticides production/formulations, vermicomposting biotechnology, and production of different enzymes. The emerging value-added products are at different levels of production, facing challenges in terms of process conditions, yield, scale-up or formulation. The wastewater sludge could be used as a potential source for isolation of microorganisms, and can be a very good carbon source of many microbial possesses that could add value to sludge by producing valuable metabolic products.

Chapter 9 offers an overview of the fundamentals and applications of anaerobic wastewater treatment processes. The features like resistance to toxicity, production of biogas, less accumulation of biomass and no requirement of aeration make the use of anaerobic microbes to remove contaminants from wastewater with an effective and industrially feasible manner. This chapter also gives an insight into the effects of various environmental/physico-chemical parameters, the different types of anaerobic treatment processes based on mode of microbial growth, the different types of reactors associated with anaerobic treatment processes, and the process kinetics using different kinetic models.

Constructed wetlands (CWs) are sustainable systems, and they have been designed as a widely accepted technology available to deal with various kinds of wastewater for nearly 40 years. Chapter 10 provides an extensive overview of present studies about the sustainable design, operation and maintenance of CWs, including plant selection (plant adaptability, plant tolerance and pollutants removal capacity), enhancing techniques (artificial aeration, intermittent operation and CWs combination, etc.) and plant reclamation and recycling.

Chapter 11 reviews on-site technologies ranging from simple septic tank followed by land filtration to high-tech membrane-filtration systems or sophisticated yet elegant designed ecosystems, such as constructed wetlands, for treating wastewater. These processes can be made flexible to accommodate specific nutrient removal processes offering advantage both technically and economically. This chapter also describes the evolution and evaluation of onsite technologies, the factors affecting their performance and case studies of on-site wastewater treatment systems.

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Chapter 12 focuses on anaerobic ammonium oxidation (Anammox), a recently identified short-cut biological method to convert ammonium nitrogen to nitrogen gas using nitrite as electron acceptor, which seems to be more promising than conventional nitrification-denitrification method in terms of its efficiency, low cost and eco-friendly nature. This Chapter presents a bibliographic review of historical developments in anammox process, the microbial physiology and growth requirements of anammox bacteria, combination of anammox with partial nitrification and/or denitrification, potential inhibitors of anammox process, reactor systems used for the cultivation of anammox bacteria and applications of anammox and its related processes to treat nitrogen rich wastewaters.

The industrialization development has delivered a number of anionic species as well as anionic metal complexes into ecosystems, which have received increasing concerns of environmental and human health risks. Chapter 13 provides the current state of research on the preparation and utilization of biomass materials as biomass based activated carbons and anion-exchange/chelating resins for removal of these anions. The adsorption as well as recovery capacities of the biomass adsorbents are also summarized. It is evident that these biomass-based adsorbents show comparable adsorption capacities for the removal of various anions as those of commercial adsorbents, making the biomass materials promising for the development of technically and economically feasible technology for removal anionic pollutants.

Chapter 14 concerns about P removal/ recovery from wastewater due to surface water quality deterioration and P rock reserves depletion. This chapter focuses on both fundamental and applied aspects of this practice using agricultural by-products based biosorbents (AWBs). Insights into adsorption and desorption mechanisms, the roles of process parameters, the adsorption performance of AWBs the drivers, technologies and barriers for P recovery, as well as the criteria for selecting potential AWBs are comprehensively discussed. Although P removal by AWBs has gained significant achievements, P recovery using AWBs still remains a challenge due to this practice is in its initial stage of development. Despite difficulties that currently exist, enormous environmental and economic benefits make this practice a promising green technology.

Chapter 15 is about treating trace organic contaminants (TrOCs) that can impose a range of possible acute and chronic toxicity effects on living organisms including human beings. When deployed on an individual basis, even the advanced treatment processes exhibit some inherent drawbacks and do not offer a complete barrier to a broad range of TrOCs that may occur in municipal wastewater. In this connection, the concept of combined processes such as coupling of membrane bioreactor (MBR) with high retention membranes, activated carbon adsorption or advanced oxidation processes has been tested with encouraging results. This chapter demonstrates the potential benefits of combined systems having MBR at the core to treat the wide varieties of TrOCs from wastewater.

Chapter 16 principally deals with the occurrences, usages, current regulations and disposal methods of heavy metals. Four heavy metals namely arsenic,

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chromium, lead and mercury are chosen and their environmental and health impacts due to their pollution are discussed. Further different physico-chemical remediation technologies namely chemical precipitation, ion exchange, adsorption, membrane filtration and coagulation/flocculation are reviewed. The upcoming green remediation technologies towards the future of sustainable water management, such as biosorption, biostimulation, bioaugmentation, bioleaching, biosurfactants, bioprecipitation, vermicomposting and phytoremediation, are also appraised.

Chapter 17 highlights surfactant-based separation techniques, namely micellar enhanced ultrafiltration (MEUF), in which solubilization of organic compounds into the non-polar interior of a micelle occurs. Activated carbon fibre (ACF) has a uniform micro-pore structure, faster adsorption kinetics and a lower pressure drop compared to the conventional adsorption process. MEUF process alone can remove heavy metals to certain extent, and its efficiency is further enhanced by the integrated approach of using the adsorbent like ACF. As the MEUF process generates the surfactant-rich effluent which is a major bottleneck of this process, adsorption technology using ACF as adsorbent can be the remedial measure to overcome this problem. MEUF-ACF hybrid process can be the best alternative to combat the burning issue of heavy metals.

Chapter 18 offers an innovative solution to tackle the challenging issues of membrane fouling and high operating cost of traditional electrochemical oxidation by using electrocatalytic membrane reactor (ECMR) that integrates electrochemical oxidation and membrane separation into a single processing step. The effects of main operating parameters include current density, residence time, pH and temperature and their mutual interactions on the performance of the ECMR are demonstrated. In addition, the types of electrocatalytic membrane materials and mechanism of ECMR for wastewater treatment are comprehensively specified. Finally, this chapter describes the application of ECMR to the treatment of industrial wastewater, including oily, phenolic, and dyeing wastewater.

Chapter 19 presents the fundamentals and basic principles of water reclamation by heterogeneous photocatalysis. The effects of important operational parameters on the overall treatment efficiency of photocatalytic system are addressed in terms of photocatalyst loading, pollutant concentration, pH and temperature of water, dissolved oxygen and light intensity. A brief introduction into the kinetics of the photocatalytic reactions associated with the photocatalytic water treatment processes is also discussed. Photocatalytic hybrid systems and future prospects for their application and development are finally embraced.

Sewage sludge as a by-product of wastewater treatment plants has become a major concern due to its large quantity and difficult disposal. In recent decades, attempts on the recycling of it include composting, energy generating, building material producing, water treatment material manufacturing, etc. Focusing on the potential techniques for conversing sewage sludge into environmentally benign materials, Chapter 20 mainly describes the application of it in the production of sludge-based ceramic particles (SBCP) and sludge-based activated carbon (SBAC). In wastewater treatment technique, SBCP as filter media material perform better

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than commercial ceramic particles due to the higher porosity and larger surface area. SBAC is a highly promising adsorbent that can be widely used, and the disparity in property dependent upon both the production method and the character of the sludge itself.

Impacts of climate change and climatic variability are evident in many parts of the world and will result in significant impacts on our water resources. Chapter 21 presents a methodology based on kernel regression for downscaling General Circulation Model (GCM) output to predict precipitation under IPCC SRES scenarios. Downscaling models are developed using kernel regression approach for obtaining projections of precipitation to lake-basin scale in an arid region, which is considered to be a climatically sensitive region in India. Strategies for future sustainable water supplies for mitigation and adaptation are discussed.

Chapter 22 promotes sustainable resource management based on the principle of materials flow management, especially the separation of highly concentrated partial streams (source separation) such as faeces and urine with a subsequent recycling represents a suitable approach with high resource efficiency. It describes a resource economic approach to evaluate the economic value of the wastewater borne resources as well as a model to determine the pollution dependent (conventional) treatment costs for single wastewater parameters (COD, N and P). Such a model can be used as an economic steering instrument for strengthening the implementation of green technologies by identifying their resource economic potential.

Under an ever-increasing demand for energy supply, societies are seeking sustainable, renewable, economically viable and environmentally safe energy sources. Chapter 23 gives insight into bioenergy generated from wastewater as well as energy recovery mechanisms in wastewater treatment such as anaerobic processes for biogas production, microbial fuel cells for bio-electricity and algae cultivation for biofuel. In addition, this chapter also assesses the wastewater treatment systems with biomass utilization and biogas energy recovery acting as a net carbon sequestration process.

Chapter 24 delineates both the scientific and practical implications of obtaining sustainable green energy through fermentative biohydrogen production. Fermentative hydrogen production is one of the emerging techno-economic options for substituting the depleting fossil fuel energy sources with biofuels. Recently, the use of organic-rich wastewater for biohydrogen production has proven to be cost-effective and sustainable. For sustainable development, a complete understanding on biohydrogen production is essential. Several parameters that govern the successful operation of a biohydrogen process are discussed, that includes the biochemical pathways involved in anaerobic digestion, physico-chemical, biological parameters, and biochemical processes. In addition, the different types of bioreactor configurations, their performances, rate kinetics and modeling of the biohydrogen process using data driven and process based models are comprehensively discussed.

Chapter 25 summarizes the state of the art with respect to the fundamentals of Anaerobic Membrane Bioreactors (AnMBRs), including its evolutionary history,

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and membrane and process design, the application development of AnMBRs in domestic and industrial wastewater treatment, opportunities for biogas production and waste minimization, and membrane fouling researches. The analysis of literature demonstrates the enormous competitive advantages of AnMBRs over the other available technologies in terms of environmental and economic perspectives, but AnMBRs' commercial applications are still pending due to membrane fouling issues and other challenges. Based on this review, the future research perspectives relating to its application, membrane fouling control, methane recovery and economic feasibility are proposed.

The Onsite Wastewater Differentiable Treatment System is an ecological sanitation approach with high potential to achieve sustainable treatment and management of domestic wastewater. In this system, the treatment of toilet wastes by using the composting toilet is an essential and key process because several benefits are expected to obtain if implemented, such as conservation of fresh water, elimination of sources of pathogens from the domestic wastewater stream, recovery and recycle of nutrients contained in excreta. Chapter 26 reviews some achievements of research work to describe the decomposition process of feces and urine in the composting toilet aiming the establishment of criteria for the proper design and operation of the system. The contents covers several aspects on composting of human feces which include characterization of feces, modeling of the aerobic biodegradation process, fate of water, compost safety and criteria for the design of the composting toilet.

Palm oil mill is one of main agro-industry in Indonesia. The primary product from palm oil mill is crude palm oil which usually not more than 25% of the fresh fruit bunches. Therefore, waste management is very important to minimize environmental risk and optimize added value from the mill. The major environmental risk of palm oil mill was caused by Palm Oil Mill Effluent (POME). Chapter 27 demonstrates successfully sustainable POME management based on zero waste approach. Through this approach, POME is observed as a resource which can be utilized to prevent environmental pollution and produce valuable materials, such as energy or organic fertilizer, simultaneously. The appropriate technology of sustainable POME management for each palm oil mill is depending on the condition of palm oil mill and plantation such as energy supply and utilization, soil characteristic of oil palm plantations, and how much the management pays attention on greenhouse gases emission reduction initiative.

Nanomaterials have been developed as high-capacity adsorbents, high-efficiency nanofiltration membrane technology and high-activity catalysts for pollutants removal, water treatments and purification, improvement of fuels quality, air quality control, degradation of organic pollutants, remediation of polluted soils, and pollutant sensing and detection. Chapter 28 gives a comprehensive review on nanomaterials; nanotechnologies that have been widely applied in developing sustainable society, such as "green" industry, agriculture, food industry, environmental protection, and renewable energy, as well as health care, are reviewed and summarized in this chapter.

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1.5 SUMMARY

Sustainable water management has received great attention over the recent years due to its substantial benefits to the environment, society, and economy. Improvements in water management are likely to come from green technologies fueled by individual curiosity, dedicated effort and opportunities within a strategic program supported by national and international agencies, universities and industries. These innovations can significantly contribute to less non-renewable resource requirement, a higher level of energy and nutrient recovery, reduced carbon footprint, greenhouse gas emissions and costs, minimized water losses and enhanced removal of contaminants. Further, the application of integrated water management strategies together with holistic assessment tools that take into account of technical, environmental, social and economic issues would lead to a more robust, efficient and credible solution for prospective water market and decision making. However, the relevant policies and water use guidelines and regulations on water quality, risk control and consumption behaviors should be established and updated frequently. Besides, public communications and surveys are essential and should be primarily taken to guarantee the implementation in a cost-effective way.

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CHAPTER 2

Rainwater Harvesting in New South Wales, Australia

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2.1 INTRODUCTION

In Australia, recent droughts and concerns about climate change have highlighted the need to manage water resources more sustainably. Rainwater harvesting has emerged as a new field of sustainable water management, which offers an alternative water supply for at least non-potable uses. It complements other approaches to sustainable urban water management such as demand management, stormwater harvesting, and the reuse of wastewater and greywater.

The quality of rainwater flowing into rain tanks is beyond reasonable control. Typical collection and storage of rainwater introduces the potential for chemical, physical and microbial contamination. Table 2.1 summarizes the main water quality hazards associated with rainwater tanks, and their probable causes (Australian Government 2004).

Rainwater in tanks often contains colloidal solids, microbial pollutants and micro-pollutants. While it is generally accepted for non-potable purposes such as toilet flushing, it does not meet the Australian Drinking Water Guidelines of 2011 (ADWG 2011). NSW Health (2002) advises against the use of rainwater for drinking purposes wherever town water is available. A reliable cost-effective and relatively maintenance-free in-line treatment will allow the unrestricted use of rainwater, either as main household water supply or to augment town supply. This type of treatment must ultimately be the goal of a rainwater harvesting system that targets widespread unrestricted adoption.

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Table 2.1. Typical hazards with rainwater tanks

Hazard	*Cause*
Faecal contamination from	Overhanging branches on roof, animal access to tank
• birds and small animals	Human access to tank
• humans (above-ground tanks)	
• humans/livestock (below-ground tanks)	Surface water ingress into tank
Mosquitoes	Access to stored water
Lead contamination	Lead-based paints on roofs, lead flashing on roofs, increased corrosion of metals due to low pH from long periods of contact between rainwater and leaves, resuspension of accumulated sediment
Other contamination from roof materials	Preservative-treated wood; Bitumen based materials
Chemical contaminants from tanks, pipework, etc.	Inappropriate material that does not comply with Aust. Standards relating to food grade products or products for use in contact with potable water
Dangerous plants	Overhanging branches

2.2 SOURCES AND CHARACTERISTICS OF RAINWATER

2.2.1 Rainwater in Sydney Metropolitan Rainwater Tanks

Detailed sampling was carried out on metropolitan rainwater tanks located in different parts of Sydney (New South Wales) and in Wollongong (a town located south of Sydney). The topography of the Sydney basin follows a classic “closed” basin. It is surrounded by high-elevated ground surface to the south, west and north whereas inherited from the temperature differential between land and ocean on the eastern side. From early morning onward, air pollution is generated from primary sources (industry, road transport, etc.) and distributes over the Sydney basin. Offshore afternoon sea breezes, typically from the north-east, pick-up air pollutants and carry it inland. As a result, the most polluted region is in the south-western corner of Sydney. Air quality is the worst in this area where most of the studied rainwater tanks located, as shown in Figure 2.1 (a) (Kus et al. 2010a).

The rain tanks (T1 to T7) ranged in age from 1 to 50 years, in size from 500 L to 120,000 L, and were constructed from a variety of materials including PVC and concrete. They collected water from concrete tiled, Zincalume, fibro and Colorbond galvanised roofs. Further details are provided in Kus et al. (2010a).

The concentration of pollutants in samples collected from the metropolitan rainwater tanks (T1 to T11) are summarised in Table 2.1 (Kus et al. 2010a). Water

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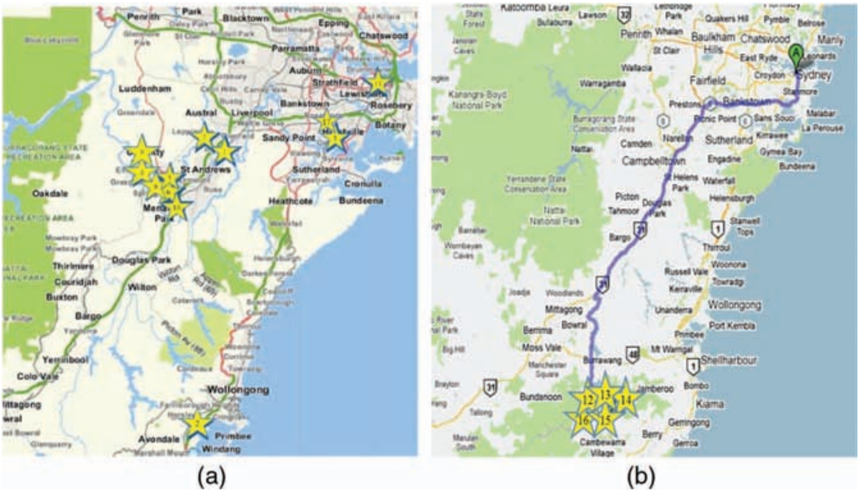

Figure 2.1. Location of (a) urban and (b) rural rainwater tanks in relation to Sydney, Australia
Source: Google Maps (2011)

quality of rain tanks located in south-western Sydney (T4, T5, T6, T8, T9, and T10) was compared with those located near the coast (T2, T3 and T11) and those along the path of the path of the onshore air current that carries pollutants to the south western suburbs (T1 and T7).

Heavy metals. The heavy metals in most of the studied water samples complied with the ADWG (2011) (hereafter referred to as ADWG), except iron and lead. The average iron concentrations in tanks T1 and T5 were under the ADWG limit (0.3 mg/L). However, each tank contained at least one sample over the iron standard, for example, 4.70 mg/L for T1 and 4.18 mg/L for T5. Lead was of particular interest when most samples exceeded the ADWG limit of 0.01 mg/L. For instance, T1 contained an average of 0.016 mg/L (upper limit of 0.033 mg/L), T4 of 0.010 mg/L (upper limit of 0.029 mg/L), T5 of 0.049 mg/L (upper limit of 0.067 mg/L), T8 of 0.007 mg/L (upper limit of 0.017 mg/L), and finally, T10 of 0.013 mg/L (upper limit of 0.021 mg/L). Other heavy metals such as arsenic, cadmium, chromium, mercury, nickel, selenium and silver were well within the ADWG standard (less than 0.001 mg/L).

If sludge at the bottom of rainwater tanks is disturbed, concentration of the heavy metals is expected to exceed the ADWG limit, due to the accumulation between periods of rainwater tank maintenance (Magyar et al. 2007).

Anions, cations, total dissolved salts. Mineral salts are a part of a human's daily dietary intake. The ADWG does not provide the maximum concentration limits for these salts in drinking water. Compared to potable water (supplied by Sydney Water), water in rain tanks was normally equivalent to or had lower concentrations of sodium, calcium, magnesium, chloride and sulphate. The only mineral salt that was higher in concentration than the potable water supply (Sydney Water) was potassium.

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A rough estimation has been done to compare the mineral content between rainwater and a commercially available multi-vitamin supplement. One tablet often contains 100 mg of potassium, 100 mg of calcium, 145 mg of magnesium and 36.3 mg of chloride. To consume these quantities of mineral salts in the typical rainwater tanks sampled in this study (with the exception of T3 and T8), more than 30 litres of water is required for the equivalent potassium dosage, more than 8 litres for calcium, more than 50 litres for magnesium and more than 7 litres for chloride; however an average person drinks approximately 2-3 L of water per day.

Ammonia, nitrate, nitrite and orthophosphate. With regards to nitrate, nitrite and ammonia, all rainwater tanks complied with ADWG. Orthophosphate is used around the world as a corrosion inhibitor in some potable water supplies, especially where it has been observed that high concentrations of lead or copper originated from potable water pipelines. Concentrations of orthophosphate are dosed at up to 1 mg/L (Edwards et al. 2002; Li et al. 2004) to reduce the metal corrosion in the water distribution pipes. All rainwater tanks contained concentrations of orthophosphate of less than 1 mg/L.

pH and water hardness. The pH analysis demonstrated that the rainwater tanks were generally within or close to compliance with the ADWG guidelines ($\mathrm{pH} = 6.5 - 8.5$) with the exception of T6 (average $\mathrm{pH} = 5.7$). The average concentrations of water hardness of T5 and T6 were rather low (0.92 mg/L and 1.26 mg/L of $CaCO_3$, respectively), which indicated that there was no water buffer. With the addition of any acidic elements such as animal or humic acids from leaves, pH of the rainwater tanks would drop rapidly. It seemed true for T5 which is actually approaching the minimum limit with a pH 6.52. High buffer or water hardness levels (with the exception of T5) of rainwater often was a result of concrete tiled roofs, whereas low buffer or water hardness levels came from Colourbond or Zincalume metal roofs.

Turbidity and Suspended Solids. The ADWG has a recommended limit for turbidity of 5 NTU. Most tanks complied with this limit. Rainwater tanks T1, T5 and T8 on average complied with this limit, although at one time this limit was exceeded with the highest individual readings of 12 NTU, 8 NTU and 6 NTU, respectively. This was due to a dirty roof on the house of T1 and T5 and the rainfall collected in tank T8 had stirred up sediments within the tank.

The ADWG does not state a limit for total suspended solids (TSS). As this is somewhat similar to turbidity, it could be assumed that if turbidity complies with the recommended limits then the total suspended solids should also be satisfactory. TSS ranged from less than 0.5 mg/l to 3.5 mg/L in most of the metropolitan tanks (except for T1, T5 and T8) when they complied with turbidity of less than 5 NTU. T1, T5 and T8 contained concentrations of 5.5 mg/L and above when their turbidity levels exceeded 5 NTU.

Conclusion. The water collected in the rainwater tanks usually complied with the ADWG limits for most parameters, except for a few individual parameters from individual rainwater tanks. These are shown in bold in Table 2.2. The majority of parameters tested were comparable to potable water.

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Table 2.2. Laboratory analysis of rainwater tank samples

Parameter	T1* Ingleburn	T2* Wollongong	T3* Kogarah	T4* Mt Hunter	T5* Kirkham	T6* Narellan	T7* Kemps Crk	T8* Cawdoor	T9* Therisa Pk	T10* Glen Alpine	T11* Newtown	Range and Average*
pH	6.89–7.30 7.13	6.71–7.49 7.12	7.13–7.48 7.28	**6.39**–8.19 7.27	**5.79**–7.09 6.52	**5.41–5.83** **5.70**	7.19–7.38 7.26	6.64–7.45 6.96	6.60–**8.62** 7.54	6.58–7.54 7.10	**6.48**–6.90 6.74	**5.41–8.62** 6.97
Conductivity (EC) (dS/m)	0.06–0.10 0.08	0.04–0.05 0.05	0.12–0.15 0.13	0.06–0.07 0.07	0.01–0.01 0.01	0.02–0.02 0.02	0.07–0.08 0.08	0.12–0.16 0.14	0.04–0.05 0.04	0.07–0.10 0.09	0.04–0.06 0.05	0.01–0.16 0.07
Total dissolved salts (mg/L)	39.44–70.72 55.3	29.92–32.64 31.05	80.24–98.60 86.36	42.84–47.60 45.33	7.48–8.84 8.39	13.60–14.96 14.45	50.32–53.04 51.91	79.56–107.44 91.80	27.20–35.36 30.15	45.56–67.32 59.16	23.80–40.12 34.68	7.48–107.44 46.23
Total suspended solids (mg/L)	0.50–17.00 6.17	1.00–2.00 1.67	1.00–2.00 1.33	0.50–2.50 1.17	1.00–12.50 4.83	1.00–1.50 1.13	1.00–3.50 1.83	2.00–5.50 3.33	1.00–2.50 1.50	0.50–3.50 1.83	0.50–1.00 0.83	0.50–17.00 2.33
Turbidity (NTU)	0.20–**12.00** **5.07**	0.20–2.00 0.87	0.20–0.60 0.33	0.20–4.00 2.07	0.80–**8.00** 3.60	0.40–2.00 1.05	0.60–2.00 1.53	0.20–**6.00** 2.73	0.20–2.00 1.07	1.00–2.00 1.67	0.60–2.00 1.13	0.20–**12.00** 1.92
Water hardness (mg/L $CaCO_3$ equivalent)	17.32–33.72 27.65	6.91–8.37 7.53	26.34–37.31 30.22	17.15–24.37 21.89	0.59–1.32 0.92	0.58–2.05 1.26	26.85–30.54 28.63	32.88–46.78 39.96	8.53–17.33 13.23	21.48–37.79 29.17	5.13–6.53 5.98	0.58–46.78 18.77
Ortho-phosphate (mg/L P)	0.00–0.03 0.02	0.01–0.01 0.01	0.00–0.00 0.00	0.01–0.36 0.24	0.00–0.00 0.00	0.00–0.01 0.00	0.00–0.01 0.00	0.03–0.03 0.03	0.01–0.02 0.02	0.01–0.02 0.02	0.01–0.01 0.01	0.00–0.36 0.03
Nitrate (mg/L N)	0.10–0.65 0.33	0.08–0.38 0.19	0.20–0.26 0.24	0.05–0.80 0.45	0.18–0.41 0.32	0.43–0.74 0.59	0.78–0.91 0.86	0.52–0.73 0.63	0.38–0.60 0.52	0.06–0.68 0.39	0.19–0.62 0.34	0.05–0.91 0.44
Ammonia (mg/L N)	0.020–0.119 0.056	0.005–0.012 0.08	0.073–0.186 0.112	0.003–0.023 0.013	0.005–0.115 0.053	0.129–0.250 0.195	0.009–0.036 0.023	0.020–0.069 0.038	0.005–0.061 0.024	0.005–0.072 0.035	0.037–0.208 0.147	0.003–0.250 0.064
Sodium (mg/L)	1.75–4.02 2.62	1.89–3.24 2.76	6.49–15.09 9.42	1.11–2.66 1.88	0.61–1.03 0.82	0.91–1.51 1.25	1.35–1.92 1.65	6.55–8.72 7.64	0.97–1.21 1.11	1.41–4.26 2.54	3.10–8.17 6.45	0.61–15.09 3.47
Potassium (mg/L)	0.98–1.82 1.29	1.83–2.85 2.18	0.94–1.57 1.17	0.48–1.41 0.80	0.16–0.32 0.25	0.01–0.25 0.13	0.10–0.44 0.27	0.85–1.38 1.14	0.46–1.01 0.78	0.03–1.15 0.57	0.13–0.34 0.21	0.01–2.85 0.80
Calcium (mg/L)	6.44–12.40 10.30	2.19–2.84 2.43	6.96–8.15 7.67	6.06–9.28 8.16	0.17–0.38 0.25	0.14–0.44 0.28	10.06–11.67 10.81	10.94–15.88 13.64	3.20–6.71 5.06	8.01–14.31 10.79	1.03–1.23 1.11	0.14–15.88 6.41
Magnesium (mg/L)	0.30–0.67 0.47	0.31–0.41 0.36	1.60–4.84 2.69	0.29–0.49 0.37	0.04–0.09 0.07	0.05–0.23 0.14	0.34–0.43 0.40	1.22–1.73 1.43	0.13–0.16 0.14	0.36–0.77 0.54	0.50–0.93 0.78	0.04–4.84 0.67

(Continued)

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Table 2.2. Laboratory analysis of rainwater tank samples (Continued)

Parameter	*T1** *Ingleburn*	*T2** *Wollongong*	*T3** *Kogarah*	*T4** *Mt Hunter*	*T5** *Kirkham*	*T6** *Narellan*	*T7** *Kemps Crk*	*T8** *Cawdoor*	*T9** *Therisa Pk*	*T10** *Glen Alpine*	*T11** *Newtown*	*Range and Average**
Chloride (mg/L)	1.91–7.66	3.94–5.67	11.59–22.81	5.37–7.34	3.86–4.98	4.45–5.11	4.56–6.08	16.03–22.96	4.26–4.90	4.53–12.93	11.19–12.94	1.91–22.96
	4.63	4.84	15.35	6.07	4.50	4.70	5.09	19.39	4.62	7.44	12.28	8.08
Sulphate (mg/L SO_4^{2-})	1.23–1.59	1.53–3.12	4.08–9.81	1.92–2.37	0.81–1.56	1.98–2.13	2.73–3.12	3.30–4.38	1.41–1.80	2.22–2.85	2.55–5.37	0.81–9.81
	1.42	2.10	6.02	2.12	1.21	2.03	2.92	4.00	1.58	2.54	4.33	2.75
Aluminium (mg/L)	0.06–0.09	0.00–0.01	0.01–0.03	0.01–0.03	0.02–0.03	0.02–0.03	0.02–0.03	0.02–0.07	0.08–0.16	0.01–0.07	0.03–0.04	0.00–0.16
	0.08	0.01	0.02	0.02	0.03	0.02	0.02	0.04	0.11	0.03	0.03	0.04
Copper (mg/L)	0.01–0.06	0.00–0.00	0.11–0.64	0.00–0.10	0.00–0.02	0.05–0.13	0.01–0.34	0.03–**2.37**	0.00–0.01	0.02–0.07	0.00–0.01	0.00–**2.37**
	0.03	0.00	0.41	0.06	0.01	0.07	0.12	1.03	0.00	0.05	0.01	0.16
Iron (mg/L)	0.05–**4.70**	0.01–0.02	0.02–0.02	0.01–0.03	0.07–**4.18**	0.00–0.08	0.01–0.06	0.03–0.11	0.00–0.01	0.01–0.02	0.01–0.02	0.00–**4.70**
	1.69	0.02	0.02	0.02	**1.51**	0.03	0.04	0.07	0.00	0.01	0.01	**0.31**
Manganese (mg/L)	0.00–0.06	0.00–0.00	0.00–0.00	0.00–0.00	0.01–0.03	0.01–0.01	0.00–0.01	0.00–0.02	0.00–0.00	0.00–0.00	0.00–0.01	0.00–0.06
	0.02	0.00	0.00	0.00	0.02	0.01	0.00	0.01	0.00	0.00	0.00	0.01
Lead (mg/L)	0.006–**0.033**	0.000–0.01	0.001–0.006	0.001–**0.029**	**0.038–0.067**	0.004–0.007	0.000–0.001	0.001–**0.017**	0.001–0.001	0.008–**0.021**	0.001–0.008	0.000–**0.067**
	0.016	0.00	0.003	**0.010**	**0.049**	0.006	0.001	0.007	0.001	**0.013**	0.003	**0.010**
Zinc (mg/L)	0.04–0.31	0.01–0.02	0.03–0.56	0.07–1.41	0.04–0.05	0.18–1.16	0.01–0.04	0.09–0.29	0.01–0.03	0.09–0.63	0.38–0.77	0.01–1.41
	0.13	0.03	0.26	0.56	0.04	0.45	0.03	0.17	0.02	0.28	0.52	0.23

*1st row: range of value, 2nd row: average value; values exceeding the ADWG (2011) limit are shown in bold

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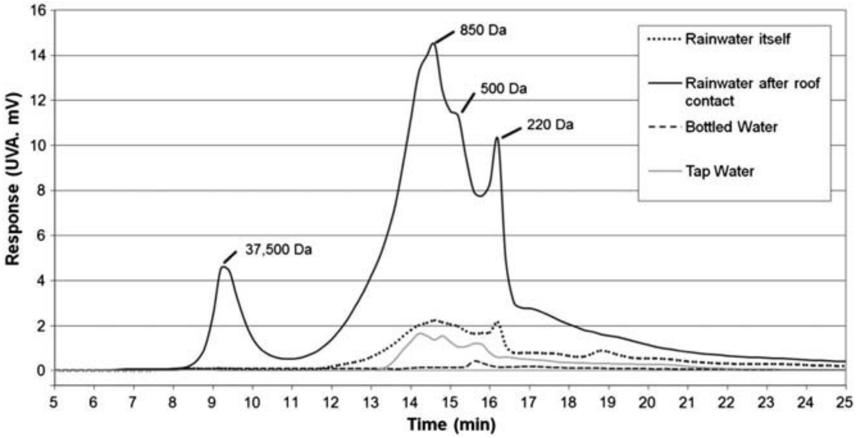

Figure 2.2. MWD of RWOM before/after roof contact of rainwater
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Organic matter. Detailed molecular weight distribution (MWD) of rainwater organic matter (RWOM) was conducted to identify the components of organic contamination. The MWD of RWOM was monitored to determine the effects of: (i) contamination of rainwater by contact with the roof, (ii) the effects of residence time of water in rain tank for the duration between storm events, and (iii) the effects of residence time of water in rain tank over a long period during which rainfall intermittently occurred (Kus et al. 2010a).

Sampling was carried out at 2-year-old rainwater tank (T1) and ceramic roof tiles from a 30-year old house, which was located near an industrial area and a freeway in Ingleburn, Sydney. The tank was made from polyethylene and was plumbed using PVC fittings from the gutter to the tank (Kus et al. 2010a).

MWD of RWOM of rainwater before/after roof contact. Figure 2.2 shows the MWD of RWOM in rainwater before it came into contact with the roof (rainwater itself), rainwater after roof contact, commercially available bottled water and tap water supplied by Sydney Water. Rainwater itself included the MWD of RWOM ranging from 850 Da to 220 Da. The origin of RWOM may be due to air pollutants dissolved in the rainwater. However, when the rainwater came into contact with the roof, the MWD of RWOM indicated a different trend compared to rainwater itself. The MWD of RWOM after the contact with the roof consisted of 37500 Da, 850 Da, 500 Da and 220 Da. A new MW of 37500 Da appeared, and the MW of 850 Da showed the highest peak intensity. Overall, the intensity of UV responses significantly increased. According to Shon et al. (2006), the MW of 37500 Da may be due to biopolymers, 850 Da to humic substances, 500 Da to building blocks, 220 Da to low MW acids, and less than 220 Da to amphiphilics. The figures suggest that after contact with the roof, the rainwater was significantly contaminated especially by biopolymers and humic substances. However there is some uncertainty concerning the origins of the RWOM, although likely by atmospheric deposition occurring between rain events.

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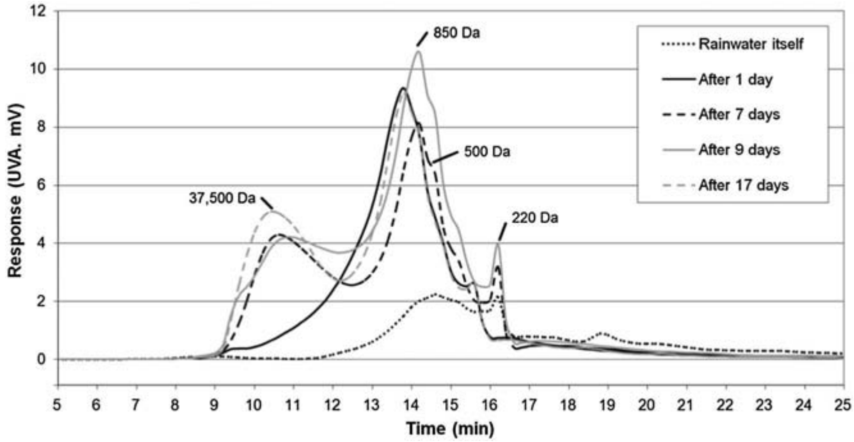

Figure 2.3. MWD of RWOM showing the effects of residence time of water in rain tank over 1-17 days
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The MWD of RWOM with rainwater before/after the contact with the roof was compared with commercially available bottled water and Sydney tap water (Figure 2.2). The MWD of organic matter from bottled and tap water showed low UV intensity compared to rainwater. Tap water mostly included humic substances and low MW acids, while bottled water only consisted of low MW acids. The results show that the concentration of RWOM before/after is higher than that of tap and bottled water.

MWD of RWOM in terms of the effects of residence time of water in rain tank for the duration between storm events. Figure 2.3 illustrates the MWD of RWOM, which shows the effect of ageing of rainwater for the durations between storm events in a residential rainwater tank (T1). From day 1 to day 17, the intensity of the MW of 37500 Da and 850 Da increased with time, showing that biopolymers (37500 Da) and humic substances (850 Da) increased during the storage period in the tank (Figure 2.3). The increase of the former could be the effect of microbial communities increasing the concentration of biopolymers and humics.

MWD of RWOM in terms of the effects of residence time of water in rain tank for long durations during which rainfall occurred. Figure 2.4 shows the MWD of RWOM as the rainwater in the tank (T1) ages during the normal operation of a residential rainwater tank over an 180-day period. During this period, the rainwater tank was used for general purposes and allowed to fill, principally during periods of rainfall, and empty, as rainwater water was consumed. Here, it should be noted that the rainwater samples in the rainwater tank were collected at set times and during the intervening periods rain may have fallen and filled the tank.

Figure 2.4 shows that from day 90 to day 180, a generalised trend of the MWD was not found. MWD for the major peaks of 850 Da, 500 Da and 220 Da

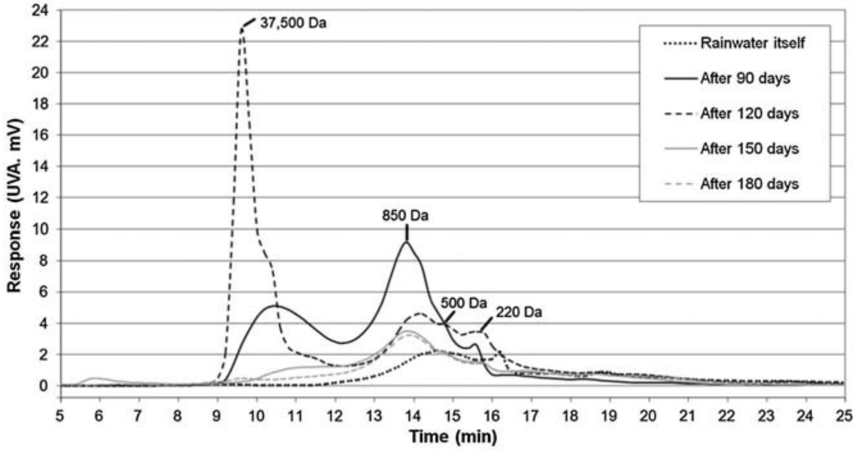

Figure 2.4. MWD of RWOM showing the residence time of water in rain tank over long durations during which rainfall intermittently occurred
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showed a decline over the period up to 180 days. Interestingly, the intensity of the MW of 37500 Da significantly increased after 120 days in an inconsistent manner during the period of sampling. This could be due to (i) uncontrollable seasonable changes which include surrounding trees not having leaves to shed on the roof in winter, (ii) the dilution effect of the frequent variation in rainfall, and (iii) the effect of microbial communities increasing the concentration of biopolymers. Further detailed characterisation of RWOM is needed to investigate this issue.

2.2.2 Rainwater in Outer Sydney Rural Rainwater Tanks

In addition to the data collected from metropolitan rainwater tanks, detailed sampling was carried out on rural rainwater tanks (T12 to T16) located in the Kangaroo Valley, approximately 160 km south-west of Sydney (Kus et al. 2011). The rainwater tanks ranged in age from 10 to 25 years and were made from various materials including PVC, concrete and galvanised steel. These tanks collected water off Colorbond galvanised roofs. The houses were located in a rural area with less vehicular activities, compared to Sydney's metropolitan area. As there was no town water supply, all residents relied on these rainwater tanks as their main household water supply. The concentrations of pollutants in the samples collected from rural rainwater tanks (T12 to T16) are described below and summarised in Table 2.3.

Anions, cations and total dissolved salts. A comparison with the potable water supply (Sydney Water Corporation) shows that rural rainwater tanks normally had low concentrations of sodium, calcium, magnesium, chloride and sulphate. The only parameter that was marginally higher in concentration than the potable water supply was potassium in the rural rainwater tanks. Total dissolved

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Table 2.3. Laboratory analysis of rural rainwater tank samples

Parameter	*ADWG (2011)*	*T12*	*T13*	*T14*	*T15*	*T16*	*Rural Average*
pH*	6.5–8.5	**6.07–6.11** **6.09**	**5.69–5.81** **5.75**	**6.02–6.03** **6.03**	6.93–7.23 7.08	**5.95–6.05** **6.00**	**5.69**–7.23 **6.19**
Total dissolved salts (mg/L)*	NA	12–15 13.5	12 12	12–13 12.5	24 24	20–21 20.5	12–24 16.5
Total suspended solids (mg/L)*	<400	<0.5 – 1 0.75	<0.5– < 0.5 < 0.5	<0.5– < 0.5 <0.5	<0.5– < 0.5 <0.5	< 0.5– < 0.5 < 0.5	< 0.5–1 < 0.5
Turbidity (NTU)*	<5	0.7–1.0 0.85	0.6–0.8 0.7	0.6–0.8 0.7	0.9–1.0 0.95	0.3–0.4 0.35	0.3–1.0 0.71
Water hardness (mg/L $CaCO_3$ equivalent)**	<200	2–2 2	2–3 2.5	3–3 3	12–12 12	4–5 4.5	2–12 4.8
Orthophosphate (mg/L P)	—	0.014–0.019 0.017	0.023–0.024 0.024	0.010–0.012 0.011	0.009–0.010 0.010	0.009–0.009 0.009	0.009–0.024 0.014
Nitrate (mg/L N)	<50	0.046–0.068 0.057	0.248–0.254 0.251	0.198–0.208 0.203	0.128–0.130 0.129	0.386–0.400 0.393	0.046–0.400 0.207
Nitrite (mg/L N)	< 3	< 0.005– < 0.005 < 0.005	< 0.005– < 0.005 < 0.005	< 0.005– < 0.005 < 0.005	< 0.005– < 0.005 < 0.005	< 0.005– < 0.005 < 0.005	< 0.005– < 0.005 < 0.005
Ammonia (mg/L)	<0.5	0.006–0.006 0.006	0.005–0.006 0.006	0.005–0.007 0.006	0.007–0.009 0.008	0.004–0.007 0.006	0.004–0.009 0.006
Sodium (mg/L)	—	1.92–1.99 1.96	1.98–4.86 3.42	2.15–2.29 2.22	2.17–2.20 2.19	3.78–6.17 4.98	1.92–6.17 2.951
Potassium (mg/L)	—	0.76–2.47 1.615	0.26–0.42 0.34	0.34–0.34 0.34	0.89–1.02 0.96	0.34–0.45 0.40	0.26–2.47 0.729
Calcium (mg/L)	—	0.25–0.29 0.27	0.37–0.64 0.51	0.38–0.40 0.39	4.29–4.43 4.36	0.72–0.99 0.86	0.25–4.43 1.276
Magnesium (mg/L)	—	0.31–0.31 0.31	0.31–0.33 0.32	0.39–0.40 0.40	0.28–0.29 0.29	0.59–0.63 0.61	0.28–0.63 0.384
Chloride (mg/L)	<400	3.4–5.3 4.35	2.6–2.9 2.75	2.9–3.1 3.0	2.9–3.0 2.95	5.5–5.6 5.55	2.6–5.6 3.72

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Sulphate (mg/L SO42-)	<400	4–6 5	4–7 5.5	3–4 3.5	5–5 5	5–10 7.5	3–10 5.3
Total coliforms (cfu/100 ml)*	<1	**20–40** **30**	**40–70** **55**	**30–40** **35**	**<10–10** **10**	**<10–10** **10**	**<10–70** **28**
Faecal coliforms (cfu/100 ml)*	<1	<10–<10 <10	**10–10** **10**	<10–<10 <10	<10–<10 <10	<10–<10 <10	<10–10 <10
Total organic carbon (mg/L)*	—	0.20–0.27 0.235	0.33–0.37 0.35	0.49–0.58 0.535	0.47–0.50 0.485	0.36–0.36 0.36	0.20–0.58 0.393
Aluminium (mg/L)	<0.2	0.016–0.017 0.0165	0.010–0.014 0.012	0.013–0.023 0.018	0.022–0.023 0.0225	0.009–0.010 0.0095	0.009–0.023 0.016
Copper (mg/L)	<2	0.004–0.004 0.004	0.013–0.022 0.0175	0.011–0.028 0.0195	0.024–0.032 0.028	0.010–0.013 0.0115	0.004–0.032 0.018
Iron (mg/L)*	<0.3	<0.01–<0.01 <0.01	<0.01–<0.01 <0.01	<0.01–<0.01 <0.01	<0.01–<0.01 <0.01	<0.01–<0.01 <0.01	<0.01–<0.01 <0.01
Manganese (mg/L)	<0.1	0.002–0.003 0.0025	0.004–0.008 0.006	0.003–0.005 0.004	0.001–0.001 0.001	0.016–0.022 0.019	0.001–0.022 0.0115
Lead (mg/L)*	<0.01	<0.001–<0.001 <0.001	<0.001–<0.001 <0.001	<0.001–<0.001 <0.001	<0.001–<0.001 <0.001	<0.001–<0.001 <0.001	<0.001–<0.001 <0.001
Zinc (mg/L)	<3	0.514–0.586 0.550	0.514–0.586 0.550	0.539–0.586 0.5625	0.085–0.122 0.1035	0.125–0.415 0.270	0.009–0.586 0.2975

*1st row: range of value, 2nd row: average value; values exceeding the AGWR (2009) are shown in bold

**$CaCO_3$ equivalent

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salts (TDS), a combined parameter of all anions and cations, in rural rainwater tanks had considerably lower levels which are about one fifth or less than that of metropolitan tanks.

pH and water hardness. Water hardness is another parameter that follows TDS closely as they are, to some extent, related parameters. Water hardness acts as a buffer to prevent the acidification of water. All of the rural rainwater tanks had considerably lower water hardness at one third less than that of the metropolitan potable water supply. The rural rainwater tanks all drained from galvanised Colourbond roofs and rain tanks were constructed from PVC with the exception of T15, which was a concrete rainwater tank. T15 had the highest level of water hardness. Having considerably low water hardness, it is not surprising that all rainwater tanks (except T15) did not comply with pH requirement (below pH 6.5), thus resulting in acidic rainwater conditions.

Ammonia, nitrate, nitrite and orthophosphate. All rural rainwater tanks complied with the ADWG limits for ammonia, nitrate, nitrite and orthophosphate.

Turbidity and total suspended solids. The ADWG states that 5 NTU is the recommended limit of turbidity. All rural rainwater tanks complied well below the 5 NTU limit. In general, the bigger the rainwater tank volume, the lower the turbidity was (Tables 2.1). T1, the smallest rainwater tank, contained the highest turbidity levels. Because the rural rainwater tanks were larger than most metropolitan rainwater tanks, the rural rainwater tanks had lower turbidity levels with an overall average of 0.71 NTU. The larger tanks had longer hydraulic residence time, resulting in better turbidity levels. Furthermore, a larger rainwater tank captures cleaner water from a rainfall event. The small rainwater tanks would collect relatively more of the first portion of the rainfall event which typically contains more polluted wash-off from the roof.

The ADWG does not propose a limit for total suspended solids. TSS mostly ranged from less than 0.5 mg/l to 3.5 mg/L in most of the metropolitan tanks (except for T1, T5 and T8) when they complied with the turbidity limit of less than 5 NTU. All samples from the rural rainwater tanks were at 1.0 mg/l or less.

Total organic carbon. The ADWG does not recommend a limit for total organic carbon. The influent rainwater samples from the rural rainwater tanks contained an average value of 0.393 mg/L (ranging from 0.20 mg/L to 0.58 mg/L). By comparison, metropolitan rainwater tanks contained an average value of 9.44 mg/L (ranging from 2.17 mg/L to 13.26 mg/L).

Heavy metals. Rural rainwater tanks did comply with the heavy metals' requirement. For example, while lead was a concern for the metropolitan tanks, all of the rural rainwater tanks satisfied ADWG with all samples were below the detectable limit (0.001 mg/L). The other heavy metals were well within the guideline's recommended limits. The concentration levels of arsenic, cadmium, chromium, mercury, nickel selenium and silver all indicated negligible concentrations (less than 0.001 mg/L).

Total Coliform and Faecal Coliform. The ADWG recommends a limit of <1 CFU/100 mL for faecal and total coliform counts. All rural rainwater samples had counts exceeding the recommended limits.

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Overall. The water collected in the rural rainwater tanks complied with the ADWG for most parameters except for a few such as the pH, total coliform and faecal coliform. These are shown in bold in Table 2.3.

2.2.3 First Flush in Sydney Metropolitan Rainwater Tanks

"First flush", a term commonly used in stormwater management, occurs when large proportions of pollutants are transported in the first part of the rainfall runoff. Because these pollutants are easily disturbed, they become suspended in surface runoff early on in the storm event. An analysis of the first flush was conducted to determine whether a first flush exists in rainfall runoff from the roof of a residential house and whether bypassing it could help improve the quality of rainwater collected in tanks. There is a lack of experimental data to determine these aspects (Kus et al. 2010b).

A first flush sampling was carried out in a rainwater tank located in the south-western corner of the Sydney basin, specifically the suburb of Ingleburn (T1, Table 2.1, and Figure 2.1a) where air pollution was the worst. Samples of runoff from the residential roof (T1) were also collected and analysed. The rain events summarised in Table 2.4 were analysed for this investigation had to comply with the following conditions:

- A previous significant storm event washed the roof;
- At least a two-week dry period followed the significant storm event; and
- Adequate and consistent rainfall occurred after two-week dry period to enable at least 5 mm of the first flush sample to be collected for laboratory analysis.

The samples were collected from the downpipe approximately every 2.5 minutes for up to 25 minutes (Table 2.3). The records of both one on-site electronic weather station and one on-site manual rain gauge were examined to determine how many millimetres of rain fell during the sampling processes. Samples were taken directly from the downpipe from the gutter before reaching the integrated first flush device. Samples of rainfall (before contacting with the roof) were also analysed. In short, there were three types of sampling: (1) T1-rainwater: rainwater collected before contacting with the roof;

Table 2.4. Summary of rain events that were monitored for first flush runoff

Date	*Rain Start Time*	*Number of preceding dry days*	*Rain Duration (minutes)*	*Total Rainfall (mm)*	*Average Intensity (mm/hr)*
15/11/08	19:37	15	24	5	13
11/01/09	18:40	22	83	3.5	3
9/02/09	22:58	19	11	3	16

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(2) T1-runoff: rainwater after contacting with the roof and before reaching to the first flush system inside the tank; and (3) T1-tankwater: rainwater captured inside the tank.

The results of pollutant concentration over the depth of rainfall are given in Figure 2.5 (a-h) and Tables 2.5 to 2.7 for all three monitored rainfall events, in comparison with their applicable concentration limits (provided by the ADWG), potable tap water and rainwater. Measurements for the pollutant concentrations in T1-rainwater are also provided.

Turbidity and total suspended solids. Except for the first sample, TSS values were below the limit of 400 mg/L (Figure 2.5 (a)). Therefore, bypassing the first 0.5 mm to 1 mm of roof runoff will improve the rain tank water by reducing TSS during a filtration process.

To obtain the turbidity less than 5 NTU as specified in ADWG, the first approximately 5 mm of rainfall should be bypassed (Figure 2.5 (b)). The concentration of turbidity in the T1-rainwater exceeded the ADWG value for the first 1 mm of rainfall. Although turbidity is not necessarily a health hazard, it may constitute a health risk if suspended particles hosted pathogenic micro-organisms or toxic compounds. Bypassing the first flush substantially improves the visual aesthetics of the water, which is also an important step in achieving public acceptance. 5 NTU would appear slightly milky-looking in a drinking glass (ADWG 2011).

According to previous studies in Australia, some rainwater tanks did not comply with the ADWG limit of turbidity (Magyar et al. 2007, 2008). Most of these tanks were smaller ones which did not serve daily potable needs. In general, the larger the rainwater tank, the less the effects are of the first flush, thanks to its dilution. Furthermore, a larger tank capacity was able to capture more water from a longer-lasting storm event.

Water hardness and conductivity. Figure 2.5 (c) shows that all samples of water hardness were below the limit of 200 mg/L ($CaCO_3$ equivalent). Tables 2.5 to 2.7 indicate that their conductivity values satisfied the ADWG limit of 0.8 dS/m.

Heavy metals. Figure 2.5 (d-f) and Tables 2.5 to 2.7 show the data for metals. The iron and manganese in the first 1–1.5 mm of T1-runoff exceeded ADWG limits of 0.3 and 0.1 mg/L, respectively. Iron is an essential trace element for humans. The concern relating to iron is more an aesthetic one due to iron's tendency to stain objects it comes in contact with or because it can lead to the water having a rust-brown colour (ADWG 2011). The aluminum concentration in T1-runoff shared the same trend.

Lead, the metal of most concern, exceeded the ADWG limit of 0.01 mg/L until the runoff from the first 5-6 mm of rainfall is bypassed. Figure 2.5 (f) indicates the concentration of T1-rainwater lead in the first 3-4 mm of rainfall was 0.02 mg/l which was above the ADWG limit. The lead concentration in T1-runoff was probably due to atmospheric deposition on the roof. In the intervening dry days, the concentration of lead on the roof built up from atmospheric deposition. Lead is a health hazard to humans (ADWG 2011). There was no lead flashing on the roof of the house used for this analysis.

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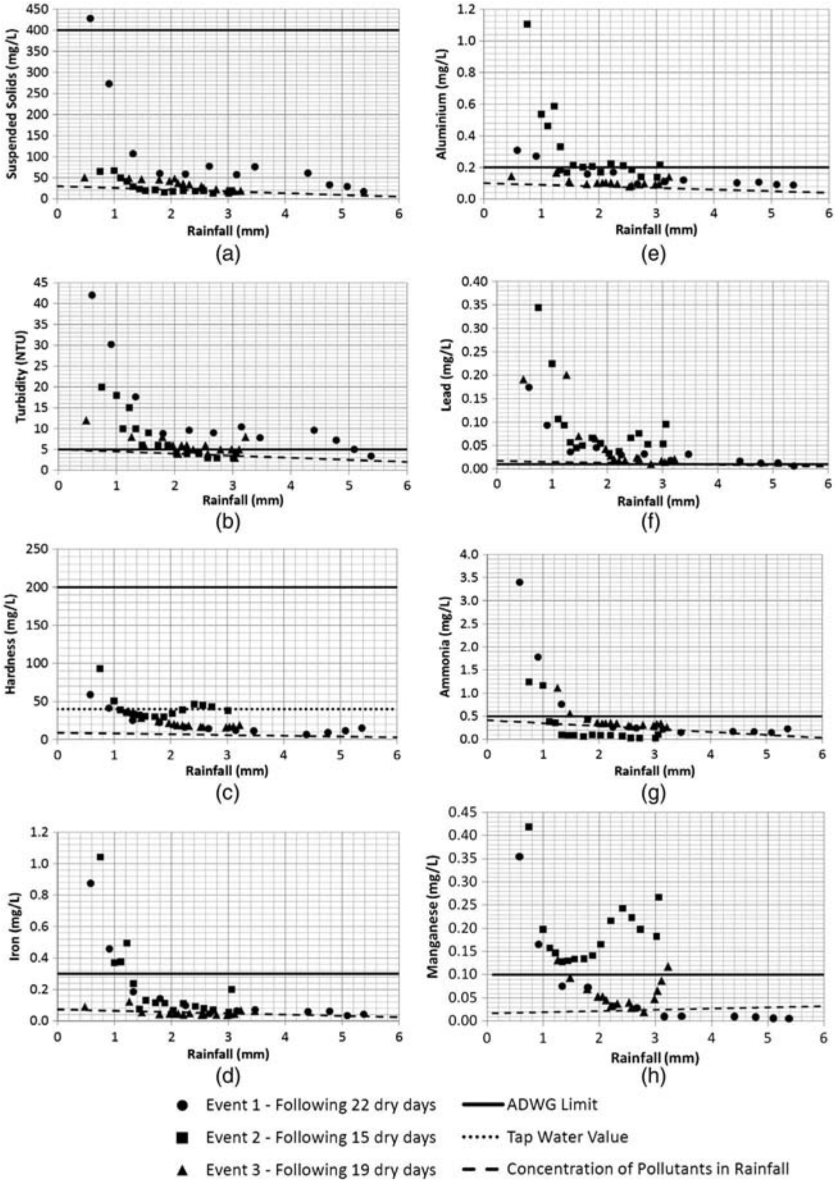

Figure 2.5. Physical and chemical characteristics of wash-off values from a concrete tiled roof of an urban house compared with ADWG limit values. The concentration of pollutants in rainfall (before contact with the roof) was the worst of the three events sampled

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Table 2.5. First flush rainwater samples from Event 1

Parameter	*pH*	*Conductivity (EC)*	*TDS (mg/L)*	*Orthophosphate (mg/L P)*	*Nitrate (mg/L N)*	*Nitrite (mg/L N)*	*Sodium (mg/L)*	*Chloride (mg/L)*	*Sulphate (mg/L SO_4^{2-})*	*Potassium (mg/L)*	*Calcium (mg/L)*	*Magnesium (mg/L)*	*Zn (mg/L)*
ADWG Limit	6.5–8.5	<0.8	—	—	<50	<3	<300	<400	<400	—	—	—	<3
0.58 mm	6.51	0.24	160	0.003	0.022	0.005	9.4	16.6	18.7	4.6	21.1	0.355	0.190
0.91 mm	6.53	0.17	117	0.005	0.016	0.003	7.6	12.4	15.4	3.0	14.9	0.167	0.123
1.33 mm	6.55	0.12	84	0.001	0.014	0.002	5.8	6.5	10.5	2.1	9.1	0.077	0.057
1.8 mm	6.57	0.11	72	0.001	0.016	0.003	5.2	5.1	9.2	1.9	8.0	0.074	0.056
2.25 mm	6.62	0.08	56	0.005	0.361	0.063	4.0	3.3	6.7	1.2	5.7	0.033	0.042
2.67 mm	6.55	0.08	53	0.005	0.260	0.021	3.4	2.5	5.0	1.0	5.2	0.029	0.049
3.15 mm	6.61	0.06	44	0.004	0.389	0.020	2.9	2.0	3.7	0.8	4.4	0.010	0.033
3.47 mm	6.58	0.06	41	0.004	0.333	0.018	2.6	1.7	3.4	0.6	4.1	0.012	0.035
4.4 mm	6.66	0.04	29	0.006	0.248	0.012	1.7	1.2	2.5	0.3	2.4	0.009	0.019
4.78 mm	6.64	0.05	36	0.008	0.175	0.004	2.3	1.8	3.0	0.6	3.3	0.008	0.039
5.09 mm	6.59	0.06	41	0.005	0.186	0.005	2.6	1.5	3.5	0.8	4.2	0.006	0.021
5.38 mm	6.59	0.08	52	0.023	0.114	0.005	3.2	3.1	4.2	1.2	5.4	0.007	0.021
Rain Water (0–3 mm)	6.70	0.05	30	0.037	0.334	0.011	2.0	2.3	4.8	0.3	2.1	0.026	0.047
Rain Water (3–6 mm)	6.75	0.03	16	0.003	0.086	0.005	2.2	2.2	1.7	0.2	1.3	0.008	0.019
Tap Water	6.93	0.18	122	0.000	0.193	0.051	10.3	26.1	3.6	0.8	11.6	1.600	0.024

Notes: 1) Arsenic, Cadmium, Chromium, Copper, Mercury, Nickel, Selenium and Silver were either not detected or less than 0.002 mg/L, and 2) Rain Water–rainwater before contact with roof

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Table 2.6. First flush rainwater samples from Event 2

Parameter	*pH*	*Conductivity (EC)*	*TDS (mg/L)*	*Orthophosphate (mg/L P)*	*Nitrate (mg/L N)*	*Nitrite (mg/L N)*	*TOC (mg/L)*	*Sodium (mg/L)*	*Chloride (mg/L)*	*Sulphate (mg/ L SO_4^{2-})*	*Potassium (mg/L)*	*Calcium (mg/L)*	*Magnesium (mg/L)*	*Zn (mg/L)*
ADWG Limit	6.5–8.5	<0.8	—	—	<50	<3	—	<300	<400	<400	—	—	—	<3
0.75 mm	6.34	0.35	240	0.026	6.926	1.954	39.6	16.2	58.4	28.1	7.2	33.0	0.418	0.151
1.00 mm	6.38	0.21	142	0.005	3.579	0.900	22.8	10.1	27.4	15.9	4.3	18.0	0.198	0.107
1.11 mm	6.32	0.17	112	<0.005	1.894	0.258	21.1	8.6	21.1	12.2	3.8	13.7	0.159	0.058
1.22 mm	6.27	0.15	104	0.019	1.855	0.138	20.9	8.5	19.5	10.7	3.8	12.2	0.147	0.056
1.33 mm	6.24	0.14	95	0.015	1.650	0.290	19.6	8.3	17.3	9.4	3.9	11.8	0.128	0.043
1.44 mm	6.24	0.14	92	0.015	1.311	0.274	20.3	8.4	17.3	9.1	4.1	11.2	0.131	0.039
1.55 mm	6.28	0.13	90	0.023	1.285	0.208	22.3	8.1	16.6	8.4	4.0	10.5	0.135	0.042
1.72 mm	6.28	0.14	97	0.020	0.854	0.057	21.0	7.9	15.9	8.0	3.9	10.3	0.134	0.045
1.88 mm	6.29	0.13	91	0.032	1.366	0.348	21.2	7.8	15.9	7.9	3.9	10.2	0.143	0.042
2.03 mm	6.32	0.15	101	0.053	1.210	0.352	25.6	9.0	18.4	8.8	4.8	11.7	0.167	0.048
2.21 mm	6.34	0.17	112	0.085	0.366	0.103	31.6	10.4	23.0	10.1	5.5	13.4	0.217	0.065
2.42 mm	6.45	0.19	130	0.096	0.418	0.116	34.1	11.5	25.4	10.9	6.4	15.8	0.244	0.076
2.57 mm	6.53	0.18	123	0.074	0.693	0.023	26.6	10.4	21.2	9.8	5.5	15.4	0.223	0.065
2.73 mm	6.11	0.19	128	0.070	0.585	0.018	24.8	9.8	19.9	8.8	5.2	15.0	0.198	0.054
3.01 mm	6.50	0.16	108	0.071	0.447	0.018	20.1	8.4	16.2	7.8	4.8	13.1	0.182	0.051
3.06 mm	6.48	0.21	143	0.025	1.188	0.078	27.7	10.6	26.8	11.6	5.5	17.8	0.268	0.066
Rain Water (0–3 mm)	5.88	0.05	35	<0.005	0.604	<0.005	7.5	4.2	6.9	4.1	0.9	1.2	0.032	0.032
Tap Water	6.93	0.18	122	0.000	0.193	0.051	2.7	10.3	26.1	3.6	0.7	11.7	0.004	0.024

Notes: 1) Arsenic, Cadmium, Chromium, Copper, Mercury, Nickel, Selenium and Silver were either not detected or less than 0.002 mg/L, and 2) Rain Water–rainwater before contact with roof

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Table 2.7. First flush rainwater samples from Event 3

Parameter	*pH*	*Conductivity (EC)*	*TDS (mg/L)*	*Orthophosphate (mg/LP)*	*Nitrate (mg/LN)*	*Nitrite (mg/LN)*	*Sodium (mg/L)*	*Chloride (mg/L)*	*Sulphate (mg/ L SO_4^{2-})*	*Potassium (mg/L)*	*Calcium (mg/L)*	*Magnesium (mg/L)*	*Zn (mg/L)*
ADWG	6.5–8.5	<0.8	—	—	<50	<3	<300	<400	<400	—	—	—	<3
0.48 mm	6.49	0.22	150	0.13	1.182	0.013	9.8	27	19	9.1	15.7	1.8	0.126
1.26 mm	6.53	0.17	116	0.12	0.986	0.021	6.9	17	15	5.2	12.8	1.3	0.111
1.48 mm	6.52	0.13	86	0.05	1.161	0.023	4.8	10	11	3.2	10.0	0.9	0.058
1.79 mm	6.51	0.11	73	0.03	1.056	0.016	4.2	8	9	2.6	8.4	0.8	0.046
1.97 mm	6.48	0.10	67	0.02	0.870	0.010	4.0	8	7	2.7	7.6	0.7	0.036
2.06 mm	6.46	0.09	64	0.02	0.805	0.010	4.0	7	7	2.6	7.0	0.7	0.029
2.12 mm	6.50	0.09	61	0.03	0.768	0.011	3.8	7	6	2.6	6.5	0.6	0.026
2.21 mm	6.45	0.08	57	0.03	0.770	0.010	3.7	6	6	2.5	6.5	0.6	0.024
2.32 mm	6.41	0.08	52	0.03	0.739	0.010	3.8	6	6	2.4	6.3	0.6	0.024
2.53 mm	6.41	0.08	52	0.03	0.649	0.010	3.2	5	5	2.1	5.9	0.5	0.022
2.57 mm	6.40	0.07	50	0.03	0.642	0.009	3.1	5	5	2.1	5.8	0.5	0.020
2.79 mm	6.56	0.07	50	0.03	0.565	0.009	3.3	5	5	2.4	5.6	0.5	0.017
2.98 mm	6.35	0.07	53	0.04	0.522	0.008	3.5	5	5	2.5	5.8	0.6	0.021
3.04 mm	6.31	0.08	56	0.05	0.491	0.011	3.7	6	5	2.7	6.0	0.6	0.023
3.11 mm	6.30	0.08	62	0.06	0.449	0.014	4.2	7	5	3.2	6.5	0.7	0.027
3.22 mm	6.29	0.09	72	0.09	0.195	0.016	5.1	9	6	4.1	7.2	0.9	0.036
Rain Water (0–3 mm)	6.49	0.14	18	0.01	0.535	0.019	1.5	2	2	0.4	0.8	0.2	0.039
Tap Water	6.93	0.18	122	0.000	0.193	0.051	10.3	26.1	3.6	0.8	11.6	1.600	0.024

Notes: 1) Arsenic, Cadmium, Chromium, Copper, Mercury, Nickel, Selenium and Silver were either not detected or less than 0.002 mg/L, and 2) Rain Water–rainwater before contact with roof

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Other metals such as arsenic, cadmium, chromium, copper, mercury, nickel, selenium and silver were either not detected or less than 0.002 mg/L.

Ammonia, nitrate, nitrite and orthophosphate. Figure 2.5 (g) demonstrates that levels of ammonia were above the ADWG limit of 0.5 mg/L in T1-runoff during the first 1.5 mm of rainfall. The other nutrients, i.e. nitrate, nitrite and orthophosphate, did not show any consistent pattern and randomly varied with ongoing rainfall (Tables 2.5 to 2.7). Nitrate concentrations were low, ranging between 0 and 2.0 mg/L with two outlying samples at 3.5 and 7 mg/L (the ADWG limit is 50 mg/L). Nitrite concentrations were also low ranging between 0 and 0.35 mg/L with two outlying samples at 0.9 and 1.95 mg/L (the ADWG limit is 3 mg/L). Orthophosphate concentration ranged between 0 and 0.2 mg/L (Tables 2.4 to 2.6).

Anions and cations and total dissolved salts. Similar to the other tested parameters, the first flush parameters of anions and cations were typically also more concentrated in the first 3-5 mm of T1-runoff compared to the typical T1-tankwater.

First flush devices. Based on the results of this study, a typical first flush device for rainwater tanks should allow sufficient storage to capture the first few millimetres depth of runoff from a roof. To bypass 1 mm of runoff from the rainwater tank, for each square metre of roof catchment area, 1 litre of storage is required in a first flush system. An average new Australian dwelling has an estimated roof area of 250 m^2 (Australian Bureau of Statistics 2007). A first flush device installed in a rainwater tank typically consists of a 100mm diameter PVC pipe with a maximum length of 1.8m, which has a storage capacity of 14 litres. Clearly, the results of this study showed that these first flush systems cannot adequately divert first few millimetres depth of first flush runoff from the roof.

Further, the amount of water that is required to divert the first few millimetres of runoff is large and is essentially wasted. Given the quality of rainwater in the tank, the quality of the first flush and available water treatment systems, it is a viable option to treat all the rainwater including the first flush.

Organic matter in the first flush. Understanding how RWOM varies in the first flush of the roof runoff can provide valuable information for the design, maintenance, and operation of a treatment system of rain tank water. A detailed variation of molecular weight distribution (MWD) of RWOM was monitored during a period of continuous rainfall (rainfall event 15/11/08; see Table 2.4) falling on the roof (Figure 2.6). The first flush generated from up to 2 mm rainfall after contact with the roof (T1-runoff) was collected and analysed.

As rainfall fell on the roof and washed the pollutants off it, the diversion of the first part of the runoff from the roof also diverted organic contaminants away from the rainwater tank. A detailed variation of MWD of RWOM was monitored during a period of continuous rainfall on the roof (Figure 2.6). The first flush generated from up to 2 mm rainfall after contact with the roof was investigated.

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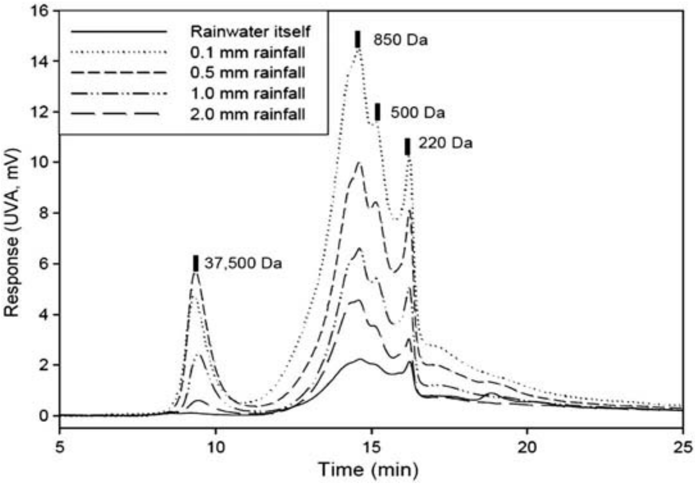

Figure 2.6. MWD of RWOM with the effects of continuous rainfall after the roof contact

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Overall, the intensity of UVA responses significantly increased following rain contact with the roof. At 0.1 mm of roof runoff, the MWD of RWOM included five major peaks, namely 37500 Da, 850 Da, 500 Da and 220 Da. According to one study, the MW of 37500 Da may be due to biopolymers, 850 Da to humic substances, 500 Da to building blocks, 220 Da to low MW acids, and less than 220 Da to amphiphilics, (Shon et al. 2006). As the roof runoff increased up to 2 mm, the intensity of the MWD of RWOM normally decreased. However, a preferential removal of specific MW was not detected, suggesting that the initial flushing carried the majority of organic contaminants. The concentration of organic matter decreased with further runoff. After 2 mm of continuous roof runoff, the intensity of the MWD peaks from the start of the runoff reduced, to the extent that it began to resemble results for T1-rainwater. This implies that diverting the initial 2 mm of rainfall from the roof can reduce the magnitude of RWOM removal process.

2.2.4 Comparison of Various Rainwater Sources

Table 2.8 compares the water quality collected in T1-tankwater, T1-first flush, T1-rainwater, urban and rural rain tank water and tap water. As described previously, the quality of the water in rainwater tanks is comparable with potable supply water with the exception of heavy metals (lead and iron) and turbidity level in the metropolitan tanks and pH in the rural tanks. In Table 2.8, non-compliance with ADWG is shown in bold. Bypassing the first flush can have a significant influence on improving the water quality in the rainwater tank. However, minimal forms of treatment will still be required especially for the metropolitan rainwater tanks.

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Table 2.8. Comparison of water quality at T1 with ADWG, rainfall and potable water

Parameter	*ADWG*	*T1 RWT**	*T1 first flush*	*Rain fall at T1*	*Rural Average*	*Urban Average*	*Ingleburn tap water (T1)*
pH	6.5-8.5	7.13	6.51	6.66	**6.19**	6.97	6.93
Conductivity (EC) (dS/m)	<0.8	0.08	0.24	0.06	—	0.07	0.179
Total dissolved salts (mg/L)	—	55.31	160	39	16.5	46.23	122
Total suspended solids (mg/L)	<400	6.17	428	6.7	<0.5	2.33	0.5
Turbidity (NTU)	<5	**5.07**	**42**	**5**	0.71	1.92	0.2
Water hardness (mg/L $CaCO_3$ equivalent)	<200	27.65	59	9	4.8	18.77	36
Orthophosphate (mg/L P)	—	0.02	0	0.07	0.014	0.03	0
Nitrate (mg/L N)	<50	0.33	0.022	0.352	0.207	0.44	0.193
Nitrite (mg/L N)	<3	0.00	0.005	0.020	<0.005	0.00	0.051
Ammonia (mg/L N)	<0.5	0.056	**3.401**	0.413	0.006	0.064	0.205
Sodium (mg/L)	<300	2.62	9.4	1.7	2.951	3.47	10.3
Potassium (mg/L)	—	1.29	4.6	0.5	0.729	0.80	0.8
Calcium (mg/L)	—	10.30	21.1	3.4	1.276	6.41	11.6
Magnesium (mg/L)	—	0.47	1.5	0.2	0.384	0.67	1.6
Chloride (mg/L)	<400	4.63	16.6	1.5	3.72	8.08	26.1
Sulphate (mg/L SO_4^{2-})	<400	1.42	18.7	7.3	5.3	2.75	3.6
Aluminium (mg/L)	<0.2	0.08	**0.308**	0.108	0.016	0.04	0.013
Copper (mg/L)	<2	0.03	0.009	0.006	0.018	0.16	0.247
Iron (mg/L)	<0.3	**1.69**	**0.875**	0.072	<0.01	**0.31**	0.007
Manganese (mg/L)	<0.1	0.02	**0.355**	0.017	0.0115	0.01	0
Lead (mg/L)	<0.01	**0.016**	**0.174**	**0.017**	<0.001	**0.010**	0
Zinc (mg/L)	<3	0.13	0.190	0.077	0.2975	0.23	0.024

Notes: 1) Average value shown, the range is given in Tables 2.1 and 2.2; and 2) values exceeding the ADWG limit are shown in bold
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2.3 RAINWATER TREATMENT TECHNOLOGIES

Some rainwater tanks incorporate simple sand filtration devices to improve water quality for potable uses. While sand filters remove suspended solids, they cannot remove most dissolved matter. By contrast, membrane filtration can remove most of these contaminants. Membrane materials have improved significantly so that they last longer, are stronger and provide higher fluxes at low pressures. In recent years, the cost of membranes has fallen significantly, and they are now affordable for the rainwater tanks application. A smart way of operating the membrane in the rainwater tank is under gravity static head. The system naturally adapts its treatment capacity to the demand for potable water. Additionally membrane backwashing will take advantage of the same pump used for water supply to the building i.e. no additional pump is necessary from an existing rainwater tank system. Further, Granular Activated Carbon (GAC) adsorption is used for pretreating rainwater as this would reduce the rate of membrane fouling and enhance the longevity of MF membrane operation.

2.3.1 Adsorption

Adsorption filtration is a well-recognized field with previous studies on wastewater, stormwater, seawater and rainwater, either with synthetic water parameters or actual water sources. The performance of filtration using GAC to determine the long term effectiveness of filtration as pretreatment for removing suspended solids, organics and heavy metals from a domestic rainwater tank was investigated.

Raw Rainwater. The raw rainwater was taken from the residential dwelling rainwater tank (T1) (see Section 2.2.3). Further details are given in Kus et al. (2010a).

Laboratory Analysis. The methods used to measure the pollutants were according to standard methods (Eaton et al. 2005). Total organic carbon (TOC) concentration of raw water and treated water was measured by using the Multi N/C 2000 analyzer (Analytik Jena AG).

GAC Adsorption Filter. The apparatus setup is shown in Figure 2.7. The GAC flow column was 500 mm in height with an internal diameter of 20 mm. The column contained tap junctions at 100 mm increments along both sides of its length with an open top for the influent hose and a tap junction at the base for the effluent. This experiment utilised the GAC adsorption filter media (Table 2.9) which was packed in the column up to a bed depth of 300 mm. The flow-rate was 5 mL/min or 1 m/hr. The water height above the GAC adsorption media was 100 millimetres. Overflow would be drained back into the raw feed tank. The raw feed tank in the laboratory was periodically topped up from the T1-tankwater when required.

During the adsorption operation, backwashing was applied to remove excess particles that can cause filter clogging. The backwashing was conducted when the flow rate of GAC filter was below 1 m/hr. During the backwashing process, the overflow pipe was rerouted from the feed tank to a waste tank. The GAC adsorption bed expanded up to approximately 30% for 2 minutes. Excess free

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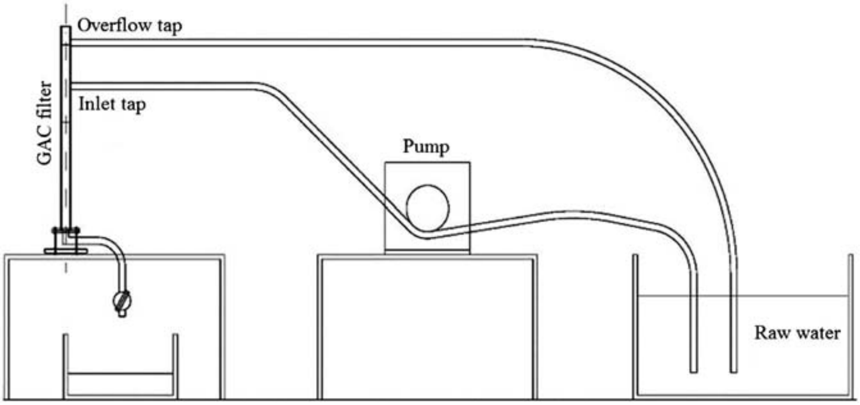

Figure 2.7. Schematic diagram of GAC adsorption filter apparatus

Table 2.9. Physical properties of granular activated carbon used

Specification	*Estimated Value*
Iodine number, mg/(g: min)	800
Maximum Ash Content	5%
Nominal size, m	3×10^{-4}
Maximum Moisture content	5%
Bulk density, kg/m^3	748
BET surface area, m^2/g	1112
Average pore diameter, Å	26.14

particles were removed from the column through the overflow pipe along with the tap water. This experiment was repeated twice.

Total Organic Carbon. Two long-term GAC adsorption filter experiments were carried out for 60 and 180 days. The experiments were monitored over the experimental period (Figure 2.8 (a)). Actual raw rainwater was used in the experiments and the water quality varied with the time of collection and varied over the duration of the experiments. During this period, the TOC of the influent (raw rainwater) fluctuated between 0.5 and 10 mg/L. Despite that, the TOC of the effluent satisfied the ADWG limit of 5 mg/L for a majority of time. Figure 2.8 (b) shows that the overall trend over the 180-day period is a decline in the TOC removal efficiency from 60% to approximately 18% at Day 180. The removal efficiency was generally over 30%, with some exceptions, for over the first 120 days. On days 35, 60, 100, and 140 the flow-rate of the filter column declined to less than the desired 1 m/hr and so a backwash cycle was initiated. Following each backwash cycle, there was a slight improvement of TOC removal before the filter reverted to the pre-backwash pattern of a general decline until day 180.

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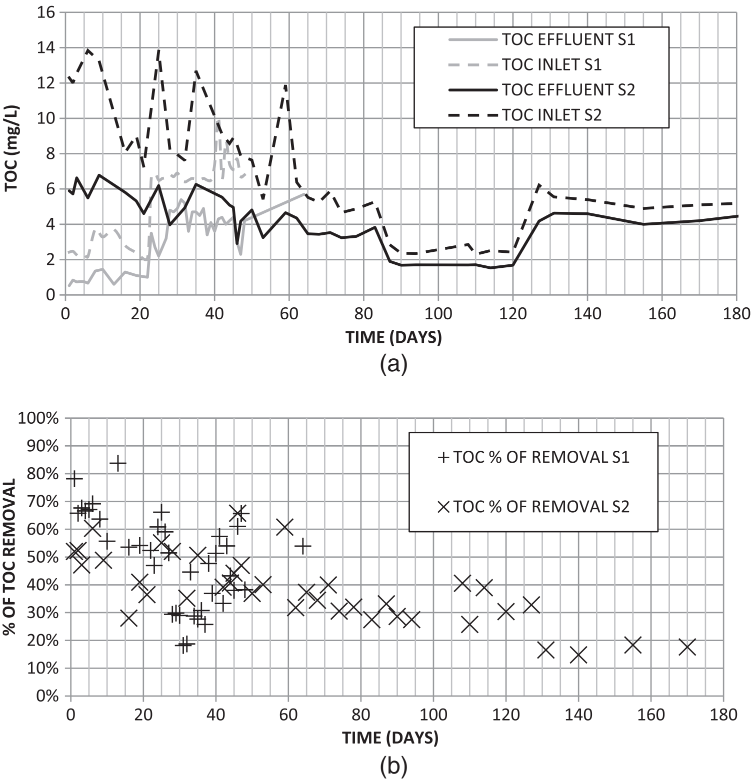

(a)

(b)

Figure 2.8. (a) TOC influent and effluent of GAC adsorption filter experiments. S1: the first experiment; S2: the second experiment. Backwash carried out on Day 25 (for S1) and Days 35, 60, 100, and 140 (for S2); (b) Graph combining TOC removal efficiency from both GAC adsorption filter experiments. S1: the first experiment; S2: the second experiment. Backwash carried out on Day 25 (for S1) and Days 35, 60, 100, and 140 (for S2)

Turbidity and Total Suspended Solids. The GAC adsorption filter performed effectively in removing turbidity (Table 2.10). The influent concentration of turbidity ranged between 6.0-0.5 NTU. The concentration of turbidity in the effluent samples was always below the ADWG limit. The results indicated low removal efficiencies during periods of low influent turbidity levels and an average removal efficiency of 39%. When the influent turbidity was higher, the removal efficiency quickly increased up to 56%.

The influent concentration of TSS all samples complied with the ADWG limit of 400 mg/L and were less than 5.5 mg/L. With an average removal efficiency (following GAC filtration) of 42%, the effluent TSS concentrations in all effluent samples were less than 3.5 mg/L.

Heavy Metal. The average concentrations of lead, iron, manganese, zinc, aluminum and copper in the influent raw rainwater was 0.009 mg/L, 0.138 mg/L,

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Table 2.10. GAC adsorption pollutant removal efficiencies

			Multiple Experiments			
Parameter	*ADWG (2011)*	*Detect Limit**	*# Samples*	*Influent*	*Effluent*	*% Removal*
Total Suspended Solids	<400	0.5	36	1.47 0.5–5.5	0.85 0.5–3.5	42%
Turbidity (NTU)	<5	0.2	36	2.03 0.5–**6.0**	1.23 0.1–4.5	39%
Orthophosphate(mg/L)	NA	0.005	36	0.048 0.004–0.152	0.028 0.005–0.096	43%
Nitrate (mg/L)	<50	0.005	36	0.514 0.011–1.025	0.320 < 0.005–0.350	38%
Nitrite (mg/L)	<3	0.005	36	0.009 0.005–0.038	0.008 0.005–0.081	NQ
Ammonia (mg/L)	<0.5	0.005	36	0.103 0.005–**1.364**	0.073 0.005–0.306	32%
Aluminium (mg/L)	<0.2	0.001	36	0.040 0.016–0.090	0.050 0.012–0.130	NQ
Copper (mg/L)	<2	0.001	36	0.009 0.004–0.016	0.004 0.001–0.010	59%
Iron (mg/L)	<0.3	0.005	36	0.138 0.006–**0.830**	0.108 0.003–**0.610**	22%
Manganese (mg/L)	<0.1	0.001	36	0.040 0.001–**0.140**	0.022 0.001–0.096	46%
Lead (mg/L)	<0.01	0.001	36	0.009 0.001–**0.031**	0.004 0.001–**0.025**	48%
Zinc (mg/L)	<3	0.001	36	0.039 0.018–0.070	0.016 0.002–0.035	58%

Notes: 1) NQ – not quantified, this parameter is not reduced by adsorption; 2) Arsenic and Cadmium were not detected; 3) 1st row - average value, 2nd row - range of value; 4) values exceeding the AWDG (2004) are shown in bold, and 5) *Detectable limits

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0.04 mg/L, 0.039 mg/L, 0.04 mg/L and 0.009 mg/L respectively (Table 2.10). While the average concentrations were all below the ADWG limit, some influent samples of lead, iron, and manganese were above this limit.

The average removal efficiency of the GAC adsorption filter for lead, iron and manganese was 48%, 22% and 46%, respectively. The concentration of manganese in all effluent samples complied with the ADWG (less than 0.1 mg/L). The concentration of lead and iron in some effluents did not comply with the ADWG limit (Table 2.10). The average removal efficiency for zinc and copper was 58% and 59%, respectively. The GAC filter was not effective in removing aluminum.

Orthophosphate, Nitrate, Nitrite and Ammonia. Orthophosphate, nitrate, nitrite and ammonia were all detected in the influent and effluent samples (Table 2.10). The average concentration of orthophosphate, nitrate, nitrite and ammonia in the influent were 0.048, 0.514, 0.009 and 0.103 mg/L and in the effluent were 0.028, 0.320, 0.008 and 0.073 mg/L, respectively. The average removal efficiency for orthophosphate, nitrate, nitrite and ammonia was 43%, 38%, NQ and 32%, respectively.

2.3.2 Membrane Filtration

Membrane filtration as post-treatment was studied to assess its performance on rainwater from a domestic rainwater tank that was pre-filtered by GAC. The effluent pollutant concentrations were compared with the ADWG.

Raw rainwater. Raw rainwater was sourced from rainwater tank (T1). Actual rainwater was used, and the water quality varied through the duration of the experiments.

Laboratory Analysis. Detailed laboratory analyses were carried out in a manner outlined in section 2.3.1.

Membrane filtration with pre-treatment. Membrane filtration experiments were carried out using a polymeric membrane from Ultra Flo, Table 2.11. It was operated in a dead-end mode of filtration. This helped to assess the relative benefits that could be obtained by pre-treating the water from rainwater tanks in

Table 2.11. Physical properties of Ultra Flo hollow fibre microfiltration membrane

Name	*Membrane*
Membrane Manufacturer	Ultra Flo
Material	Polysulfone
Pore Size	0.1 µm
Outer diameter	1.9 mm
Inner diameter	0.7 mm
No. of fibres	40
Length of fibre	400 mm
Filter Area	0.3 m^2
Method	Out - in

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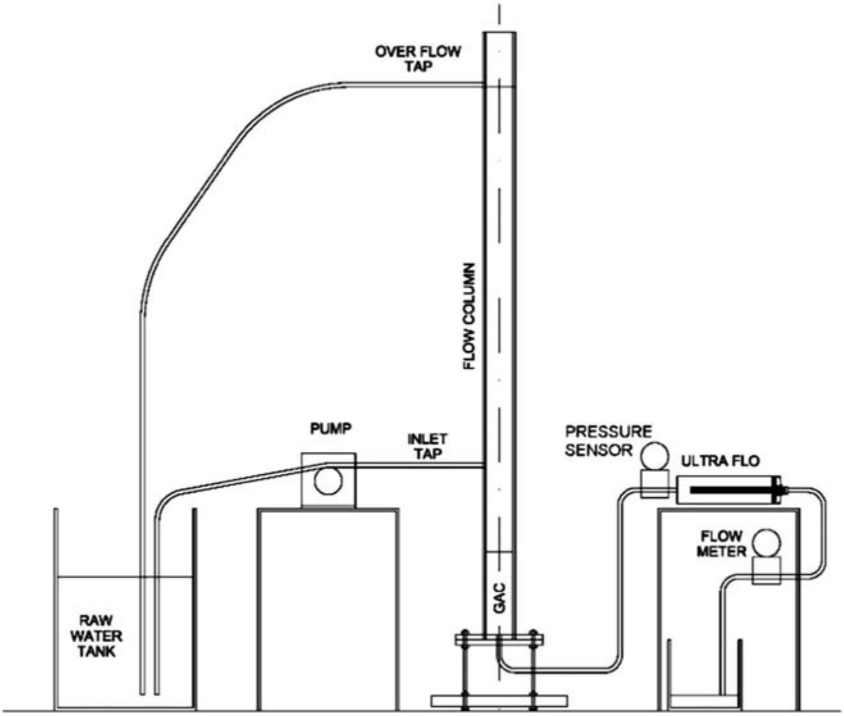

Figure 2.9. Schematic diagram of Ultra Flo hollow fibre micro-filtration membrane under the gravitational head with GAC adsorption pre-treatment
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terms of reducing membrane fouling, reducing flux decline and improving filtration performance. The experimental apparatus setup is shown in Figure 2.9. Firstly, rainwater was pre-treated by GAC adsorption filter column. Water samples of the influent raw rainwater, the pre-treated water and the effluent were collected at various times during the treatment process.

Flux Decline. Each flux decline test was analysed under a constant pressure for the entire test at 1.5, 10 and 20 kPa respectively. These results show that the GAC adsorption pre-treatment of rainwater prolonged membrane flux decline. Regardless of the driving head, a long-term flux was around 4–5 L/m^2-hr.

Raw water quality. While monitoring the flux decline of the Ultra Flo membrane filter, grab samples of the influent (rain water) and effluent from the membrane filter were collected to analyse pollutant removal efficiencies. The results of the parameters tested are shown in Table 2.12. The concentration of the water quality parameters in the raw rainwater varied significantly as the actual rainwater was used. The influent quality typically complied with most of the ADWG parameters tested (Table 2.12), except microbiological (total and faecal coliforms), iron, and lead.

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Table 2.12. Laboratory analysis of Ultra Flo hollow fibre microfiltration membrane pollutant removal without pre-treatment

			Ultra Flo Membrane filtration with GAC Pre-treatment, (14 samples)		
Parameter	*ADWG Limit*	*Detect Limit**	*Influent*	*Effluent*	*%*$^{+}$
Total Suspended Solids (mg/L)	400	0.5	1.4 (<0.5–5.0)	<0.5 (<0.5–< 0.5)	>64%
Turbidity (NTU)	5	0.2	1.8 (0.5–5.9)	0.10 (0.1–0.2)	94%
Ortho-phosphate (mg/L P)	—	0.005	76 (1–276)	15.3 (1–46)	80%
Nitrate (mg/L N)	50	0.005	0.038 (0.004–0.152)	0.016 (0.006–0.047)	58%
Nitrite (mg/L N)	3	0.005	0.538 (0.02–1.022)	0.318 (< 0.005 – 0.854)	40%
Ammonia (mg/L N)	0.5	0.005	0.008 (<0.005–0.038)	0.005 (<0.005–0.015)	28%
Total Coliforms (cfu/100 ml)	1	1	**182** (**20–1000**)	**74** (<10–**160**)	59%
Faecal Coliforms (cfu/100 ml)	1	1	**108** (<10–**1000**)	< 10 (<10–<10)	>90%
Total Organic Carbon (mg/L)	—	0.001	2.66 (2.10–3.73)	0.56 (0.068–2.12)	79%
Aluminium (mg/L)	0.2	0.001	0.038 (0.016–0.090)	0.020 (0.010–0.020)	46%
Copper (mg/L)	2	0.001	0.009 (0.004–0.016)	>0.001 (<0.001–<0.001)	>90%
Iron (mg/L)	0.3	0.005	0.135 (0.006–**0.830**)	0.0057 (<0.005–0.011)	>98%
Manganese (mg/L)	0.1	0.001	0.033 (<0.001–0.140)	0.018 (0.004–0.079)	44%

Table 2-12. Laboratory analysis of Ultra Flo hollow fibre microfiltration membrane pollutant removal without pre-treatment (Continued)

Parameter	*ADWG Limit*	*Detect Limit**	*Ultra Flo Membrane filtration with GAC Pre-treatment, (14 samples)*		
			Influent	*Effluent*	*%⁺*
Lead (mg/L)	0.01	0.001	0.008 (0.001–**0.031**)	<0.001 (<0.001–<0.001)	>87%
Zinc (mg/L)	3	0.001	0.038 (0.018–0.070)	0.012 (0.005–0.040)	67%

Notes: 1) NQ – not quantified, this parameter has not been reduced; 2) Arsenic and Cadmium were not detected; 3) 1st row: range of value, 2nd row: average value; 4) Values exceeding the AWDG (2004) are shown in bold; 5) *denotes Detectable Limits; and 5) ⁺denotes % removal

Turbidity and total suspended solids. The influent had an average of 1.8 NTU whereas the effluent from membrane filtration ranged between 0.1 and 0.2 NTU (with an average of 0.1 NTU). The overall reduction rate in turbidity was 94%.

TSS in the influent samples were quite low with an average concentration of 1.4 mg/L. The effluent from membrane filtration had a TSS concentration of less than 0.5 mg/L (instrument detection limits) or an overall average reduction of 64%.

Total organic carbon. The influent contained an average concentration of 2.66 mg/L. The GAC adsorption pre-treatment achieved an average concentration of 0.95 mg/L or a removal efficiency of 64%. The membrane filtration reduced the concentration of TOC to 0.56 mg/L giving an overall reduction of 79%. This reduction could be due to the absorption of TOC onto the membrane.

Heavy metals. While the average influent concentrations of iron, manganese and lead at 0.135 mg/L (0.06–0.83 mg/L), 0.033 mg/L (<0.001–0.140 mg/L) and 0.008 mg/L (0.001–0.031 mg/L) respectively were below the ADWG limits, some individual samples exceeded the ADWG limits. The GAC adsorption pre-treatment followed by membrane filtration reduced the average concentration of iron, manganese and lead to 0.0057 mg/L, 0.018 mg/L and 0.001 mg/L respectively, giving an overall reduction of 98%, 44% and 87% respectively.

The effluent concentrations of aluminum, copper and zinc all showed very low to negligible concentration. The removal efficiencys were greater than 67%. The concentration levels of arsenic, boron, cadmium, chromium, mercury, molybdenum, nickel selenium and silver were all negligible with concentrations <0.001 mg/L.

Microbiology. The ADWG recommend a limit of <1 CFU/100 mL for faecal and total coliform counts. Membrane filtration reduced the faecal coliform count reduced to under the detection limit (less the 10 CFU/100 mL). Total coliform

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count reduced by 59% though still more than the ADWG recommended limit (Table 2.12). Further treatment is thus required.

Orthophosphate, Nitrate, Nitrite and Ammonia. The concentration of nitrate, nitrite and ammonia in raw water samples were below the ADWG limits except one sample of the later (ammonia) being at 1.364 mg/L which was approximately two times higher than the ADWG limit (0.5 mg/L). Orthophosphate, nitrate and ammonia concentrations were reduced by 42%, 38% and 36% respectively with the GAC adsorption pre-treatment. Membrane filtration was able to reduce orthophosphate, nitrate and ammonia concentrations further with a total reduction of 58%, 40% and 39% respectively. Meanwhile, nitrite had negligible improvement. It but was reduced by 28% following membrane filtration, most likely due to the very low influent concentration which was often already near detectable limits.

Summary. Ultra Flo membrane treatment with GAC adsorption pre-treatment was able to reduce the concentration of all water quality parameters to below that specified in the ADWG. The exception was for faecal and total coliforms. Further disinfection is required as micro-filtration membrane treatment does not remove viruses.

2.3.3 Pilot Scale Application of Rainwater Treatment

A pilot scale rainwater treatment system consisting of a gravity fed GAC filter and membrane filter (Ultra Flo) was operated for a period of 120 days (Kus et al. 2013a, b). The performance of this system was assessed in terms of membrane flux and the improvement in water quality compared to the ADWG. Determination of the flux, especially in the later stages of membrane operation, was important to size the filters in a manner that meets the expected demand.

Rainwater tank and treatment configuration. A typical domestic residential rainwater tank was selected for the operational simulation of a GAC filter and membrane filter system. The rainwater tank was located within the Sydney Metropolitan basin at Peakhurst, approximately 1 km south of a heavily trafficked motorway and 10 km west of Sydney's domestic and international airport. The tank and house (with a typical concrete glazed tile roof and aluminium guttering) are five years old. The rainwater tank was a PVC tank with a total volume of 3000 litres, PVC plumbing and brass fittings. For the duration of the pilot trial, the rainwater tank was connected directly to feed the treatment system (GAC filter and membrane filter) (Figure 2.10). Potable grade hose lines were installed between the rainwater tank and the filter system connections.

Filter configuration. Detailed characterisation of the rainwater tanks (Kus et al. 2010a, b) had highlighted that turbidity and heavy metals and in particular lead, were not compliant with the ADWG. These findings have been reflected in other studies (Magyar et al. 2007, 2008). Further, dissolved organic carbon (DOC) is known to cause membrane fouling. Therefore, reducing its concentration will improve membrane performance and prolong membrane life. The GAC filter was used as a first step to remove DOC in particular and also to reduce the turbidity (see section 2.3.1). The DOC and lead associated with particulates were also removed. Membrane filtration removed any remaining solids and concentrations

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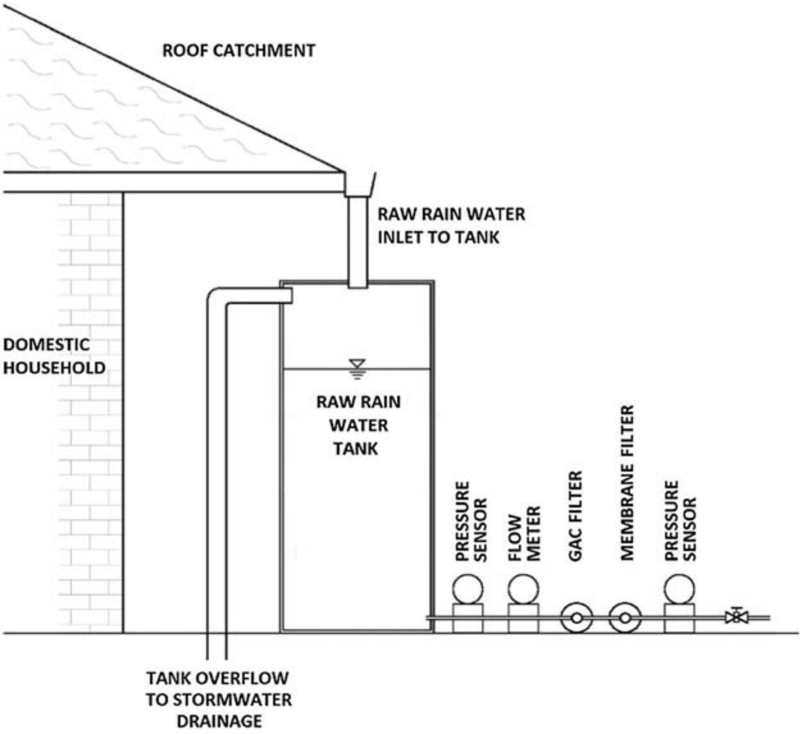

Figure 2.10. Schematic diagram of the household rainwater harvesting system with a pilot scale gravity driven membrane based filter system
Source: Kus et al. (2013a, b); reproduced with permission from IWA Publishing

of turbidity, DOC and lead (see section 2.3.1). Further, the membrane filter can screen coliforms although it is acknowledged that further disinfection treatment (with very small dose) is required to guarantee all viruses are removed.

A pilot-scale treatment system was developed and comprised of a pre-treatment of GAC filter (Watts-Ultraflo) followed by a membrane filter (Ultra Flo). The characteristics of the GAC and membrane filter are given in Table 2.13 and Table 2.14 respectively. GAC of 0.3 mm was packed in a column. The volume of GAC was 0.4 L. The membrane had a surface area of 0.4 m^2 and pore size of 0.1 µm. This system was operated in dead-end mode. The raw water was passed through the two filters, each with a volume of 0.4 L. As the pilot scale system was operated under gravity head, the 2 filter columns were placed horizontally and located at the base of the rainwater tank to take advantage of the full water head available from the rainwater tank (Figure 2.10).

The raw rainwater was passed through two filters in a continuous operating system where the effluent from the GAC filters passed through to the membrane filter. An available water head of up to 2 m in the rainwater tank drives the flow though the GAC filter and membrane filter. The pilot scale treatment system was

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Table 2.13. Physical properties of granular activated carbon used

Specification	*Property*
Manufacturer	Watts
Specified Treatable Capacity	1500 Gallons (~5700 L)
Iodine number, mg/(g: min)	800
Maximum Ash Content	5%
Nominal size, m	3×10^{-4}
Maximum Moisture content	5%
Bulk density, kg/m^3	748
BET surface area, m^2/g	1112
Average pore diameter, Å	26.14
Media Volume	4×10^{-4} m^3

Table 2.14. Physical properties of Watts (Ultra Flo) hollow fibre micro-filtration membrane

Specification	*Property*
Membrane Manufacturer	Ultra Flo
Material	Polysulfone
Specified Treatable Capacity	1500 Gallons (~5700 L)
Pore Size	0.1 μm
Outer diameter	0.45 mm
Inner diameter	0.25 mm
No. of fibres	1000
Length of fibre	300 mm
Filter Area	0.4 m^2
Method	Out - in

operated continuously for 120 days. In this pilot scale study, the GAC filter and membrane filter were not backwashed except on two occasions (day 8 and 12). This was done to determine the performance of the treatment system under low maintenance conditions, determine how long the filters would operate effectively without backwash and quantify the flux. Determination of the flux in the final stage of membrane operation (with no backwash) was important to be able to size the membrane area in a manner that meets the expected demand. Both filters were backwashed for 30 seconds on two occasions, eighth day and 12th day, to observe the impact of backwashing on the flux and what improvement it made. During the backwashing process, the flow was passed through the two filters in the reverse direction from normal operation. The influent flow pipe was rerouted from the rainwater tank to a waste drain. Excess free particles were removed from the column filter along with the tap water.

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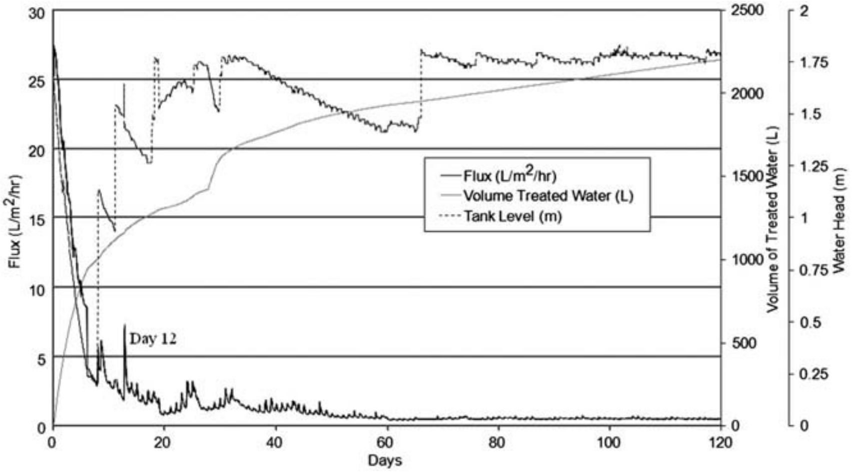

Figure 2.11. Membrane flux decline over the duration of the pilot sale study. Also shown is the water head in the rainwater tank, and the volume of water treated
Source: Kus et al. (2013a); reproduced with permission from IWA Publishing

Detailed laboratory analyses were carried out to determine the concentration of individual pollutants in a manner outlined in section 2.3.1. Data logging equipment was utilised to monitor the flow rates (Endress & Hauser Promag 10 H) and the driving head on the membrane. The flow rate was only controlled by the flux limitation through the treatment system and the available driving head. The available head was monitored using a calibrated pressure transducer (Endress & Hauser PMC 131) connected to a data logger (Endress & Hauser Eco Graph T RSG30) which represented the head available from the membrane to the top of water level in the rainwater tank. The tanks water level only increased when there was rainfall.

Flux decline. The membrane flux decline was monitored over 120 days as shown in Figure 2.11. During this period, the membrane was backwashed twice (on day 8 and day 12) for a period of 30 seconds. On both occasions, there was an increase in flux which lasted only several hours before it reduced to levels that existed prior to the backwash. No other backwash was undertaken. The flux reduced from 27 L/m^2/hr to a stable flux of 0.47 L/m^2/hr over a period of 60 days. The membrane filter ran at steady state conditions for the remaining 60 days where the flux was nearly constant.

Turbidity. The treatment train of the GAC filter followed by membrane filtration reduced the turbidity by 78% (0.6-0.41 NTU) (Figure 2.12, Table 2.16). The GAC filter achieved significant reductions in turbidity (Figure 2.12). Membrane filtration provided additional turbidity removal of up to 20%. The turbidity following membrane filtration was small and below 0.4 NTU whereas the ADWG limit is 1 NTU.

DOC. The GAC treatment was capable of reducing the influent DOC concentrations from an average of 0.42 mg/L to 0.12 mg/L (Figure 2.13,

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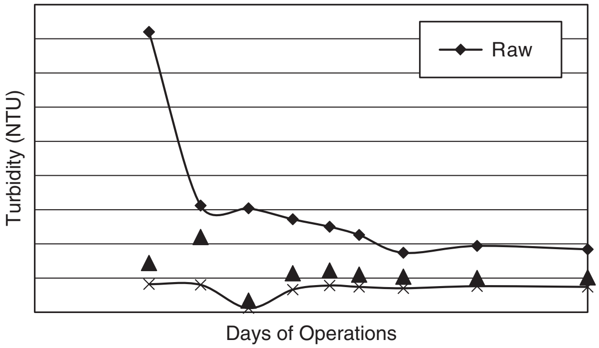

Figure 2.12. Turbidity results with GAC filter followed by membrane filter filtration. DOC following sand filter not shown

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Table 2.15). The ADWG limit for DOC is 0.2 mg/L. In the initial period, during the first 30 days of operation, the DOC in the effluent was higher at approximately 0.4 mg/L. This corresponds to a period of the development of biofilms on the GAC. Beyond this initial period, after 30 days of operation, the concentration of DOC reduced to below detectable limits. The removal efficiency of DOC during this period was at times more than 99%. The membrane filter system used as post-treatment to the GAC filter indicated only a small improvement in the DOC removal, particularly during the initial period of the first 30 days. DOC is known to cause membrane fouling (especially organic and subsequently bio-fouling) and reducing its concentration will improve membrane performance and prolong membrane life in treatment systems that incorporate it. Further, organic matter in the water caused membrane fouling and led to carcinogenic compounds upon chlorination.

Heavy metals. The influent (raw rainwater) itself generally had low concentrations of heavy metals (Table 2.15). There were even no traces of cadmium, selenium, silver or mercury detected in the samples. The concentration of aluminium, arsenic, copper, iron, manganese, and nickel were below ADWG limits. However, the concentration of lead was notably above the ADWG limit.

The treatment system performed effectively with significant reductions in most heavy metals. The lead concentration in the effluent was reduced to below 0.005 mg/L, which was below the ADWD limit of 0.01 mg/L. Aluminium, iron and manganese were reduced to below detection limits. The concentration of these heavy metals in the effluent was well within the ADWG limit (Table 2.15).

It was observed that the levels of both copper and zinc were not improved by filtration and actually increased from the initial raw rainwater samples taken from the tank. This is due to the in-situ connections of the rainwater tank, and effluent tap comprising of brass fittings which are a copper/zinc alloy. As brass is the

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Table 2.15. Turbidity and DOC results based on samples taken during the pilot trial

Parameters	*ADWG Limit*	*Detectable Limit*	*Tap Water*	*Raw Water**	*GAC Filter*	*Pre-Treatment + Membrane**	*GAC + Membrane Filter Removed (%)**
Turbidity (NTU)	1^+	0.2	<0.5	1.52 (0.87–4.1)	0.58 (0.17–1.1)	0.34 (0.06–0.41)	78%
Dissolved Organic Carbon (mg/L)	0.2	0.001	<5	0.42 (0.16–0.84)	0.12 (<0.001–0.56)	0.09 (<0.001–0.42)	78%
Aluminium (mg/L)	0.2	0.005	0.013	0.011	0.010	<0.005	>55%
Copper (mg/L)	2	0.001	0.247	0.004	0.018	0.027	No Improvement
Iron (mg/L)	0.3	0.005	0.007	0.006	0.010	<0.005	>16%
Manganese (mg/L)	0.1	0.001	<0.001	0.002	0.002	<0.001	>50%
Lead (mg/L)	0.01	0.001	<0.001	0.011	0.005	0.005	55%
Zinc (mg/L)	NA**	0.001	0.024	0.033	0.514	0.504	No Improvement

* average value followed by range of values; ** Insufficient data to set a guideline value based on health considerations. Water for aesthetic use has a guideline limit of 3 mg/L; $^+$ to maintain effective disinfection a limit of 1 NTU is necessary

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Table 2.16. Fractionation of organic compounds by LC-OCD

Sample	*DOC Dissolved mg/l, % DOC*	*HOC Hydrophobic mg/l, % DOC*	*CDOC Hydrophilic mg/l, % DOC*	*BIO-polymers mg/l, % DOC*	*Humic Substances mg/l, % DOC*	*Building Blocks mg/l, % DOC*	*LMW Neutrals mg/l, % DOC*	*LMW Acids mg/l, % DOC*
Raw rainwater	1.74 100%	0.53 30.3%	1.20 69.7%	0.09 5.2%	0.44 25.3%	0.21 12.0%	0.43 24.6%	0.05 2.6%
GAC filter and membrane filter	1.14 100%	0.38 32.9%	0.77 67.1%	0.04 3.8%	0.50 43.3%	0.09 8.2%	0.01 9.7%	0.02 2.1%

LMW = low molecular weight

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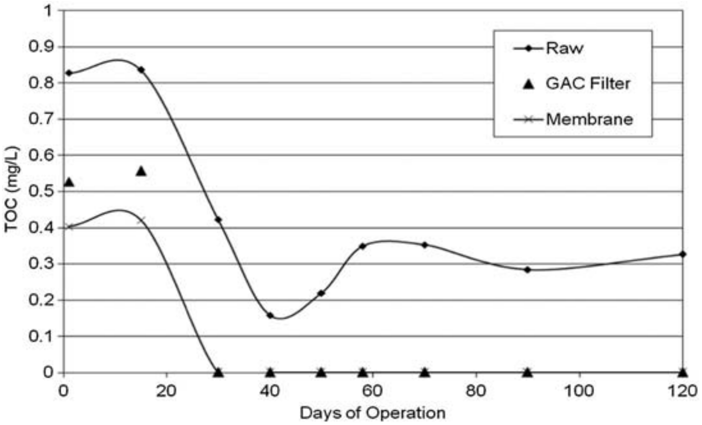

Figure 2.13. DOC results with GAC filter followed by membrane filter filtration. DOC following sand filter not shown
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common material used for connections in domestic residential tanks in Australia, and also copper for the internal plumbing of houses, it is expected that both higher levels of copper and zinc is likely found in samples collected from a residential tap. The concentration of copper and zinc in the effluent remained below ADWG limits.

Organic matter characterization. Categorisation of organic matter was conducted for raw rainwater and after treatment (Table 2.16). It was found that the concentration of DOC of the raw rainwater was 1.74 mg/l out of which 30.3% was hydrophobic and remaining 69.7% was hydrophilic. In hydrophilic portion, the majority of the substances was biopolymers (5.2%), humic substances (25.3%), building blocks (12%) and lower molecules neutrals and acids (24.5 and 2.6 respectively).

After treatment of raw stormwater through GAC filtration followed by membrane filtration, the concentration of DOC was found to be 1.14 mg/l which represents a 34% removal. The majority of organic matter was hydrophilic (32.9%) compared to 67.1% of hydrophobic organic matter. In hydrophilic portion, the majority of the substances were biopolymers (3.8%), humic substances (43.3%), building blocks (8.2%) and lower molecules neutrals and acids (9.7% and 2.1% respectively). It was found that rainwater treated with the GAC filter had a majority of organic substances removed. GAC filter removed all types of organics. In general, membrane filtration can remove only the small amount of organics that is associated with suspended particles.

Summary. This study reported the results of monitoring and evaluation of the improvement in rainwater quality and quantified the flux decline from a gravity fed GAC and membrane filter system during a 120 day pilot scale trial at a residential household within the Sydney metropolitan area.

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This study followed a detailed water quality characterisation of rainwater tanks within the Sydney metropolitan area (Kus et al. 2010a) which identified turbidity, DOC and heavy metals and in particular lead, as these parameters did not comply with the ADWG. A comparison with tap water showed a similar result. A treatment system was configured to reduce the concentrations of these parameters.

The treatment system of GAC filter and membrane filter was effective in reducing turbidity, DOC and heavy metals. The system reduced the turbidity by an average of 78% (0.6-0.41 NTU), below the ADWG limit of 1 NTU. The concentration of DOC was reduced to below the ADWG limit of 0.2 mg/L. The concentration of lead was reduced to an average of 0.005 mg/L and below the ADWD limit of 0.01 mg/L. The concentration of all other heavy metals was well within the ADWG limit. The GAC filter was necessary to reduce the turbidity, lead and DOC. The use of micro-filtration was as a security filter is relevant to achieve physical disinfection and removal of solids in emergency situations where there is a high turbidity load. The micro-filtration will reduce the disinfectant dose significantly. Further, the GAC filter removed a majority of the organic substances from raw rainwater. After an initial flux decline, the stable flux achieved was 0.47 L/m^2/hr over the final 60 days of the experiment.

2.4 PRACTICAL IMPLICATIONS

In urban areas, rainfall events and the stormwater arising from them do not last for more than several hours. Stormwater discharge is relatively high and, therefore, needs to be treated at a high rate. The alternative to a high rate treatment is to collect and store the stormwater before treatment. Raw stormwater in storage will degrade under anaerobic and anoxic condition while pretreatment of stormwater adds value to the stored water and can be beneficially reused. When stormwater is treated at a high rate the need to store stormwater before treatment is alleviated. These high rate treatments include media filters, and these are given in Kus et al. (2012a, b). The filters performed at a high rate (10 m/hr) and were able to remove suspended solids, organic matter and heavy metals in a consistent manner despite fluctuation in the influent concentration of these pollutants. The effluent was of similar quality to raw rainwater and suitable for non-potable purposes such as irrigation of gardens and lawns, car washing and so on (Kus et al. 2013a, b). Stormwater, which can be typically collected from the property surrounding the building, treated in this manner can be stored together with raw rainwater in a manner shown in Figure 2.14.

The treated stormwater in storage may be augmented by roof rainwater (Figure 2.14) which has commensurate quality, and both can be stored in the same tank. In this way, the contributing catchment increases from just the building roof to the whole site increasing the amount of water that can be captured and stored for reuse. In medium-scale developments, rainwater tanks typically empty quite quickly due to demand and often are augmented by town water.

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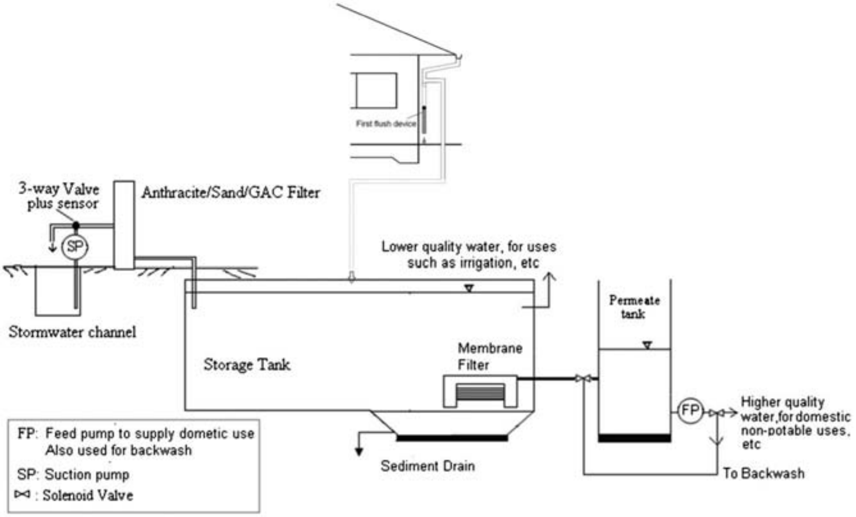

Figure 2.14. Possible prototype application of high rate media filtration followed by membrane filtration membrane (operated under the gravitational head)

The stored water (both treated stormwater and rainwater) can be filtered under gravity through membrane filters. Though the filtration rate is slow, the water quality of the effluent is high, and for many parameters achieves drinking water standard (Tables 2.16 to 2.17 and Figures 2.12 to 2.13). The volume of water required for potable purposes is less compared to non-potable uses. This system can be suitably configured to meet these different demands.

Concentrated pollutants remaining after treatment and sludge can be discharged to the sewer alleviating sludge disposal problems and is attractive in creating a low maintenance system. Further, it significantly reduces the stormwater pollution leaving the site and transported downstream into the receiving water. It is possible to create a sustainable development with a low demand for town water, low stormwater pollution export and reduce stormwater discharges. It is vital as such a system is ideal for inner city areas for application in medium scale development such apartment complexes, business parks and so on. The benefits of a successful harvesting scheme are reductions in (i) demand for town water; (ii) stormwater pollution loads to downstream waterways and estuaries; and (iii) stormwater volumes, flows and the frequency of run-off.

2.5 ACKNOWLEDGMENTS

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CHAPTER 3

Stormwater Treatment Technology for Water Reuse

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3.1 INTRODUCTION

With the world's total population predicted to increase to 9.3 billion by 2050, the majority of whom will live in urban areas (UNDESA 2012), pressure on urban water resources will increase significantly. For example, water demand for Australia's five largest cities is projected to increase by over 40% by 2030 (Cook et al. 2012) in a moderate growth scenario. These five cities have already experienced severe water shortages resulting in water restrictions (e.g. Sydney 2000-2009). Managing scarce and unpredictable water resources will therefore be a major challenge for policy makers, water resource managers, scientists and engineers, noting that future climate change will also increase the variability of both rainfall and runoff (Kamruzzaman et al. 2013). A key strategy is to shift from conventionally derived water resources to alternative water supplies such as recycled wastewater, seawater reverse osmosis and stormwater harvesting and to build a diversified water supply portfolio that increases resilience. Here we will focus on stormwater harvesting and reuse.

While roof water harvesting and reuse is common in many parts of the world, local harvesting and reuse of stormwater from hard surfaces is a relatively new practice. In many of Australia's capital cities, the annual volume of stormwater runoff is comparable to the total potable water demand (Mitchell et al. 1999), hence harvesting of this resource can potentially provide a significant alternative water supply (Philip et al. 2008). As only a fraction of water used needs to be of drinking water standard (Mitchell 2004; DEC 2006), many water uses can be supplied by water of a lesser quality. Community acceptance of using treated stormwater is also higher than that using treated wastewater (DEC 2006), and a number of government programs have aimed to encourage both roof water harvesting and stormwater harvesting in Australia. The overall objective of these

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[1] Univ. of Technology, Sydney, Australia.

[2] Univ. of Technology, Sydney, Australia.

[3] Univ. of Technology, Sydney, Australia.

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programs has been to relieve pressure on scarce water resources and the uptake by local government organisations and other large water users has been significant. Roof water often can be used without further treatment, especially for non-potable purposes. In contrast, stormwater generally contains higher concentrations of pollutants and in most cases, treatment is required.

In addition to helping relieve stress on the main water supply, stormwater harvesting schemes can also have other benefits such as reducing the impact of urban development on local waterways by improving water quality and helping to maintain a natural flow regime and stream flows (Fletcher et al. 2007). The practice of stormwater harvesting also has the potential to provide water at less ongoing energy consumption per unit of water supplied than if mains water is used (refer to Case Studies 3.1 and 3.2). While stormwater reuse can be environmentally beneficial, impacts on local ecosystems in the receiving water from which stormwater is extracted needs to be considered (Fletcher et al. 2007), for example, the environmental impact of producing the infrastructure and constructing the stormwater harvesting system. The overall result of a system will be site-specific. Ongoing energy consumption will be influenced by the quality of the source water, the level of treatment required and the treatment technology implemented to achieve the specified management objectives.

A number of case studies of operating stormwater harvesting schemes are used throughout this chapter to illustrate how currently operating schemes compare to requirements and guidelines. These include:

- Turramurra stormwater harvesting scheme, refer Case Study 3.1. Stormwater is treated using conventional stormwater treatment techniques (biofiltration) and is used only for outdoor irrigation without disinfection.
- Greenway Park stormwater harvesting scheme, refer Case Study 3.2. Stormwater is treated using conventional treatment methods (Gross pollutant trap) and disinfected before reuse for outdoor irrigation.
- Blackmans Swamp Creek stormwater harvesting project, refer Case Study 3.3. Stormwater is harvested to supplement potable water supply.

The literature reviewed has been sourced mainly from Australia as stormwater harvesting is relatively common, and there is a large body of research in this field. The literature on stormwater treatment technology associated with stormwater harvesting has also been sourced mostly from Australia and the U.S. along with data on stormwater quality augmented with literature from other parts of the world.

3.2 SOURCES AND CHARACTERISTICS OF STORMWATER

Stormwater is surface runoff from both pervious and impervious surfaces, predominantly in an urban environment from man-made hard surfaces such as roads and carparks (Philip et al. 2008). As the runoff travels overland, it picks up

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pollutants that are ultimately transported to the receiving water. The catchment's characteristics will have a great impact on the chemical characteristics of the stormwater (Eriksson et al. 2007). Stormwater can contain a wide range of pollutants that can be physical, chemical and biological. These include gross pollutants, suspended solids, nutrients, metals, chemicals of concern such as pesticides/herbicides, alkyl phenols, pharmaceutical and personal care products, surfactants, phenols, aromatic hydrocarbons, etc. (Aryal and Lee 2009; Kaczala et al. 2012; Zgheib et al. 2012; Gasperi et al. 2013; Loganathan et al. 2013; Sidhu et al. 2013; Tang et al. 2013).

While concentrations of pollutants in stormwater vary considerably between storm events and between individual catchments, roads are generally a major source of contaminants in urban runoff while agricultural catchments generate the highest concentrations of suspended solids, total nitrogen and total phosphorus (Duncan 1999). Table 3.1 for example shows mean concentrations with standard deviation for suspended solids, total phosphorus, total nitrogen and copper respectively for different catchments types from selected studies and is compared to stormwater quality data from Case Study 3.1.

Critical to stormwater reuse is the ability of any treatment system to cope with a highly variable pollutant concentration. At the same time, it must provide treated water of a consistent and acceptable quality suitable for the end-user. There is also growing evidence that stormwater drainage systems can be contaminated with sewage due to failing sewer infrastructure and cross-connections between stormwater and sewage networks (Noble et al. 2006; Rajal et al. 2007; Sercu et al. 2009). This can lead to an increased risk of pathogen exposure from stormwater harvesting schemes (Sidhu et al. 2013).

3.3 WATER QUALITY TREATMENT CRITERIA

3.3.1 Non-Potable Water Guidelines

The most common application of stormwater reuse in Australia is for outdoor irrigation (Hatt et al. 2006; NRMMC 2009), but treated stormwater can also be used to supplement other non-potable uses such as flushing toilets, washing clothes, firefighting and in cooling towers. More recently instances have emerged where stormwater has been harvested for indirect potable reuse (see Case Study 3.3). The water quality criteria will depend on the application, and the treatment required to meet these standards will be influenced by the source of the stormwater. As noted in the previous section, stormwater quality can vary significantly between different catchments and between different storm events.

The Australian Guidelines for Water Recycling, Stormwater Harvesting and Reuse – Phase 2 (NRMMC 2009) include treatment criteria for a range of uses, and has been developed on the basis that most stormwater reuse schemes in Australia are relatively small and are operated by organisations rather than water utility companies, for example, local councils and golf clubs (DEC 2006). If a

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Table 3.1. Pollutant concentration for different land uses expressed as mean EMC (mg/L)

	Suspended Solids			*Total Phosphorus*			*Total Nitrogen*			*Total Copper*			
Catchment type	*Sample[1] size*	*Mean*	*Std. dev.*	*Sample[1] size*	*Mean*	*Std. dev.*	*Sample[1] size*	*Mean*	*Std. dev.*	*Sample[1] size*	*Mean*	*Std. dev.*	*Source*[*]*
High urban road	29	779	0.46										[1]
Low urban road	8	229	0.66										[1]
All roads				20	0.42	0.44	12	2.70	0.30	23	0.17	0.44	[1]
Roofs	11	47	0.38							16	0.06	0.56	[1]
Residential				6	0.15	0.34				59	0.06	0.42	[1]
High urban	247	294	0.48				139	3.40	0.28				[1]
Non-residential High urban				116	0.46	0.4				81	0.13	0.49	[1]
Low urban										6	0.04	0.19	[1]
Parking lot	29	152		29	0.18		29	1.96					[2]
Parking lot	23	49.5		23	0.19		23	1.68		23	0.013		[3]
Suburban residential (case study 6.1)	4	70		4	0.1775		4	1.225		4	0.027		[4]

[*] [1] = Duncan (1999); [2] = Brown and Hunt (2011); [3] = Hunt et al. (2008); [4] = Turramurra stormwater harvesting system, NSW, Australia. Note that Sample Size in Duncan (1999) is number of studies, each comprising a number of storm events, while for Hunt et al. (2008), Brown and Hunt (2011) and the case study, Sample Size refers to the number of storm events

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stormwater-reuse scheme is for open-space irrigation only, the process of complying with the guidelines is relatively straight forward. A more stringent assessment is required where stormwater is plumbed into buildings for toilet flushing or other indoor uses. This is due to the risk of cross-connection, as the potential exposure due to such an accidental occurrence would be much higher than the exposure from any intended use.

Water quality criteria will also vary for different elements of a stormwater reuse scheme. For an outdoor irrigation system, the main pollutants of concern for the irrigation infrastructure itself will be objects that can damage pipes and sprinkler heads such as gross pollutants, coarse particles and suspended solids. Excessive nutrient concentrations may also lead to biofilm growth that can block irrigation lines. Hard water may cause calcification and blockage of irrigation lines in the long term. Elevated iron levels may cause problems with iron bacteria that can clog or damage irrigation infrastructure. Stormwater quality criteria for open space irrigation infrastructure are presented in Table 3.2 along with data from Case Study 3.1. As shown in Table 3.2, based on the parameters tested, stormwater from the Turramurra scheme is unlikely to cause problems for the irrigation system during the life of the infrastructure.

For the vegetation being irrigated, the main concerns will be environmental health where the predominant environmental hazards from stormwater irrigation are cadmium, hydraulic loading, iron, nitrogen and phosphorus (NRMMC 2009). The primary pollutants of concern for people using the facility and who could potentially be exposed to the irrigation water are human-derived pathogens, mainly originating from sewer overflows or cross-connections.

Where stormwater is used to substitute non-potable uses such as toilet flushing or washing clothes and where water is returned to the sanitary sewer after use, the main concern is also the exposure to pathogens. Aesthetic appearance will also be important in such applications. While both metals and organic chemicals could potentially pose a risk to human health even in non-potable reuse schemes, it is likely that they will be present at such a low concentration that they will not pose an acute risk to human health when pathogens have been removed satisfactorily (NRMMC 2009; Page and Levett 2010). The risk of exposure to pathogens from reused stormwater is based on a tolerable dose (maximum number of infectious organisms per person per year) and is the product of concentration multiplied by the volume of water consumed per year. Where no site-specific data is available, standard values can be used, these being available in NRMMC (2009).

As an example, the potential exposure (volume of water consumed) from combined toilet flushing and laundry use is much lower than the potential exposure from open-space irrigation (NRMMC 2006). This would suggest that a lower level of treatment is required. However, the treatment requirements for any use where stormwater is plumbed into a building are stringent. This is due to the risk of cross-connection, as the potential exposure should an accidental cross-connection occur would be much higher than the exposure from any intended use.

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Table 3.2. Indicative stormwater treatment criteria for public, open space irrigation for managing operational risks

	Stormwater treatment Design life[1]		*Turramurra stormwater reuse*		
	up to 20 years	*up to 100 years*	*Raw stormwater*	*Treated stormwater*	*Duncan (1999)*
Suspended solids	<50 mg/L	<30 mg/L	38–90 mg/L	6–9 mg/L	2.8 – 14,541 mg/*L*
Coarse particles (⊘)	<2 mm	<1 mm	Not tested	Not tested	Not reported
Iron (total)	<10 mg/L	<0.2 mg/L	Not tested	Not tested	0.22–38 mg/L
Phosphorus (total)	<0.8 mg/L	<0.05 mg/L	0.07–0.44 mg/L	0.05–0.09 mg/L	0.01–4.7 mg/L
Hardness ($CaCo_3$)	<350 mg/L	<350 mg/L	15–36 mg/L	33–60 mg/L	Not reported

[1] NRMMC (2009)

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Treatment requirements for a range of stormwater reuse applications are presented in Table 3.3, along with data from Case Study 3.2 where disinfection is used. As shown, even though stormwater is only used for irrigation, the inclusion of disinfection (ultraviolet (UV) light) in the design could potentially allow reuse for other purposes as well.

The presence of Faecal Coliforms and specifically the indicator bacteria *E. coli* may indicate sewerage contamination. However, *E. coli* can be present in stormwater from sources other than sewerage such as animal droppings. No statistically valid relationship has been found to exist between levels of pathogens and *E. coli* (NRMMC 2009). Nevertheless, it is routinely measured for two reasons. Firstly, its test is relatively cheap and easy. Secondly, guidelines often include recommended maximum or median values on *E. coli* concentration for stormwater reuse. Reduction in *E. coli* concentration may indicate the effectiveness of the disinfection systems in removing pathogens present in the treated water as well. Stormwater treatment criteria for managing the public health risk for open-space irrigation schemes are shown in Table 3.4 along with data from Case Study 3.2. The results show that, even though the design had complied with typical requirements for outdoor irrigation, the measured effluent water does not meet the water quality criteria. This may indicate a problem with the treatment system or with ongoing maintenance.

It is worth noting that treatment requirements for public health are generally expressed as a $\log_{10}$ reduction rather than as an absolute concentration, reflecting the variable concentration of pathogens found in stormwater. The equivalent reduction in exposure to pathogens can be achieved by both treatment and control of on-site exposure. Table 3.5 includes a summary of the equivalent log reduction from on-site exposure control measures along with information from Case Study 3.1.

When determining a suitable treatment strategy, it is important to consider all aspects of the system as the water quality requirements may be different. The risk of accidental exposure and cross-connection with the potable water supply (and hence, increased treatment requirements) must also be weighed against the potential benefits derived from adding such uses to the reuse scheme. For example, adding toilet flushing as a part of an outdoor irrigation scheme will require a higher level of treatment whereas the potential volume of water saved is likely to be small compared to the volumes used for irrigation. The cost, both capital and for ongoing maintenance, of providing the additional treatment will have to be weighed against the potential benefits to water conservation from adding toilet flushing to the scheme.

3.3.2 Potable Water Guidelines

While most current stormwater harvesting systems are merely for outdoor irrigation, with an increased population and pressure on water resources, stormwater harvesting for indirect potable reuse is likely to become more common. Indirect potable reuse refers to diverting previously treated stormwater to a raw water source before it is later harvested for potable water. As such, treatment

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Table 3.3. Tolerable pathogen levels and required reductions for stormwater reuse and design compliance from Greenway Park stormwater harvesting scheme (see Case Study 3.2)

Use	*Reference pathogen*	*Tolerable concentration (infectious Units/L)*[1]	*Required reduction*[1]		*Greenway Park stormwater reuse, applying UV disinfection*
Municipal, including open-space irrigation and nonpotable construction activities (e.g. dust suppression, earthworks compaction) (exposure = 50 mL/person/year)	Rotavirus	0.050	95.0%	1.3 log	>3.0 log
	Cryptosporidium	0.32	82.2%	0.8 log	>3.0 log
	Campylobacter jejuni	0.76	95.9%	1.3 log	3.0–4.0 log
Dual reticulation for indoor and outdoor use: (exposure = 667 mL/person/year) Toilet flushing: 11 mL Laundry use: 1 mL Garden irrigation: 200 mL Garden food crops: 90 mL Cross-connection: 365 mL	Rotavirus	0.0037	99.6%	2.4 log	>3.0 log
	Cryptosporidium	0.024	98.7%	1.9 log	>3.0 log
	Campylobacter jejuni	0.057	99.6%	2.4 log	3.0–4.0 log
Firefighting: (exposure = 1000 mL/person/year)	Rotavirus	0.0025	99.8%	2.6 log	>3.0 log
	Cryptosporidium	0.016	99.1%	2.1 log	>3.0 log
	Campylobacter jejuni	0.038	99.8%	2.6 log	3.0–4.0 log
Commercial food crops (exposure = 490 mL/person/year)	Rotavirus	0.0051	99.5%	2.3 log	>3.0 log
	Cryptosporidium	0.033	98.2%	1.7 log	>3.0 log
	Campylobacter jejuni	0.078	99.5%	2.3 log	3.0-4.0 log
Non-food crops (e.g. trees, turf, woodlots, flowers) (exposure = 50 mL/person/year)	Rotavirus	0.050	95.0%	1.3 log	>3.0 log
	Cryptosporidium	0.32	82.2%	0.8 log	>3.0 log
	Campylobacter jejuni	0.76	95.9%	1.3 log	3.0-4.0 log

[1] NRMMC (2009)

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Table 3.4. Stormwater treatment criteria for public health, open-space irrigation (no access control) for managing health risks

Parameter	*Stormwater treatment criteria*[1]	*Greenway Park harvested stormwater after treatment and UV disinfection*[2]
Disinfection	>1.5 $\log_{10}$ (96%) reduction of virus and bacteria	
	>0.8 $\log_{10}$ (82%) reduction of protozoan parasites	
	E. coli <10 colony forming units (CFU)/100 mL (median)	*E. coli* 15 CFU/100 mL (median)
Turbidity	<25 NTU (median)	3.5 NTU (median)
	100 NTU (95th percentile)	18 NTU (80th percentile)
	Provided the disinfection system is designed for such water quality that, during operation, the disinfection system can maintain an effective dose.	
Iron	<9.6 mg/L (median)	0.38 g/L (mean)[3]

[1]NRMMC (2009);[2] Water quality data from Greenway Park (Case study 6.2), UV treated stormwater in header tank, monthly testing July 2011 to June 2012), HSC (2012); and[3] Based on four samples, median not reported

techniques for stormwater harvesting are able to meet more stringent requirements. To date, there is only one indirect potable reuse scheme in NSW if not Australia; this being the Blackmans Swamp Creek stormwater harvesting project in Orange, NSW (see Case Study 3.3).

The Australian Drinking Water Guidelines (NHMRC 2011) listed 238 physical and chemical parameters for drinking water. Most of these are not reported in the literature. Hence it is difficult to judge to what extent urban stormwater meets the guidelines. Regularly tested pollutants in urban stormwater are presented in Table 3.6, along with guideline values from NHMRC (2011), and values reported in Case Study 3.1.

For the tested parameters, with the exception of turbidity and *E. coli* (as well as marginally low pH), the stormwater from Turramurra, NSW, complies with the drinking water guidelines. However, only four storm events were included in the result. Therefore, further testing is required to ensure that other guideline values are not exceeded. Toxicity of stormwater can be high due to the presence of chemicals not regularly tested, originating either from urban runoff or from sewerage contamination (Tang et al. 2013).

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Table 3.5. Indicative exposure reductions provided by on-site preventive measures and design compliance from Turramurra stormwater harvesting scheme (Case Study 3.1)

	Reduction in exposure to pathogens[3]		*Turramurra stormwater harvestings scheme*	
Control measure	*On-site*[1] *exposure*	*Off-site*[2] *exposure*	*On-site*[1] *exposure*	*Off-site*[2] *exposure*
Drip irrigation of crops	2 log			
Subsurface irrigation of above-ground crops	4 log			
Withholding periods for irrigation of parks/sports grounds (1–4 hours)	1 log		1 log	
Spray drift control (micro sprinklers, anemometer systems, inward-throwing sprinklers, etc.)		1 log		1 log
Drip irrigation of plants/shrubs	4 log			
Subsurface irrigation of plants/ shrubs or grassed areas	5–6 logs			
No public access during irrigation	2 log		2 log	
No public access during irrigation and limited contact following irrigation (e.g. food crop irrigation rather than public open space)	3 log			
Buffer zones (25–30 m)		1 log		1 log
Total			**3 log**	**2 log**
Design requirement (per Table 3.4):			Min 1.5 log	Min 1.5 log

[1]exposure for those present on the irrigated site NRMMC (2009); [2]exposure for those not present on the irrigated site, i.e. exposure due to wind drift, etc.; [3]summary from NRMMC (2009)

While stormwater can meet the drinking water guidelines for many parameters that are regularly tested, high variability in values may pose a problem because the guideline values (NHMRC 2011) are maximum concentrations. Consequently, any treatment must be designed for the worst case scenario which may increase requirements on the water treatment system. While stormwater would be mixed with conventional water sources (e.g. groundwater, river water) in an indirect potable water reuse scheme where the impact of fluctuating quality is reduced, a subsequent treatment system may still be adjusted to account for a

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Table 3.6. Pollutants regularly tested for in urban stormwater along with guideline values and values for local stormwater harvesting schemes in Sydney

Water quality parameter	*Raw stormwater Turramurra stormwater reuse (case study 6.1)*	*ADWG 2011*[1]
Traditional (physical & chemical)		
pH Value	6.3–7.1	6.5-8.5
Sodium Adsorption Ratio	0.67–0.85	
Electrical Conductivity at 25°C	80–119	
Total Dissolved Solids (Calc.)	52–81	600
Suspended Solids (SS)	38–90	
Turbidity	9.9–39.6	5
Total Hardness as $CaCO_3$	15–36	200
Dissolved Salts		
Sulfate as SO_4 - Turbidimetric	1–6	500
Chloride	11–20	250
Calcium	5–11	
Magnesium	0–2	
Sodium	6–8	180
Potassium	1–5	
Metals		
Arsenic	0	0.01
Cadmium	0	0.002
Chromium	0–0.002	0.05
Copper	0.011–0.041	2
Nickel	0–0.003	0.02
Lead	0.003–0.01	0.01
Zinc	0.051–0.146	3
Mercury	0–0	0.001
Fluoride	0–0	1.5
Nutrients		
Ammonia as N	0–0.31	0.5
Nitrite as N	0–0.04	3
Nitrate as N	0–0.17	50
Total Nitrogen as N	0.7–2	
Total Phosphorus as P	0.07–0.44	
Bacteriological		
Faecal Coliforms	2200–17000	
Escherichia coli	2200–17000	0
Coliforms	15000–65000	

[1] NHRMC (2011)

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broader range of pollutant concentrations. Treatment of stormwater, before it reaches the water reservoir, is therefore recommended.

3.4 CONVENTIONAL STORMWATER TREATMENT TECHNOLOGIES IN STORMWATER HARVESTING

Conventional stormwater treatment systems commonly utilized in harvesting schemes include gross pollutant traps (GPTs), vegetated swales, sediment ponds, constructed wetlands and biofiltration systems (Hatt et al. 2006; Burns and Mitchell, 2008). Sand filters also have the potential to provide a high level of treatment (Birch et al. 2005; Kandasamy et al. 2008). Conventional technologies for treating stormwater are traditionally incorporated into a management strategy to meet stormwater quality objectives for discharge to receiving water (e.g. rivers, estuaries). As such, they are not designed to achieve a quality suitable for reuse. Objectives for stormwater treatment alone in Australia are commonly based on a minimum mass reduction of pollutants discharged to receiving waters such as gross pollutants, total suspended solids and nutrients such as nitrogen and phosphorus (calculated on an annual basis). For example Total Phosphorus (TP), both dissolved and particulate has a goal of attaining the ambient receiving water quality concentration objective but has an effluent water quality criteria of 45% retention of the average annual load. In a similar manner total nitrogen (TN), both dissolved and particulate has a similar goal as TP and has an effluent water quality criteria of 45% retention of the average annual load, Singh et al (2009). This is contradictory to stormwater reuse water quality requirements that are given as a maximum or mean concentration of pollutants or in the case of pathogens, a $\log_{10}$ reduction.

Conventional stormwater treatment systems are commonly combined in “a treatment train”. A treatment train consists of a number of treatment devices, each providing a different level of treatment. The standard treatment train would include primary treatment, followed by secondary treatment and tertiary treatment. A particular treatment device or system may overlap two or more treatment levels, depending on its specific design feature. In most situations, a treatment train combines treatment techniques that reduce pollutants through different processes for the best overall treatment.

Stormwater treatment requirements are aimed at environmental protection rather than reuse, Singh et al (2009). The focus is on capturing litter, sediments and nutrients, whilst pollutants of concern for reuse schemes such as metals and pathogens are commonly not adopted as treatment criteria. Nevertheless, as the treatment system targets at smaller and smaller particles, these pollutants of concern will be captured. Table 3.7 summarizes the typical treatment performance of a number of stormwater treatment measures.

Of the conventional systems commonly used in harvesting applications, biofiltration and constructed wetlands have the highest potential in terms of

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Table 3.7. Indicative percentage of pollution retained in the treatment system for a range of stormwater treatment measures

Stormwater Treatment Measure	*Suspended Solids*	*Total Phosphorus*	*Total Nitrogen*	*Turbidity*	*E. coli*[1]	*Source*[*]
Gross Pollutant Trap	0–70%	0–30%	0–15%	0–70%	Negligible	[1]
Swale	55–75%	25–35%	5–10%	44–77%	Negligible	[1]
Sand filter	60–90%	40–70%	30–50%	55–90%	−25–96%	[1–3]
Bioretention	70–90%	50–80%	30–50%	55–90%	−58–95 + %	[1, 4–6]
Pond	50–75%	25–45%	10–20%	35–88%	40–98%	[1]
Wetland	50–90%	35–65%	15–30%	10–70%	−5–99%	[1, 3, 7–10]

[*] [1] = DEC (2006); [2] = Kandasamy et al. (2008); [3] = Birch et al. (2005); [4] = Zhang et al. (2010); [5] = Zhang et al. (2011a); [6] = Chandasena et al. (2012); [7] = Davies and Bavor (2000); [8] = Mendez et al. (2009); and [9] = Hathaway et al. (2009, 2011)

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addressing pollutants relevant for risk management [i.e., pathogen, according to the Australian guidelines (NRMMC 2006, 2009)] as well as operational risk (nutrients and suspended solids). One of the benefits of adopting conventional stormwater treatment techniques is that they typically rely on gravity for their functions, which do not require pumps or electricity. They can, however, require significant areas of land for their construction and can be difficult to retrofit into an already developed area.

Constructed wetlands, Constructed wetlands are most commonly used for large stormwater harvesting schemes. They can provide a cost-effective treatment per unit of harvested stormwater (A. Deletic, unpublished data, 2011). A substantial volume of water storage is available within the wetlands while other treatment techniques, such as biofiltration, will require additional storage of treated water. Wetlands have been shown to effectively remove nutrients, suspended solids (Greenway 2010; Malaviya and Singh 2012), and metals (Malaviya and Singh 2012). Constructed wetlands can also provide reasonable reduction of faecal coliforms concentrations. It should be noted, however, that their removal efficiency is highly variable. For example in a brief summary of wetland systems reviewed in Malaviya and Singh (2012) (Tampa, Florida, USA; Washington, USA; Manassas, Virginia, USA; Port Jackson, Sydney, Australia; Putrajaya wetlands, Malaysia; Crete, Greece; and Danshui River Basin, Taipei, Taiwan) the variation in TP removal was between 16–90%, TN removal between 9–82% and TSS removal between 57–94%. Overall, constructed wetlands function well as pre-treatment systems for stormwater harvesting applications.

Vegetated Biofilter. Biofiltration is a common treatment technique in urban areas as the amount of land involved is smaller than for constructed wetlands. It also has greater potential to provide treatment for stormwater harvesting schemes at a local scale. Laboratory studies have shown that biofilters have the potential to remove a large proportion of TSS and metals from stormwater (Hatt et al. 2007; Read et al. 2008; Hatt et al. 2008; Blecken et al. 2010). These results have been largely confirmed by field studies (Hatt et al. 2009; Brown and Hunt 2011). While the removal of nutrients can also be beneficial (Dietz and Clausen 2006; Davis et al. 2006; Henderson et al. 2007; Zhang et al. 2011b), there are examples where biofilters have been net producers of nutrients, especially nitrogen. This includes both laboratory studies (Hatt et al. 2007; Hatt et al. 2008; Read et al. 2008; Blecken et al. 2010; Kim et al. 2012) and field studies. A summary of field studies of biofilters receiving natural stormwater is presented in Table 3.8.

Regarding the removal of pathogens in biofilters, less data is available. A pilot study into the performance of vegetated biofilters using a number of different plant species indicated 48-97% removal of *E. coli* (Kim et al. 2012). Another laboratory testing of different biofilter configurations have shown log removal of in excess of 3 $\log_{10}$ to a mean of 2 $\log_{10}$ for a number of different pathogens (Li et al. 2012). Field testing of the Turramurra stormwater harvesting system in the Ku-ring-gai Local Government Area, NSW (Case Study 3.1) using biofiltration as pre-treatment demonstrated the reduction of Faecal Coliforms of around 1 $\log_{10}$ (refer to Table 3.9).

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Table 3.8. Stormwater biofilter field studies, receiving natural stormwater. Negative values indicate an export of pollutants

	*TSS***			*TP*			*TN*	
References	*RMC (%)*	*MMR (LR) (%)*	*RMeC (%)*	*RMC (%)*	*MMR (LR) (%)*	*RMeC (%)*	*RMC (%)*	*MMR (LR) (%)*
Hatt et al.	87.2	76		−214.3	−398		−18.2	−7
(2009)	89.1	93		82.5	86		18.5	37
			80.0			50.0		
Hunt et al.				−409.1			−224.4	
(2006)		−170		−2900.0	−240		−311.8	40
					65			40
Davis et al.		59	47.1		79	75.4		
(2006)		54	61.8		77	72.1		
Passeport et al.				62.8	53		54.3	56
(2009)				57.7	68		54.5	47
Brown and		71			5.3			12
Hunt (2012)*		79			12			35
Brown and		84			44			13
Hunt (2012)*		89			19			32
Brown and	58.9			−12.5			57.8	
Hunt (2011)								

[*] Systems tested pre- and post-restorative maintenance, pre-restorative presented first; ** RMC = reduction in median concentration; MMR (LR) = mean mass removal (load reduction); and RMeC = reduction in mean concentration

Table 3.9. Reduction of Faecal Coliforms and turbidity at stormwater biofilter in Turramurra, NSW (Case Study 3.1)

	Faecal Coliforms				*Turbidity*		
Date	*EMC In*	*EMC Out*	*Removal conc. (%)*	*Equivalent log removal*	*NTU In*	*NTU Out*	*Reduction (%)*
25/05/2012	~17,000	~350	97.94%	1.69	39.6	18.7	52.78%
29/01/2013*	~15,000	~1,600	89.33%	0.97	9.9	16.6	−67.68%
11/11/2013	~2,200	1,200	45.45%	0.26	12.9	17	−31.78%

[*] Samples out of holding time, applies equally to both in and out samples

Despite constructed wetlands and biofilters showing high potential for reducing pathogens, they are not currently recommended as treatment techniques for compliance with the Australian guidelines (NRMMC 2009). Unlike treatment techniques specially developed for water supply systems such as media filters and

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disinfection systems, conventional stormwater treatment methods are not continuously monitored against a critical control point. It is worth noting that for the Turramurra stormwater reuse system (case study 3.1), as a conservative measure, the biofilter has not been included as a treatment strategy in the risk assessment for people's health. The biofilter does, however, provide one additional barrier for public health protection. Specifically, the biofilter provides treatment that (1) ensures that the storage and irrigation infrastructures are not subjected to elevated sediment loads; and (2) protects the irrigated vegetation by removing metals in the stormwater. It also provides additional protection for the harvesting system against any accidental spills within the catchment such as chemicals or fuel.

Other conventional treatment techniques in stormwater harvesting. GPTs, sediment ponds and swales are commonly used as a pre-treatment for wetlands and biofilters, but it is also common that stormwater is harvested after only primary treatment by a GPT. Greenway Park (Case Study 3.2) is one such system. In these cases, relatively dirty water is conveyed to a storage facility, commonly by pumping due to the low elevation of the stormwater treatment infrastructure. After storage, water is often treated by disc or media filters, sometimes followed by activated carbon filters, and in most cases, disinfection before being used for irrigation or toilet flushing. Little information is available in the public domain regarding how efficient these systems are in removing target pollutants. Verification testing after installation is recommended but there is little information available on how often this is actually undertaken, nor if ongoing monitoring is carried out.

Irrespective of whatever treatment technology is adopted, where treatment is relied upon for risk management, additional pathogen removal through disinfection is required. Treatment by UV light is currently the most common treatment technique used in stormwater harvesting. UV requires water of a relatively high quality in order to provide the prescribed level of disinfection. This results in the need for prior treatment, in addition to primary treatment. Wetlands and biofilters, on the other hand, can provide a safe level of pre-treatment adequate for effective UV disinfection with minimal or no further treatment.

It should also be noted that, in most cases, a stormwater treatment system is implemented to meet environmental objectives or requirements rather than for the sole purpose of water reuse. Harvesting of the treated water is then merely an additional benefit to the environmental benefits, which are already provided by the infrastructure through the reduction of stormwater flow-rate and associated pollutants.

Operation and maintenance requirements of conventional stormwater treatment systems and life cycle cost. The ongoing maintenance of any treatment system forming part of a stormwater harvesting scheme is vital for their continuous function. If not properly maintained, treatment devices may become blocked, preventing stormwater from entering the harvesting system. In addition, captured pollutants may be re-suspended, adversely affecting the harvested water quality. The maintenance frequency and cost will be site-specific. Therefore, a

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thorough life cycle cost assessment should be carried out at the planning stage to ensure all involved parties can make a sound decision. It is important to note, however, that conventional stormwater treatment systems (that form part of a stormwater harvesting scheme), if effective, will provide environmental benefits beyond that of the harvesting component. It is important that any operational and maintenance costs associated with the operation of the conventional stormwater treatment devices are appropriately allocated among the harvesting components and other environmental services.

As the vegetation forms a vital part of the treatment system for both constructed wetlands and biofiltration systems, vegetation management is critical and should include weed removal and replacement of any die-off. For biofilters, the root activity of the plants ensures ongoing permeability of the filter media that otherwise can become blocked, significantly reducing the treatment capacity. Plant density and biological activity is likely to fluctuate over the life of the filter, which will impact on its performance. Long-term data on the field performance of biofiltration systems are not currently available since most systems are less than 10 years old, and very few systems in the area are monitored. From the systems that have been monitored, it is clear that performance will vary, not only between systems but performance is also likely to be impacted by other variables such as temperature, as shown in laboratory studies (Blecken et al. 2010). Different plants will also exert different influences on the removal of pollutants (Read et al. 2008). Non-vegetated areas of a filter are likely to be less effective in capturing pollutants than vegetated areas and may in some cases be a net exporter of some pollutants (Hatt et al. 2007, 2008; Read et al. 2008). As vegetation cover and density vary, so will the performance.

Where UV disinfection is relied upon for managing public health risk, weekly *E. coli* testing to verify the performance of the disinfection system is recommended in the Australian guidelines (NRMMC 2009). If its levels comply with the guidelines over a three month period, the frequency can be reduced to a quarterly basis. Such testing is labor-intensive and requires appropriate resource allocation. Information on common frequencies for *E. coli* testing for operational systems is not available.

Items to include in a life cycle cost analysis include: (i) concept development; (ii) detailed design; (iii) construction and other capital costs; (iv) management plans; (v) commissioning and verification testing; (vi) ongoing monitoring as required by guidelines; (vii) vegetation management (if applicable); (viii) maintenance of treatment devices/disposal of captured pollutants; (ix) desilting of storage; (x) corrective maintenance; and (xi) decommissioning and disposal.

3.4.1 Case Studies

Case study 3.1. Turramurra stormwater harvesting scheme. Comenarra playing field is a 0.9-ha sports field in Turramurra, NSW, used mainly for soccer and cricket. The Comenarra stormwater harvesting scheme was constructed in 2008 and collected stormwater from an 8.9 ha residential catchment. The catchment was sewered and there were no designed sewer overflow points within the

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catchment, and hence the land uses within it were not considered to pose any significant risks in terms of water quality. All inlet pits have been fitted with pit litter baskets. However, some of the baskets have been removed due to flooding concerns and damage. The baskets are maintained under the local government council's stormwater quality improvement device maintenance contract. Regular stormwater maintenance such as street cleaning and pit cleaning are important preventative measures so that the scheme remains reliable.

Water is diverted from a 600 mm diameter pipe and passed through a 5 mm screen before being treated in a terraced stormwater biofilter, which is located in the car park adjacent to the sports field. Stormwater that has been treated through the biofilter is conveyed to a 250 kL storage tank located underneath the playing surface. Flows in excess of the capacity of the biofilter bypass the system and are directed back to the drainage system. Stormwater stored in the tank is used to irrigate the sports field. A process flow chart is provided in Figure 3.1.

Local monitoring has shown that the biofilter provides approximately 1 $\log_{10}$ reduction in indicator bacteria (*E. coli*). However, as a conservative measure, treatment was not included as a risk management strategy in the risk assessment for public health. This is because such treatment is not amenable to validation and process control against a continuously monitored critical control point. The public health risk is managed through access control, including signage on site, spray drift control and buffer zones and irrigating at night.

The system supplies approximately 2,000 kL of irrigation water per year. Since its commissioning, the harvesting system has not had any problems concerning the stormwater harvesting procedure. An ongoing maintenance has been provided for the stormwater biofilter, but no additional maintenance of the irrigation system was required. Sports field personnel are responsible for periodically checking the irrigation program and ensuring that all signage is in accordance with the management plan.

As the harvesting component is gravity-driven, no energy is required to divert, treat and convey stormwater to storage. Once in storage, pumping is needed to supply water to the irrigation system, which is still required even if mains water is used. This is because the pressure and flow rate in the mains system are not enough to drive the irrigation system. With an average energy intensity of

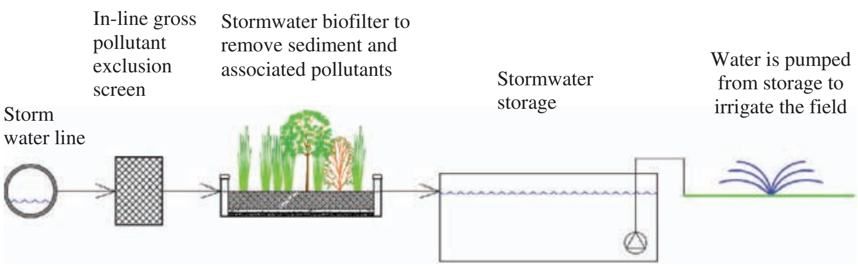

Figure 3.1. Process flow chart, Turramurra stormwater harvesting system

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water supply of 0.65 kWh/kL (Cook et al. 2012), the project provides water with less energy consumption compared to a scheme that relies on mains water supply.

Case study 3.2. Greenway Park, Hornsby, NSW, Greenway Park is located in Cherrybrook and consists of two playing fields. Stormwater flows from an 8.0 ha catchment. The catchment is dominated by open space parklands, and includes some residential and commercial areas. Surface runoff from the catchment drains via the pit and pipe network to an off-take. The land-uses within the catchment are not considered to pose any significant risks to water quality. A regular stormwater maintenance such as street cleaning and pit cleaning is an important preventative measure to retain the scheme's reliability.

Water is drained through an existing 600 mm stormwater pipe. A gross pollutant trap (GPT) has been installed on the pipe for the primary treatment of harvest flows. Treated flows are diverted into a 5 kL sump where pumps transfer stormwater to 4 × 110 kL underground concrete storage tanks. Stormwater is delivered to a treatment room where it receives UV disinfection prior to distribution for irrigation. Treated water is stored in a header tank before being pumped to the irrigation system. The stormwater harvesting project was completed in 2009. The system was designed to supply up to 5,000 kL per year of recycled stormwater. A process flow chart is provided in Figure 3.2 and identifies the main elements of the scheme.

While supplying stormwater for irrigation, the system has experienced some problems along the way. This often relates to issues of poor water quality causing the system to shut down. In addition, sports field maintenance staff lack technical skills to understand how the system operates. Often the system has been checked in accordance with the management plan. It is also noted that alarms for pump failure or issues with the disinfection have been triggered, yet no further action is taken to rectify the problem. This has caused the system to be idle at times when irrigation water must be supplied by the mains supply instead. There have also been issues with the UV lamp. Its recommended replacement schedule of every 12 months was not followed. Consequently, the effectiveness of the disinfection was doubtful. The council conducts monthly water quality tests in the irrigation tank (treated water), which have resulted in variable outcomes.

Acknowledging that the sports field staff often do not have the technical skills to assess maintenance requirements or to carry out maintenance of the stormwater harvesting system, Council has placed the scheme on an external

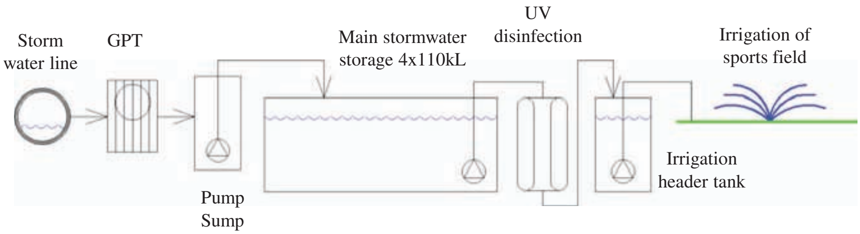

Figure 3.2. Process Flow Chart, Cherrybrook stormwater harvesting system

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preventative maintenance contract. This has significantly improved the ongoing function of the scheme.

Pumps are used for transferring water to the central storage and the header tank. Once in the header tank, water is pumped to the irrigation system. This would be the case even if mains water was used as the water source, as the pressure and flow rate in the mains system are not enough to drive the irrigation system. Furthermore, the overall power required for pumping is approximately 0.30 kWh/kL. Comparing to an average energy intensity of water supply of 0.65 kWh/kL (Cook et al. 2012), the project saved half of the energy consumption.

Case Study 3.3: Blackmans Swamp Creek stormwater harvesting project, Orange, NSW. The Blackmans Swamp Creek Stormwater Harvesting Scheme is one of the first large-scale, indirect-to-potable stormwater harvesting project in NSW, Australia. This project provides Orange, a regional town in NSW, with up to 1,300–2,100 ML of raw water or 40% of the city's water demand (OCC 2009).

The basic concept of the Blackmans Swamp Creek Stormwater Harvesting Scheme involves capturing a portion of the high flows in Blackmans Swamp Creek during storm events, and transferring it to the main water supply reservoir at Suma Park Dam for augmentation of the city's bulk water supply. Blackmans Swamp Creek lies in close proximity to Suma Park Dam. The stormwater catchment supplying the scheme is approximately 3,417 ha, 24% of which is impervious (Sidhu et al. 2012). The catchment's large impervious area in the catchment produces a significant runoff during rainfall events. The treatment system includes gross pollutant traps, settling and chemically assisted sedimentation before pumping into Suma Park Dam. The water then passes through Council's central water filtration plant which includes ozonation and biologically activated carbon and chlorination (Sidhu et al. 2012).

Summary. Harvesting and reuse of stormwater from hard surfaces is a relatively new practice that can potentially provide a significant alternative water supply. The stormwater characteristics are affected by the catchment and weather patterns. For this reason, it is important that treatment systems are able to cope with a highly variable concentration range while providing treated water of a consistent and acceptable quality suitable for the end-user. The most common application of stormwater reuse in Australia is outdoor irrigation. However, stormwater can also be used to supplement other non-potable functions such as flushing toilets, washing clothes, fire-fighting and in cooling towers. There are also examples of stormwater being used to supplement potable water supplies. The water quality criteria will depend on the applications, and the treatment required to meet these standards will be affected by the source of the stormwater.

The conventional technologies for treating stormwater are traditionally incorporated into a management strategy to meet stormwater quality objectives aiming to protect estuaries and streams. As such, they are not designed to achieve a stormwater quality suitable for reuse. While objectives for stormwater treatment are commonly based on a minimum mass reduction of pollutants, typical stormwater reuse water quality requirements are given as a maximum or mean concentration of pollutants or in the case of pathogens, a $\log_{10}$ reduction.

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Criteria for stormwater reuse vary depending on the application and other site-specific conditions (Table 3.3), and compliance with guidelines can be achieved by limiting exposure to the reclaimed water as well as through treatment (Table 3.5). For any use other than irrigation, however, stormwater must go through a treatment system to manage risks to public health. Where stormwater is used for supplementing potable supplies, even more stringent water quality requirements will be imposed.

The great variability in both the quality and quantity of stormwater is a big problem as any employed treatment system must be able to cope with these fluctuating flows and water quality while delivering required volumes of water at a consistent quality. This may lead to systems being over-designed in order to cope with the worst possible scenario. For conventional treatment systems such as constructed wetlands and biofiltration, a significantly large amount of land required may pose a problem, especially in retrofit situations, unless stormwater harvesting is added to systems designed mainly for pollutant reduction purposes.

Long-term data on field performance of biofiltration system is currently not available, as most systems are less than a decade old and very few systems in the field are being monitored. It is clear that performances of the monitored systems vary greatly, not only between systems but also due to the impact of seasonality and temperature. Different plant species, vegetation cover and density may affect the removal of pollutants as well.

Currently, there are no specific design procedures for conventional stormwater treatment techniques as a part of the harvesting system. As monitoring of stormwater harvesting systems for non-potable purposes is not mandatory, data on their performance is usually not collected due to budgetary constraints. The variation in treatment performance is likely to be even more enormous than what has been reported from monitored systems. Operational and maintenance procedures are also often inconsistent. There is anecdotal evidence from operators in NSW that maintenance is not carried out in accordance with the Australian guidelines. This may be a result of the fact that most organisations adopting stormwater harvesting have not been involved in the water supply or water treatment. Additionally, only limited resources have been allocated to train staff members, who until then had only maintained assets such as sports fields but are now required to maintain water treatment systems.

In a reuse application where minimum standards or treatment criteria are set (such as those shown in Tables 3.2, 3.3 and 3.4), this variability in performance and lack of a critical control point means that the conventional techniques should not be used without further treatment in a stormwater harvesting scheme if treatment is used to manage public health risk. Where other management strategies are used to manage public health risk such as access control, conventional stormwater treatment techniques can, however, provide treatment suitable for managing operational risk. Constructed wetlands and biofilters can also provide effective pretreatment for subsequent treatments. Stormwater harvesting may be added to the existing treatment systems, which were mainly designed to manage environmental impacts. In such cases, harvesting will help to improve the

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system's environmental performance while the treatment will provide pre-treated water at low cost for the harvesting scheme.

3.5 HIGH-RATE STORMWATER TREATMENT TECHNOLOGIES

Stormwater management treatment devices such as wetlands, bioretention, permeable pavement, etc., are widely used. According to Hatt et al. (2006), the current stormwater management treatment systems employed in Australia for stormwater pollution control do not provide the reliability of water quality necessary for recycling. Furthermore, these systems include a storage component, which takes up a considerable large amount of land that is not available in urban inner-city areas.

Stormwater discharge is relatively high and, therefore, needs to be treated at a high rate. The alternative is to store the stormwater before treatment in a manner similar to current stormwater management treatment systems. Raw stormwater in storage has low value and will degrade under anaerobic and anoxic conditions while pretreatment of stormwater adds value to the stored water, which can be beneficially reused.

High rate treatment yields an effluent stormwater of similar quality to roof rainwater, and both can be stored in the same tank. This raises the contributing catchment from just the building roof to the whole site, thus increasing the amount of water that can be captured and stored for reuse. In medium scale developments, rainwater tanks empty quite quickly due to demand and often need to be augmented by town water.

Physio-chemical treatment systems such as fibre filters, deep bed filters and GAC (granular activated carbon) biofilters can achieve a relatively high pollutant removal at a high rate (see Table 3.9). These high rate systems are targeted to enhance water quality suitable for at least non-potable purposes. The details of these systems are briefly described. Further details can be found elsewhere [fibre filter (Lee et al. 2006, 2007; Johir et al. 2009a); deep bed filter (Vigneswaran et al. 1990; Johir et al. 2009b); membrane hybrid systems (Johir et al. 2009b); biofilters (Mohammad et al. 2011)].

Fibre Filter. High rate fibre filters were successfully used in the tertiary wastewater treatment. In fibre filter, instead of sand, fibre media consisting of bundles of U-shaped fine polyamide fibres are used. Compared to the conventional rapid sand filter, the filtration velocity of a fibre filter is more than 5 times faster and the specific surface is more than twice as large (Lee et al. 2006, 2007). The fibre packing combines two advantages of a large specific surface area and a very large porosity (more than 90%) which results in high removal efficiency and low pressure drop despite the high filtration velocity (Lee et al. 2007). In-line additions of flocculants enhance the pollutant removal capacity for both dissolved organics and trace metals.

Deep Bed Filter. Deep bed filtration is often referred to as media filtration or rapid filtration. It has been widely used for water treatment as a final clarification

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unit to remove particles. Deep bed filtration is an effective process for removing particles of various natures and sizes in water and wastewater. Deep bed filtration finds its greatest application in the clarification of dilute suspensions of particles (less than 500 mg/l) ranging in size from about 0.1 to about 50 μm (Vigneswaran et al. 1990). Deep bed filter usually operates under pressure or gravity (Wilf 2007), and its filtration velocity is between 5–20 m/h. Depending on the number of filter media used, deep bed filters can be single media or dual media filters. In the latter case, the influent passes through one media filter followed by another.

Membrane filtration and Membrane Hybrid systems. Advances in low pressure-driven membrane technologies such as microfiltration (MF) and ultrafiltration (UF) have encouraged their use in stormwater due to their high efficiency, ease of operation and small footprint (Qin et al. 2006). MF that is generally used has a pore size of 0.1–0.2 μm, although there are exceptions, as MF membranes with pore sizes of up to 10 μm are available. For UF, pore sizes generally range from 0.01–0.05 μm or less (Wagner, 2001). Again, with reference to pore size, the lower cutoff for a UF membrane is approximately 0.005 μm (Wagner 2001). MF typically remove particles, clay and bacteria. UF typically remove macromolecules, proteins, polysaccharides, virus The operating pressure for MF is 100–1000 KPa and UF is more than 200 KPa.

Membrane filtration is usually coupled with a pre-treatment of fibre filter or deep bed filter, and such systems are called membrane hybrid systems. This significantly improved the removal efficiency of the system yielding high-quality reuse water.

GAC Biofilter. An adsorption biofilter typically comprises a column of support media onto which microbes grow. In the initial stage of operating the biofilter, adsorption of substances including micro-organisms is the dominant process, while in the later stages, organic degradation by microbial activities becomes more important. The activities of microbes determine the performance of biological filtration in removing pollutants.

3.5.1 Treatment Systems for Stormwater Harvesting and Reuse in Inner City Areas

These high rate systems can form a part of the stormwater filtration system (Figure 3.3). Stormwater is collected in a stormwater pit and is diverted through a gross pollutant screen to remove rubbish and coarse sediments. Following a pre-treatment with high rate fibre filter or buoyant media flocculator/filter, the effluent is stored in a storage tank. Water in this tank may be augmented by roof rainwater which has a quality commensurate with the treated stormwater effluent, and the storage tank will also serve as a rainwater tank (Figure 3.3). The rationale for mixing of rainwater with treated stormwater (which may be high in organic content and solids) is based on the potential use of the water and on cost consideration.

Water from the storage tank passes through a submerged membrane filter (SMF) placed inside the storage tank. The quality of permeate from the SMF should be at least equivalent to potable level. The gravity driving head, or the

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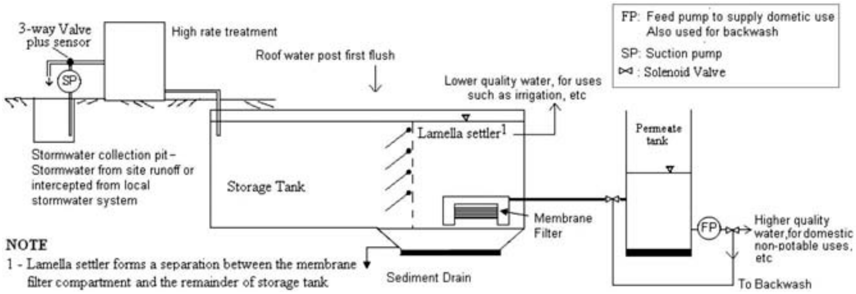

Figure 3.3. Scheme of the stormwater harvesting treatment system (not to scale)

difference in water levels between the storage tank and the permeate tank will be used to drive treated stormwater through the membrane filter, and eliminate the need for pumping. The permeate tank need not be a separate tank as shown in Figure 3.3 but may be a compartment within the storage water tank so long as there is no mixing of water between compartments. The driving head will decrease as water filters through the SMF into the permeate tank and raises the water level there. This reduces the flow through the SMF until it stops. The flow resumes when the water level in the permeate tank drops as water is pumped for domestic use, or if there is more inflow to the storage tank. The innovative feature of the system is that it naturally adapts its treatment capacity to the demand for treated water.

3.5.2 Treatment Systems for Stormwater Harvesting and Reuse in Sub-Urban Areas

The treatment system is a sand/GAC filter as an on-site treatment strategy for removing pollutants for potential water recycling and reuse. The sand/GAC filter (SFD) is shown in Figure 3.4.

The SFD consists of several components including a diversion pit on the main stormwater pipeline, a gross pollutant trap located upstream of the SFD (not shown), in-line coagulation, an above ground storage basin, sand filter compartments, a porous pipe contain GAC and a monitoring pit at the filter outlet (Figure 3.4). The diversion pit diverts stormwater discharges from rain events up to the 6-month average recurrence interval (ARI) or return period to the sand filtration compartments. An orifice plate within the diversion pit (not shown) will regulate the flow diverted to the SFD. The gross pollutant trap is a litter basket and provides pre-screening of stormwater to remove gross pollutants and gravel. This helps prevent clogging of the SFD. The surcharge pit provides access to the stormwater inflow for monitoring and directs the stormwater into the above ground storage basin. An overflow weir diverts away inflow volumes greater than this capacity.

The sand filtration unit consists of concrete masonry block walls on a reinforced concrete slab. The filter bed will be divided into two compartments,

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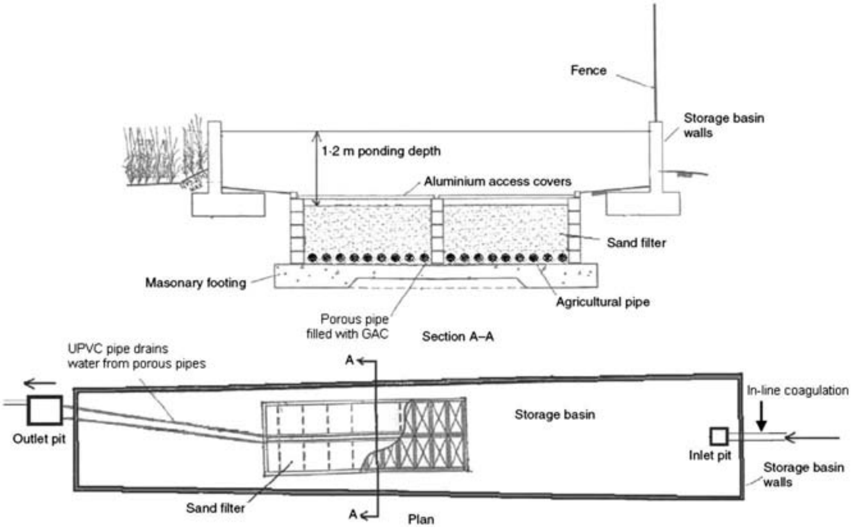

Figure 3.4. Schematic of the pilot plant

Table 3.10. Indicative percentage of pollution retained in the treatment system and indicative levels of pollutants in the outflow for a range of high rate treatment measures

High rate system	*Fibre filter*[1]	*Deep bedfilter*[1]	*Submerged Membrane hybrid systems*	*GAC Biofilter*
Suspended Solids	98%	99%	99%	—
Heavy Metals	90%	40–54%	-[2]	90%
Total Phosphorus	90%	50%	-[2]	74%
Total Nitrogen	90%	38%	-[2]	34%
Turbidity[3]	95%	95%	98%	75%
TOC	40%	30–45%	40%	100%
E. coli[3]	93%	80%	99.9%	—
Reference	[1]	[2]	[2]	

[1] in conjunction with in-line flocculent ferric chloride addition; [2] at least equal to fibre filter, deep bed filter or biofilter depending on the system the membrane filter is coupled to. Usually, membrane systems are combined with in-line flocculent or adsorbent addition; [3] influent and effluent pollutant concentrations in mg/L except for turbidity (NTU) and *E. coli* (cfu/100 mL); and reference: [1] = Johir et al. (2009a); [2] = Johir et al. (2009b)

which allows testing of two types of filter bed material. The sand filter bed overlays an underdrain porous pipe system containing GAC (biofilter). The effluent from the porous pipe drains into UPVC pipes. The entire sand filtration unit is covered with removable aluminium grates.

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The downstream monitoring pit provides access for sampling of the treated water. The pit is divided so that the discharge from each SFD compartment is kept separate for monitoring purposes. The downstream monitoring pit can be drained back into the main stormwater trunk line or to a storage pit to collect the treated water for reuse. The indicative performance of this system is shown in Table 3.10.

3.5.3 Applications of High Rate Systems and Performance

These high-rate treatment systems can be used to create a sustainable urban development with a low demand on town water, low stormwater pollution and reduced stormwater discharges. Residues of the treatment process (concentrated pollutants and sludge) can be discharged to the sewer, thus alleviating sludge disposal problems and is attractive in creating a low maintenance system. The use of these treatment systems for water reuse can significantly reduce the transport of stormwater pollution from a site to receiving water bodies.

Table 3.10 shows how high-rate treatment systems are suitable for treatment for stormwater harvesting and reuse. They have relatively high removal rates of nutrients (total nitrogen and total phosphorus), physical (suspended solids or turbidity), heavy metals (such as iron, manganese and lead), and organic matter.

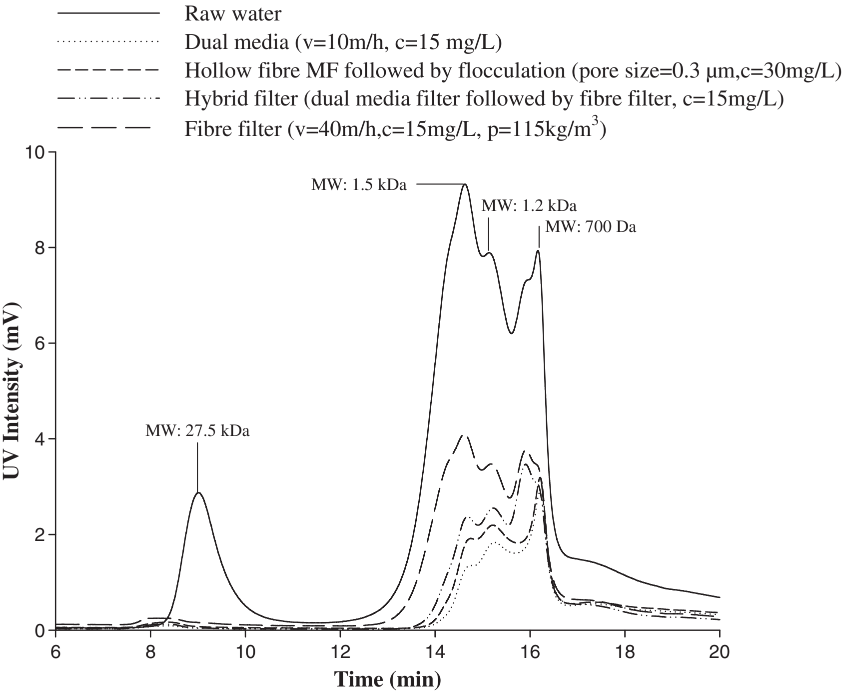

Figure 3.5. Effect of pre-treatments on organic matter (OM) removal (v = filtration velocity; c = flocculants dose; p = packing density; MF = microfilter)

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These systems are so compact that they do not require a significant land footprint as there is no need to store water before pre-treatment.

Figure 3.5 illustrates the molecular weight distribution of organic matter of raw stormwater and various forms of high rate treatment. Although not shown here, biofilters are also effective in removing organic matter. The GAC biofilter, in particular, is an environmentally friendly pre-treatment which can remove the majority of organic matter in stormwater. This biofilter (1) removes the majority of dissolved organic matter and reduces/eliminates the problem of biofouling in the subsequent membrane process; (2) requires only a small amount of energy; (3) does not require regeneration of GAC; (4) does not involve any chemical requirement; (5) achieves significant removal of dissolved organics for a long period of time with little operation and maintenance; and (6) is simple to construct and operate.

3.6 CONCLUSION

Stormwater for harvesting and reuse should be assessed primarily for nutrients, physical properties (suspended solids, turbidity), bacteriological properties (total and faecal coliform), heavy metals (such as iron, manganese and lead), and organic matter since it is more unlikely to meet these water parameters. Traditional stormwater management measures alone are currently unsuitable for harvesting and reuse. However they can provide adequate pre-treatment before disinfection. These systems commonly do not have a high rate of treatment, and since stormwater discharge from urban areas can be high at short durations, storm flows will need to be temporarily stored before treatment (in, for example, a biofilter or a wetland). This can require a large land footprint, often not available in urban areas. The ability to treat water at a high rate means that a high volume of storm flow can be captured over a short period of time without the need to store flows. The treatment provided by high rate treatment systems have relatively high removal rates of nutrients (total nitrogen and total phosphorus), suspended solids or turbidity, heavy metals such as iron, manganese and lead, and dissolved organic matter. These systems are compact and do not require a significant land footprint as there is no need to store water before pre-treatment. For this reason, these systems may be better suited for stormwater harvesting and reuse systems where harvesting and reuse are the main objectives. Where conventional stormwater treatment systems are constructed for other environmental reasons, harvesting can provide additional benefits in addition to the treatment function, and can do so at a very low energy demand where systems relies on gravity for their function.

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CHAPTER 4

Sustainable Groundwater Management: Policy and Practice

William Milne-Home[1]

4.1 INTRODUCTION

Groundwater is the hidden phase of the global water cycle which is the framework for describing the circulation of water, both in liquid and vapour form, over and within the earth's surface. Figure 4.1 is a graphic summary of the global water cycle and illustrates how precipitation, runoff, streamflow and infiltration interact with groundwater flow and storage. An estimate of proportional volumes of water stored in each component shows that groundwater and soil moisture amount to 35% of the fresh water on the earth (Figure 4.2).

Sustainability is implicit in the concept of the water cycle. Shifts in the distribution of water between the cycle's phases create the requirement for management to maintain this vital resource for the planet. Oki and Kanae (2006) suggest that water resources assessment should concentrate on water flows rather than storage in the global water cycle because climate sets an upper limit to renewable freshwater resources that are unevenly distributed in space and time. At present, more than two billion people live under conditions of high water stress (Oki and Kanae 2006). The sustainability imperative is becoming increasingly urgent as climate change is likely to further push the water cycle towards uncertain outcomes by changes in seasonal rainfall distribution and the occurrence of extreme droughts and floods. GRACE (the Gravity Recovery and Climate Experiment, a joint U.S.-German satellite deployment) (Famiglietti and Rodell 2013) provides data which can be interpreted to map the changing distribution of water within the cycle (Tapley et al. 2004; Yeh et al. 2006; Famiglietti and Rodell 2013). GRACE was launched in 2002 and is comprised of two satellites, orbiting at about 500 kilometres elevation. The distance between them varies temporally as they traverse time-varying mass features of the earth's surface with differential gravitational attraction, often reflecting changes in water storage and flows in surface water and groundwater (Moore 2012). More information on GRACE is available at http://www.csr.utexas.edu/grace. Applications in Australian groundwater management are discussed by Tregoning et al. (2012).

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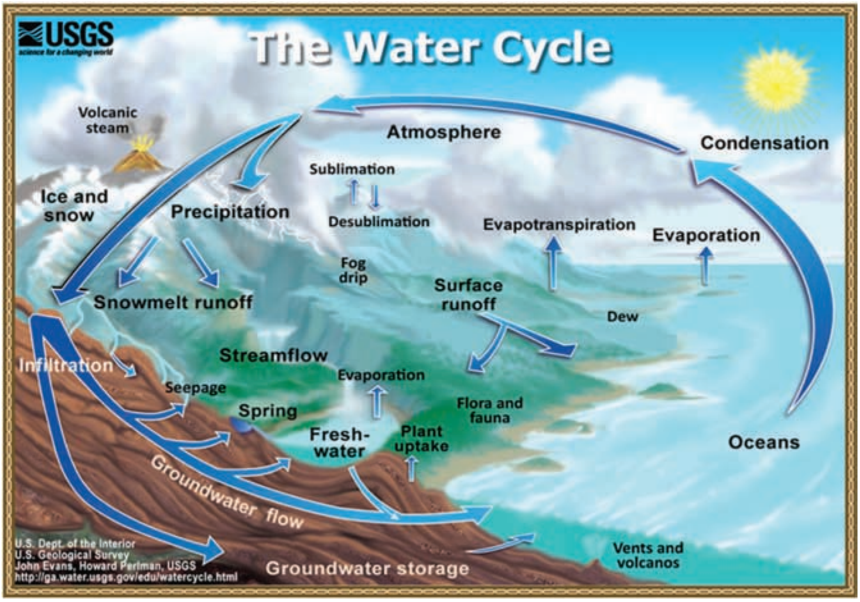

Figure 4.1. The global water cycle

Source: U.S. Geological Survey, http://ga.water.usgs.gov/edu/watercycle.html (accessed on 21 October, 2013)

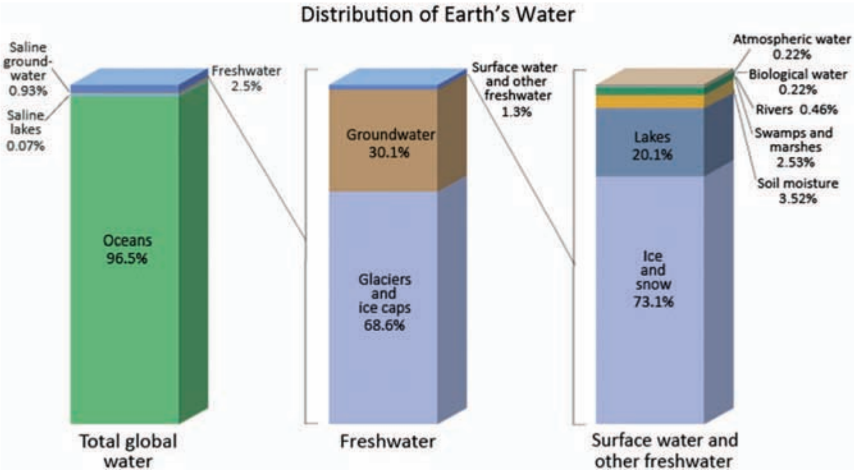

Figure 4.2. Proportion of groundwater in the total global water storage inventory

Source: U.S. Geological Survey, http://ga.water.usgs.gov/edu/watercycle.html (accessed on 21 October, 2013); data from Shiklomanov (1993)

The prediction of these climate-change related outcomes is derived largely from general circulation models (GCMs) which simulate the atmospheric and surface phases of the global water cycle. GCMs have been developed as part of major research programs investigating climate change scenarios. The output from

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some GCMs and associated data are available on the website of the Intergovernmental Panel on Climate Change (http://www.ipcc.ch). Some twenty-five GCMs are available from various sources, and there is an increasing trend in their application for the prediction of the groundwater component of the water cycle through their generated emission scenarios. GCMs may be linked to land surface models (LSMs) which simulate the fluxes of water, carbon (CO_2, CH_4), energy and momentum between the land surface – including the soil and subsoil zones – and the atmosphere (Jiménez et al. 2013). The LSM, Joint UK Land Environment Simulator (JULES), is an example of such models (Best et al. 2011; Clark et al. 2011) (https://jules.jchmr.org). An increasingly common procedure for groundwater is to apply the selected GCM scenarios of climate change in conjunction with various data downscaling methods (Wilby and Wigley 1997) and groundwater models (Allen et al. 2010).

Although GCMs are not designed to include the effects of climate change specifically on groundwater resources, researchers have incorporated model predictions under various scenarios of changing climate to investigate how the sustainability of groundwater resources might be affected (Small 2005; Döll 2009; Allen et al. 2010; McCallum et al. 2010; Jackson et al. 2011; Stoll et al. 2011; Taylor et al. 2013). Sustainability has been defined in terms of the limitations of long-term average groundwater recharge or renewable groundwater resources (Döll and Fiedler 2008). They estimated the long-term average diffuse groundwater recharge on the global scale using a modified version of the WaterGap Global Hydrology Model WGHM which is set up on a spatial resolution of 0.5 degree square grids and daily time steps. Groundwater recharge was calculated as a function of the total runoff from the land area of each grid cell, topography, soil texture, hydrogeology, permafrost and precipitation intensity (Döll and Fiedler 2008). On this basis global groundwater recharge averaged 1.27E7 gigalitres for the climate normal 1961–1990 and amounted to 32% of the total renewable water resource (broadly comparable to the groundwater storage shown in Figure 4.2).

A recent study of renewable groundwater resources found large differences between the outputs of five climate models using four greenhouse-gas scenarios in the estimation of future groundwater recharge on a global scale (Portmann et al. 2013). Crosbie et al. (2012) used sixteen GCMs and three scenarios of global warming to generate projections of aquifer recharge to 2050 across the Australian continent. The range of results was enormous for the forty-eight future climate variants generated and the authors indicated the difficulty of translating these results into water allocations for practical water resource management policy. However, on a regional scale, Almanaseer et al. (2014) showed that it was feasible to estimate 6-months-ahead groundwater levels in a relatively pristine catchment in Georgia, USA, from the *ECHAM 4.5* General Circulation Model Forced with Sea Surface Temperature precipitation forecasts. They noted that there was significant conditional bias in their modelling schemes.

GCMs are useful for projecting potential changes in available water resources across the time frame of the current century. Importantly, they allow the consideration of uncertainty, for which definitions and applicable concepts are available (e.g. Walker et al. 2003) so that water resources policy settings and

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management objectives can be planned in a framework for risk analysis. The varying availability of water in semi-arid and monsoonal climates with a pronounced dry season and periodic droughts leads to the utilisation of ground water. Shah (2009) has shown that over the past 40 years India has transitioned to dependence on large-scale, energy-intensive groundwater pumpage for irrigation, which is becoming unsustainable. The resulting depletion of groundwater resources has been mapped both by conventional groundwater monitoring techniques and satellite monitoring (Tiwari et al. 2009). These data assist the assessment of water resources into blue and green water, summarized by Falkenmark and Rockström (2006), in which blue water is the water contained in rivers, lakes and aquifers and green water is soil water, i.e. water in the vadose or unsaturated zone above the water table. Reference to Fig. 4.1 suggests that this terminology is a convenient vehicle for classifying the interconnected components of the water cycle for management purposes, as expressed previously (e.g., Winter et al. 1998; Alley et al. 1999; Sophocleous 2002, 2003). Green-blue analysis of water availability with the LPJml dynamic vegetation and water balance model (Rockström et al. 2009) has demonstrated that well-managed green water can support food production in many countries which are currently water-short.

Globally, groundwater provides essential support to humanity for water supply and irrigated agriculture to ensure food security and maintain the environment through the provision of ecosystem services. This chapter provides an overview of these issues and concepts such as the sustainable yield of aquifers and groundwater depletion from the overexploitation of aquifers in sub-chapter 4.2. Policy and methods for the sustainable management of these activities and related ecosystem services are reviewed in the context of risk in sub-chapter 4.3. The methods include various types of mathematical and socio-economic models for ensuring the participation of all stakeholders in managing a groundwater resource; modelling is discussed in sub-chapter 4.4. Also, there is the considerable challenge of mitigating the impacts of coal mining and the production of coal bed methane (coal seam gas) and shale gas on groundwater resources – topics discussed in sub-chapter 4.5. Finally, sub-chapter 4.6 brings the themes of groundwater management and mineral resource extraction together in case studies of the Great Artesian Basin and the Murray-Darling Basin of Australia.

4.2 GLOBAL GROUNDWATER RESOURCES IN A CHANGING CLIMATE

The idea of the global water cycle was introduced previously to serve as a framework within which blue and green water could be assessed, and policies developed for their sustainable management. It was shown that monitoring on the global scale by means of satellite observations combined with traditional methods of hydrological and hydrogeological investigation had provided a baseline

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inventory from which climate change scenarios can be projected. The regions of severe water stress noted by Oki and Kanae (2006) are predicted to shift geographically as climate changes so collaborative approaches to policy and management goals will be required. One such approach is unitization, borrowed from the oil and gas industry for co-operation in the development and utilization of a shared resource (Jarvis 2006, 2010a). Unitization also shares its provenance with the concept of peak oil originally introduced by Hubbert (1969) to predict (correctly) that oil production in the USA would peak in 1970. The peak oil concept has been transferred to water to define the peak water as blue and green water which is utilized beyond sustainable demand, leading to undesirable consequences for water supply, irrigation, food production and ecosystems (Gleick and Palaniappan 2010).

The availability of satellite data has demonstrated the spread of areas with peak water and highlighted the necessity to evolve policy and management. The well-established principles of integrated water resources management (IWRM) have been used to allocate blue and green water to satisfy water supply, agriculture and ecological requirements. In its current form, IWRM is implemented by developing water policy, laws for water rights, water pricing for allocation and participatory decision making on the scale of the drainage basin (Shah and Van Koppen 2006). A similar framework was outlined by the International Association of Hydrogeologists Australia (IAH Australia 2004). The adoption of IWRM principles by unilateral and multilateral development assistance agencies and donors ensures its widespread use. Giordano and Shah (2014) argue that IWRM has become unduly prescriptive in its application and discourages alternative solutions to local problems. The increase in peak water and its effect on food security and related issues adds urgency to the debate.

4.2.1 The Role of Groundwater in Water Supply, Irrigation, Food Security and Ecosystems Services

It is apparent from Figure 4.2 that groundwater represents a large part of the earth's freshwater. In arid and semi-arid areas, it is the main source of water supply and supports irrigated agriculture globally to a significant extent, contributing to food security. It also has a major role in maintaining the surface phase of the water cycle by flows to lakes and forming the base-flow of rivers (Bovolo et al. 2009). These connected surface water and groundwater systems are increasingly being managed as a single resource (SKM 2011) but their exploitation can result in unsustainable development (Alley et al. 1999).

Groundwater is a prime example of a common property resource which is available for use by more than one person or entity and which can be degraded by excessive use (Provencher and Burt 1993). In practice, the demands on groundwater often are in mutual competition and various methods of optimal allocation of a scarce resource have been applied to the problem. It is essential to develop viable policies for management of the resource to prevent overuse in the peak water sense, but they must be based on its accurate assessment, such as recharge estimation (Healy and Cook 2002). The basic principle is the hydrologic budget or

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balance, defined as the difference over a long period between inflows and outflows; if the budget is assessed on a seasonal or annual time period changes in storage (which may be positive or negative) are included. Analogous to surface water supply reservoirs a groundwater resource could be characterized by its safe yield or perennial yield, the rate at which an aquifer could be pumped without exceeding long-term recharge (zero depletion) considering all inflow and outflow factors, including water quality degradation (Lee 1915; Conkling 1946; Mann 1963; Domenico 1972; Linsley and Franzini 1972; ASCE 1987; Sophocleous 1998). There has been an on-going debate of long standing on safe yield in the context of the sustainable management of groundwater (Kazmann 1956; Bredehoeft et al. 1982; Bredehoeft 1997; Sophocleous 1997; Sophocleous 1998; Bredehoeft 2002).

The safe yield debate has shifted more recently to explicitly include the broad definition of sustainable yield as the "safe yield" of a groundwater system. Sustainable yield, therefore, is the volume which can be withdrawn in the long-term without adverse environmental and socio-economic consequences (Sophocleous 2000; Alley and Leake 2004; Maimone 2004; Kalf and Woolley 2005; Zhou 2009; Walton and McLane 2013). Gleeson et al. (2012) have extended this discussion beyond the physical groundwater system to include groundwater sustainability on global and regional scales and intergenerational equity concerns. They propose an integrated, adaptive management approach which includes all stakeholders and can be implemented locally, building on the discussion in Gleeson et al. (2010). The discussion has been expanded further by Rudestam and Langridge (2014) to include the conceptualisation and representation of sustainable yield by resource managers, specifically water agencies in California. They identified the differing understanding of sustainable yield by various stakeholders as posing a problem. Nevertheless, knowledge can be advanced through the use of GCMs, groundwater models and decision support systems in the community-based management of blue and green water. Its implementation is an example of how common property resources such as groundwater can be managed sustainably at various levels. The broad common property approach is applied in the coordinated international management of the transboundary Guaraní Aquifer in South America. Management of critical transboundary aquifers is achieved within the growing applications of international law (Dellapenna 2011; Eckstein 2011). The use of collaborative learning in sharing the groundwater within the Umatilla Basin of the northwestern United States is described in a second example.

The first case study involves the huge Guaraní Aquifer System in South America, shared by Brazil, Argentina, Paraguay and Uruguay and containing 45,000 km^3 of water (Wolf and Newton 2010). Some fifteen million people depend on the blue and green water resources of the region for water supply, irrigation and the sustainability of the region's ecosystems. Projected future water demands from population increase led to concern that uncontrolled groundwater abstraction could result in contamination from irrigation runoff and untreated municipal wastewater, and depletion of the resource. The four countries with support from the World Bank and the Global Environment Facility (GEF) of

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UNDP (http://web.undp.org/gef/) established the Guaraní Aquifer Sustainable Development and Environmental Protection Program through the Organisation of American States (OAS) in 2003. The project which ended in 2009 was to obtain scientific information on the aquifer system through five on-going pilot projects (Foster et al. 2009a). The information is compiled into a knowledge base to improve stakeholder communications for future cooperative management of this major groundwater resource. Amore (2011) describes the outcomes of the project, which was implemented at all levels of government in the participating countries and by collaborating stakeholder organisations. The current phase involves the implementation of the approved Strategic Action Program. The agreement is precautionary as there are no existing conflicts over the groundwater resource (Villar and Ribeiro 2011). Agreements of this type are part of the global groundwater governance framework being promoted by GEF with other UN agencies and the World Bank (http://www.groundwatergovernance.org) (Mechlem 2012).

In contrast to the Guaraní Aquifer situation, the Umatilla River Basin in Oregon, USA, is characterised by the competing demands for relatively limited water resources by a large number of stakeholders. The primary user of surface water is irrigated agriculture with supplies supplemented from the alluvial and basalt aquifers in hydraulic connection with the Umatilla River (Jarvis 2010b). Other uses are drinking water supply and environmental flows for maintaining salmon fisheries as required by the 1855 treaty with the now Confederated Tribes of the Umatilla Indian Reservation (CTUIR). Langford (2010) describes the development of irrigation of grain crops and pasture in the latter part of the nineteenth century, supported by the irrigation dams and channels of the Umatilla Basin Project which eliminated the salmon runs. During the 1950s, there was significant expansion of irrigation with groundwater resulting in water level declines on the order of 150 m (Jarvis 2010b). The response of the Oregon Water Resources Commission in the 1970s was to designate critical groundwater areas in which groundwater pumping was severely restricted, leading to legal conflict (Schlager 2007). More recently, the Oregon Water Resources Department has used the estimates of sustainable annual yield to restrict use to 30% of issued groundwater rights (Langford 2010). Although the salmon fishery has partially recovered through the collaboration of irrigators and the CTUIR taking water from the Columbia River and leaving the equivalent volume in the Umatilla River (Langford 2010), the problem of declining groundwater levels still exists. The proposal by the Umatilla County Planning Commission to impose a land-use overlay zone within the critical groundwater areas was countered with a change of policy suggested by the stakeholders. The policy change was to establish the Umatilla County Critical Groundwater Taskforce (UCGT) with membership drawn from the irrigators, the CTUIR, media, universities and state and federal government agencies (Jarvis 2010b). Stakeholder and public participation is included through the collaborative learning approach of Daniels and Walker (2001) which increased knowledge of the groundwater management issues. This approach facilitates the communication to stakeholders of the on-going

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hydrogeological and modelling investigations by the U.S. Geological Survey (USGS Oregon Water Science Center 2013). GCMs are part of the modelling effort to simulate projected future conditions (Vynne et al. 2010) and support proposals for policy and sustainable management (UCGT 2008).

The case studies of the Guaraní Aquifer and the Umatilla Basin represent management policies with a major input from government technical, scientific and regulatory agencies. These policies are not the only means by which sustainable groundwater management can be achieved especially where large numbers of small-scale users are involved. In these situations, the collaborative learning approach can be extended to the idea of social learning (Pahl-Wostl et al. 2007) in which learning is not confined to particular groups of experts or stakeholders. Instead, all parties collaborate in the learning process which is embedded in the structure of governance of the resource. The village of Hivre Bazaar in Maharashtra, India, is an example of the achievement of food security through community self-regulation of groundwater use for irrigation and water supply (Foster et al. 2009b). Following Shah (2008, 2009) it may be argued that the principles described in Foster et al. (2009b) and demonstrated for Hivre Bazaar can be upscaled to the national level in India. An obstacle identified by Shah et al. (2012) is the extent of subsidies which tends to encourage groundwater depletion. Policy changes must involve not only major government agencies for their scientific and engineering expertise in groundwater recharge management but also the millions of farmers and householders in their thousands of communities for an effective strategy (Shah 2009).

Garduño and Foster (2010) develop these concepts further within the context of sustainable irrigation on the global scale. The massive, world-wide increase in irrigation has largely relied on groundwater in arid areas and those with long dry seasons. In India, the area irrigated with groundwater has increased 500% since 1960; this area currently amounts to 39 million hectares, followed by China with 19 million hectares (Garduño and Foster 2010). Figure 4.3 shows the proportion by area and volume of groundwater used throughout the world. The preponderance of South Asia (mainly India), East Asia (especially China) and the Middle East is clear. The very low usage in sub-Saharan Africa may be due partly to imprecise knowledge of groundwater reserves, but this gap is being remedied (MacDonald et al. 2012). Globally the groundwater irrigation area amounts to 112.9 million hectares (38% of the total area) with annual usage of 545 cubic kilometres (43% of the total usage) (Garduño and Foster 2010). In many areas, this level of exploitation is unsustainable or is becoming so (Wada et al. 2012). Some of these areas are in the peak green and blue water situation and according to Brown (2013): “The world has quietly transitioned into a situation where water, not land, has emerged as the principal constraint on expanding food supplies”. In this context, Brauman et al. (2013) have shown that better management to improve water productivity, defined as the food produced (kcal) for each litre of water consumed, has the potential annually to feed ~110 million people (rainfed agriculture) and reduce consumption (irrigated cropland) to supply ~1 billion people. Although water for drinking supply, industry and irrigation are essential,

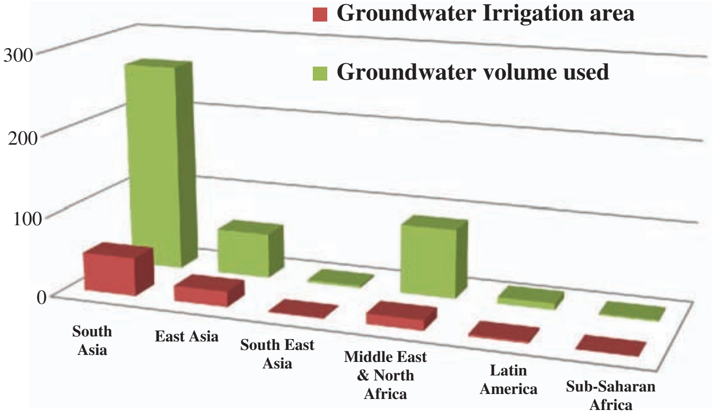

Figure 4.3. Groundwater irrigation area (M ha) *and groundwater volume used* (cubic kilometres per year)

Source: Data from Table 4.1 in Garduño and Foster (2010); original data in table from Siebert et al (2010)

environmental and ecological requirements, such as the maintenance of ecosystems which rely on groundwater–groundwater dependent ecosystems (GDEs)–are equally critical. Policies which include these components through the concept of ecosystem services are necessary for sustainable development.

Ecosystem services are defined as the benefits provided to human society by ecosystems as services for: provisioning–water, timber, food; regulation–flood and erosion control; support–formation of soil, recycling nutrients; and, culture–recreation, spiritual experience (Millenium Ecosystem Assessment 2005; Bergkamp and Cross 2006). Many of these services are interrelated with groundwater as in the transport of nutrients and dilution of contaminants in green and blue water storage, control of groundwater recharge and in the regulation of streamflow by groundwater discharge as baseflow (Eamus and Froend 2006; Eamus et al. 2006). Bergkamp and Cross (2006) show that the close linkages between groundwater and ecosystem services are often not recognised and are not valued adequately. They describe natural capital as the overall stock of material and information that is the basis of ecosystem services which must be maintained for sustainability. There is a range of economic instruments which can be applied to estimating the worth of ecosystem services: concept that water is an economic as well as a social good which can be regulated by legislation, taxes, tradeable permits for its use, and planning strategies (Bergkamp and Cross 2006; Murray et al. 2006).

The demand for increased food production may often conflict with the provision of other ecosystem services and maintenance of biodiversity in a land and water system (Maskell et al. 2013). Their work involved the spatial analysis of multiple ecosystem service interactions throughout the United Kingdom but did not include groundwater considerations. Nevertheless, it demonstrates the interactions between the various ecological constraints on biodiversity which

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should be considered in development planning. Restricting consideration to groundwater related ecosystem services reduces the complexity of the problem but at the cost of lack of knowledge about biodiversity in groundwater ecosystems populated by microbes and stygofauna (invertebrates in the aquifers). Boulton et al. (2008) pose the question of the significance of the high biodiversity in stygofauna in some aquifers and the possible effects on ecosystem services such as bioremediation and water purification. These subsurface groundwater dependent ecosystems (SGDEs) possess intrinsic scientific interest as well as a relatively unknown influence and linkages with other ecosystems (Tomlinson and Boulton 2008, 2010). Recent sampling of stygofauna in the Border Rivers region of southern Queensland, Australia has found their unexpected occurrence in saline aquifers where the electrical conductivity is close to that of seawater (Schultz et al. 2013). There is pressing need of a governance framework for SGDEs and related groundwater ecosystem services (GESs), possibly following the framework described by Knüppe and Pahl-Wostl (2013) to include groundwater ecosystem services in sustainable management while meeting water supply and irrigation objectives.

4.2.2 The Challenges of Groundwater Depletion and Resource Degradation

The concepts of peak blue and green water are becoming widely applied to global groundwater resources as it is clear that plentiful supplies of groundwater are no longer available at low socioeconomic and environmental cost. Data from satellite mapping and modelling show that water tables are falling in aquifers in the USA, China, India and elsewhere as groundwater volumes pumped exceed recharge (Giordano 2009; Rodell et al. 2009; Hu et al. 2010; Famiglietti et al. 2011; Wada et al. 2012; Voss et al. 2013). This blue/green groundwater resource is renewable but is considered to be non-renewable when the continued excess pumping results in groundwater depletion, leading to groundwater mining and ultimately, exhaustion of the resource. There may be a component of non-local water from cross-basin diversions, desalination plants and ancient groundwater (Wada et al. 2012). The contribution of the various types of water resources to the gross irrigation water demand in different countries is shown in Figure 4.4. India and China are the largest users of blue and green water, but overall India uses the greatest volume of non-renewable pumped groundwater and non-local resources. The relatively large component of non-local water use in India and Pakistan may be related to the continuing use of extensive canal distribution systems of surface- and groundwater-derived irrigation water (Shah 2008). Although the actual use by Saudi Arabia is comparatively small, its dominant water resource is the hoary, non-renewable groundwater in deeply buried aquifers. Foster and Loucks (2006) discuss the classification of non-renewable groundwater resources and supply some useful definitions of groundwater depletion. They distinguish between non-renewable and fossil groundwater. Non-renewable groundwater occurs in aquifers with large storage capacity but very low renewal rates; fossil groundwater was recharged in earlier millennia usually under more humid climates.

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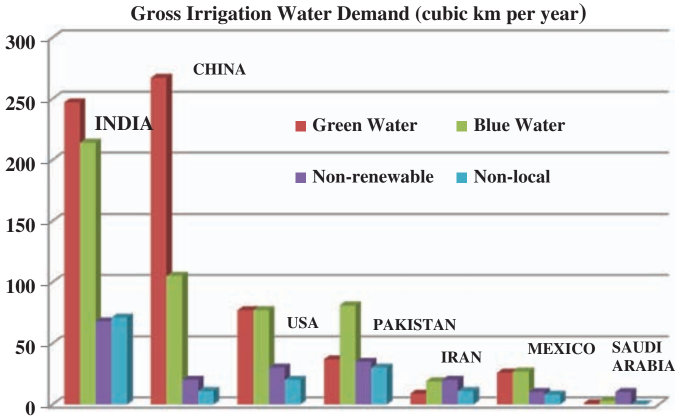

Figure 4.4. Contribution of blue, green, non-renewable and non-local water to gross irrigation water demand for the year 2000
Source: data from Table 4.2 of Wada et al. (2012)

The definitions of non-renewable and fossil groundwater are not entirely mutually exclusive as both incorporate the time period of the water storage. Non-renewability indicates that the turnover time – the time taken for water to transit from recharge to discharge zones of an aquifer – is longer than the practical time period for the exploitation of the aquifer. In contrast, fossil groundwater has a much greater age or residence time – the length of time the water has remained in the aquifer. Standard methods for characterising aquifers, described in textbooks such as Todd and Mays (2005), are coupled with carbon dating and other isotopic techniques for estimating groundwater age and recharge rates (Kazemi et al 2006; McMahon et al 2011). The major regional aquifer systems of North Africa, the North Western Sahara Aquifer System–Libya, Algeria and Tunisia–and the Nubian Sandstone Aquifer System–Chad, Sudan, Libya and Egypt, are examples of mainly fossil groundwater resources, whereas the Great Artesian Basin of Australia contains a large proportion of non-renewable resources (Ahmed 2013).

Some of the adverse quality side effects associated with groundwater depletion are (1) salinization due to irrigation and seawater intrusion into coastal aquifers, and (2) industrial pollution. Knapp and Baraenklau (2006) describe an economic-hydrologic model of groundwater salinization induced by agricultural activity. Typical industrial pollutants are nutrients, active ingredients of pesticides and persistent organic contaminants. Recently, so-called emerging contaminants derived from agriculture, pharmaceutical products, veterinary medicines and nanomaterials have generated concern about their potential to contaminate the environment. Boxall et al. (2007) have posed rhetorical questions addressing their potential risk to human health. There is increasing use of nanomaterials in cosmetics, pharmaceuticals and personal service products and studies of their toxicity and fate in the aquatic and soil environments have been undertaken (Lam et al. 2004; Dhawan et al. 2006; Liu et al. 2009). The transport in saturated, heterogeneous porous media has also been the subject of various studies (Tufenkji et al. 2003; Mehrabi and Milne-Home 2012). Boxall (2012) observes that the impact of these contaminants and their interactions will need to be considered in terms of risk management.

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4.3 RISK MANAGEMENT IN GROUNDWATER DEVELOPMENT

Risk management includes all the procedures and values which facilitate the effective management of opportunities for gains while minimising losses. The risk management process is defined by Australian Standard AS4360:1999 (now Australian/New Zealand Standard AS/NZS ISO 31000) as “the systematic application of management policies, procedures and practices to the tasks of establishing the context, identifying, analysing, evaluating, treating, monitoring and communicating risk.” Risk management can be applied to develop equitable strategies for the assessment of sustainable yield through quantifying the uncertainty in estimates of the long-term average annual recharge for input to groundwater models (Merrick 2000). Other applications can focus on avoiding or minimising the adverse effects of aquifer overexploitation, for instance, seawater intrusion into coastal aquifers. Groundwater modelling is an integral part of these management procedures, and the incorporation of risk management will ensure that risks are known and measures are taken to mitigate those risks. Also, it will allow stakeholders to make informed decisions about groundwater management and reduce planning uncertainty around future development (Staltari 2010).

A risk management strategy for the groundwater industry, including a three-level risk assessment methodology, is described by Staltari et al. (2011). The proposed risk management framework assesses a set of criteria and analyses risks to develop a risk ranking. Next, management options are assessed to reduce the risk, through a comprehensive study of the options and the activities associated with them (Level 1). Stressors, such as climate change and land use changes, which could affect management options are identified (Level 2); selected management options are analysed in depth at Level 3. The tiered approach to risk management allows the user to implement the appropriate level, ensuring that risks are captured, analysed and transparent from the early stages of planning through to more elaborate aquifer management. In order to adequately compare the risks across criteria and demonstrate these graphically, an analysis section is included in the risk assessment. A risk ranking score is calculated from the risk ranking and used for graphical summaries of the data. The risk ranking score and graphical summaries allow relationships between management options, risks, stressors and impact criteria to be demonstrated. The graphical summaries organise risks in a clear and concise manner, aiding in decision-making and prioritisation efforts. The Level 2 assessment identified the key areas of risk to the water resource, through the risk of sea water intrusion, social impacts from community concern as

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the water source is depleted, and environmental impacts from the risk to GDEs. The groundwater and seawater intrusion models MODFLOW and SEAWAT were used to estimate the risk of seawater intrusion and to evaluate sustainable groundwater pumping regimes. The models were also used for scenario analysis to examine future groundwater management options. The risk assessment framework applies a holistic approach to the assessment of risks incorporating both quantitative and qualitative assessment of risk. Groundwater modelling is an essential component of risk assessment because it can provide an indication of the uncertainty associated with each planning option by implementing a probabilistic approach.

4.4 GROUNDWATER MODELS AS TOOLS FOR SUSTAINABLE GROUNDWATER MANAGEMENT

The estimation of sustainable yield is an important part of groundwater management especially in the typical situation of interconnected surface water and groundwater systems. These systems can interact as gaining or losing and as connected and disconnected (Figure 4.5) (Winter et al. 1998).

The management of water resources involves consideration of water rights, entitlements and allocations. The definition of these terms in the Australian context are: water right is the statutory right to use water from a water resource; water entitlement is the water right issued to a person or entity; and, water allocation is the volume of water that the holder of a water entitlement is

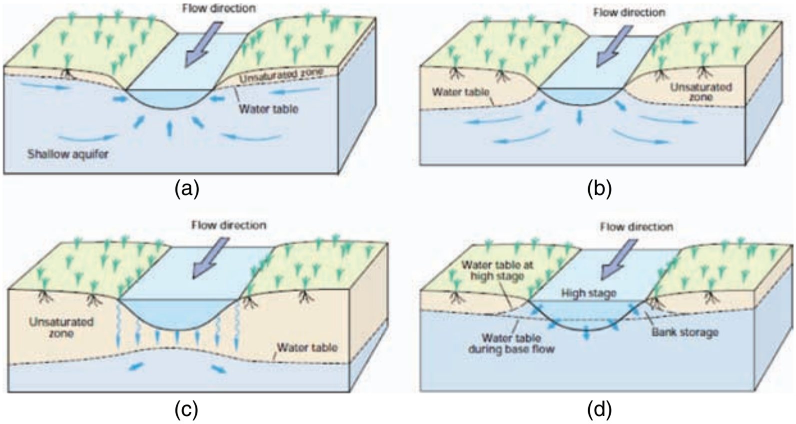

Figure. 4.5. Connection modes surface and groundwater systems, (a) connected gaining stream; (b) connected losing stream; (c) disconnected losing stream; and (d) fluctuating connected losing stream–high stage recharges bank storage which partly discharges to the stream as baseflow during low stage
Source: Winter et al. (1998)

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authorised to extract from a particular resource for a defined period of time (SKM 2011). The estimation of the sustainable yield of a resource is the basis for the issue of water allocations within existing rights and entitlements. In many instances, the lack of an accurate estimate of sustainable yield has allowed the overallocation of water with the result that the groundwater system has become stressed due to overexploitation. There may be competition among holders of rights and entitlements, including statutory allocations for environmental flows and maintenance of GDEs and SGDEs. Overallocated groundwater in New South Wales, Australia is being addressed by the State and Commonwealth (federal) governments to reduce entitlements of irrigators to sustainable yield levels through various policy instruments including cap and trade schemes (Goesch et al. 2007). The cap provides a limit to extraction of the groundwater, and trading allows water to be allocated to the usage of highest value. Application of these policies to the connected systems shown in Figure 4.5 is complicated by their susceptibility to 'double accounting', where an allowed increase in groundwater abstraction may affect surface water flows, i.e. the same volume of water has been allocated twice (SKM 2011). A wide range of groundwater models is available for application to resource management. Only a selection of commonly-used models will be discussed in this sub-chapter.

Modelling of interconnected surface water and groundwater systems requires the use of models that can simulate the behaviour of both systems based on a good understanding of the interactions between them. The interactions can be handled by the imposition of suitable boundary conditions in groundwater models but fully coupled and integrated models will provide more precise estimates of flow and mass balance in the systems. The increased precision comes at the cost of larger data requirements and computational complexity. The issues of time and space scales have to be considered: rainfall and streamflow event-based processes operate on timescales of less than a day whereas groundwater flow as it impacts on baseflow takes place over much longer periods. These considerations influence the design of the spatial and temporal discretization grid of the model. In practice, numerical simulation models are used to inform planners and stakeholders on policy and management and there has to be a trade-off between the physically detailed simulation of streams and aquifers and meeting management objectives. Risk management and the inclusion of uncertainty both in the modelling process and decision-making are also important Jakeman et al. (2006). Recommendations for the suitable use of groundwater models have been developed worldwide; the recently revised, comprehensive Australian groundwater modelling guidelines document is a good example (Barnett et al. 2012).

There are a large number of open source and commercial software codes for modelling surface and groundwater systems shown in Figure 4.5, and non-renewable aquifers. The MODFLOW open source finite-difference based package developed by the U.S. Geological Survey (USGS) has become an international informal standard for simulating saturated groundwater flow. The modular structure of the code has allowed the development of specialised packages for modelling coupled surface water and groundwater systems, land subsidence,

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seawater intrusion and groundwater management. The current core version is MODFLOW-2005 and a new version, MODFLOW-USG (for UnStructured Grid), has been released which offers flexibility of the model grid beyond the original rectangles to other shapes (USGS 2014; Panday et al. 2013). A commercially available extension of MODFLOW is the package MODFLOW-SURFACT which can simulate saturated and unsaturated flow as well as solute transport (Panday and Huyakorn 2008). MODFLOW-SURFACT was found to yield more accurate estimates of groundwater heads and unsaturated flow directly above a longwall coal mine in the Sydney Basin, Australia, than MODFLOW (Merrick 2009). MODHMS is an extended form of MODFLOW-SURFACT and is a fully integrated code including simulating two-dimensional overland flow and one-dimensional flow and solute transport in rivers (Panday and Huyakorn 2004). Panday et al. (2009) describe the application of MODHMS to the management of water flow and quality in a complex water resources system that included water reclamation plants, dams and an underlying groundwater basin in southern California. Other commercial software with broadly similar capabilities are the finite element codes FEFLOW and Hydrogeosphere (Trefry and Muffels 2007; Brunner and Simmons 2012; Sciuto and Diekkrüger 2010; Diersch 2014).

4.5 GROUNDWATER MANAGEMENT AND MINERAL RESOURCE DEVELOPMENT

Extractive mineral resource industries can have a significant environmental impact from the initial exploration activities, through the mining development and production stages to the final mine closure and rehabilitation. The entire process can last for many years with tremendous implications for groundwater and environmental management through the disruption of GDEs and SGDEs, and the diversion of water resources for consumptive use by the mining operations. Open cut coal and metals mines can change the regional groundwater flow systems by creating extensive artificial discharge areas. There is also the potential for contamination of surface water and groundwater by water produced during the mining through the impacts of natural events such as severe storms and flooding on water storages. Underground mining can cause subsidence that reduces streamflow, is responsible for the decline in groundwater levels and disruption of GDEs and SGDEs. The water quality resulting from the oxidation of sulfide minerals in mine tailings dumps can be highly variable in salinity and pH. The drainage produced as a byproduct of mining may be acid to slightly alkaline (circumneutral in nature with a high sulphate content and may contain dissolved heavy metals [International Network for Acid Prevention (INAP) 2009]. The impacts on water quality can continue for decades or centuries after a mine has closed and it is essential to implement procedures to minimise the formation of acid mine drainage (INAP 2009).

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The potential for environmental harm from mining activities has stimulated monitoring agencies worldwide to establish policies for the regulation of the industry to protect surface water and groundwater resources. In New South Wales, Australia the main policy instrument is the *NSW Aquifer Interference Policy* (NSWAIP) (NSW Department of Primary Industries Office of Water 2012) which is implemented under the *Water Management Act 2000* and related legislation. Aquifer interference is defined under the Act as penetration of an aquifer, interfering with its contained groundwater or obstructing the groundwater flow. The Act also governs the taking and disposal of groundwater during mining (NSW Department of Primary Industries Office of Water 2012) and includes coal seam gas (coalbed methane) production, water injection and any other activities – business, industry, agriculture, housing, quarrying of sand and gravel, construction dewatering – which penetrate or interfere with aquifers. GDEs are protected even in the absence of groundwater production, and any disposal of water or waste material may trigger provisions of the *Protection of the Environment Operations Act 1997*.

The requirement for proper accounting of the water taken is addressed by the issue of a water licence to ensure that the extraction limit of the applicable water sharing plan–the allocations to existing users under the rights and entitlements for the time period of validity of the policy–are not exceeded. Also, minimal impact considerations are the assessment criteria applied by the NSW Office of Water to examine the impacts on groundwater systems which may be affected by a development proposal. Review by an independent Gateway Panel is included in the application process to assess the potential impacts of a project on strategic agricultural land and water resources. In practice, the NSWAIP is an attempt to apply sustainable management principles to surface and groundwater systems in areas subject to major development proposals.

4.5.1 Sustainable Groundwater Management and Coal Mining

Coal is extracted mainly by open-cut and longwall mining methods depending on the depth of the coal resource. In the open-cut method, the coal is mined with large excavators leaving a void which gradually increases in area and depth as the mining proceeds and extends below the water table. Initially the overburden topsoil and rock strata are removed by blasting to expose the coal seams and the mine is initiated with a rectangular-shaped excavation in an area where the ratio of the overburden thickness to that of the coal seam is relatively low. As the mine develops, it is backfilled with mining spoil (waste rock) which is more permeable and has a higher storage capacity than unmined rock material, allowing infiltration of rainfall. A partially filled void remains on completion of mining and has to be rehabilitated as part of the post-mining landscape and environment. The partially filled void forms a water body or pit lake which is filled by direct void rainfall, spoil runoff and seepage, and groundwater inflow or through flow (Bowell 2002; Hancock et al. 2005). Bowell (2002) indicates that water quality can change from acid mine drainage type to circumneutral mine drainage type over time. This opens the potential for obtaining recreational or ecological

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benefits from pit lakes (Gammons et al. 2009). Hancock et al. (2005) showed by mass-balance modelling that the salinity of a pit lake in the Hunter Valley would increase from 2452 to 8909 mg/litre over 500 years due to concentration by evaporation and inflow of saline groundwater as the regional groundwater system re-equilibrated to post-mining conditions. Mackie (2009) discussed the evolution of the water chemistry of the leachate resulting from the re-saturation of the mine spoil and demonstrated from batch reaction trials on core samples of representative lithologies that a predominantly $NaHCO_3$ type of water would result. Younger and Robins (2002) provide a comprehensive review of mine hydrogeology and water quality.

While the landscape footprint of longwall mining is less because the operation takes place underground, the method has the potential to change the connectivity of surface water and groundwater systems in the affected area. In longwall mining, large, rectangular blocks–panels - up to several kilometres long and typically 150 to 400 metres wide are mined, leaving support only in the vicinity of the working face. The excavation and removal of the coal as the panels are advanced in parallel induces fracturing and subsidence above the unsupported mined area which can extend gradually to the ground surface. The subsidence affects hydraulic gradients, piezometric levels and groundwater flow paths (Booth 2002, 2006) and as confined aquifers become unconfined there are changes in water quality (Booth 2007). Adverse changes have been noted by McNally and Evans (2007) where groundwater in areas downstream of mining in the Southern Coalfield of NSW are de-oxygenated, more saline and contain high concentrations of total iron and manganese. Madden and Merrick (2009) summarise the initial hydrogeological effect of longwall mining as the formation of a collapsed and heavily fractured zone directly above the mined area draining directly into the mine. Next, a constrained zone develops, which subsides without much fracturing, remains saturated and acts as a barrier to vertical drainage from the surface and shallow aquifers to the mine. Finally, a surface zone characterised by fracturing is created and which typically does not contribute drainage to the mine. A key parameter is H, the height of complete groundwater drainage above subsided longwall panels (Tammetta 2013), mainly from the collapsed zone. Tammetta presented a generally applicable empirical expression for H (in metres):

$$H = 1438\ \ln(4.135 \times 10^{-5} u + 0.9818) + 26$$

where $u = wt^{1.4} d^{0.2}$ and t are the width and height of the mine opening, and d is the overburden thickness (all in metres). H defines the maximum height of the collapsed zone which is unsaturated and acts as a drain while the mine void remains dewatered (Tametta 2013). Although the fractured surface zone is relatively disconnected from the mine void there are potentially far-reaching effects on shallow hydrology: reduction in streamflow, increased infiltration locally and decreased runoff for regional recharge as the connectivity between surface and groundwater is enhanced due to the fracturing (Jankowski 2009). These effects have been widely documented in mining areas, e.g. Shepley et al.

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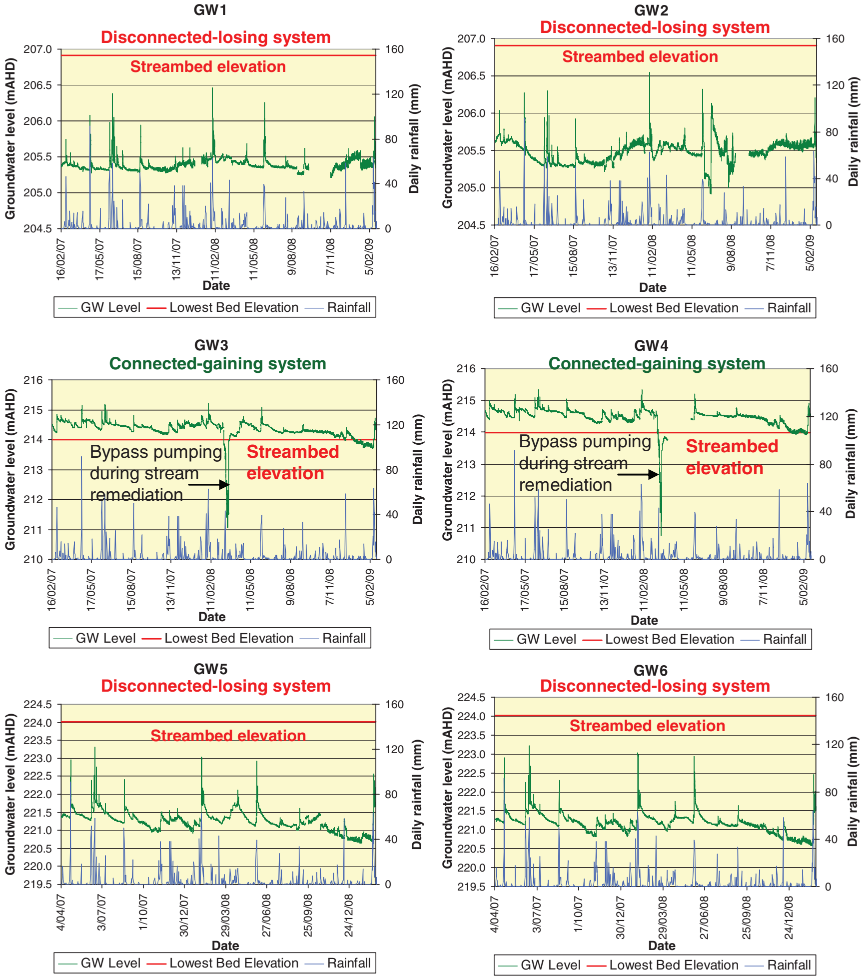

Figure 4.6. Groundwater levels, rainfall and streambed elevations in the mining area of the Southern Coalfield

Source: Figure 4.5 from Jankowski (2009); reproduced with permission from the author and International Association of Hydrogeologists (IAH)

(2008) from central England, and Sidle et al. (2000) from Utah, USA. Figure 4.6 illustrates various aspects of this connectivity for the Southern Coalfield, NSW, Australia.

The groundwater levels in Figure 4.6 were measured in shallow piezometers near the river: downstream at the edge of the mining zone (GW1 and GW2); within the mining area (GW3 and GW4); and, downstream in the area mined in 2003–2004 (GW5 and GW6). The downstream area has partially recovered from the mining but open fractures, joints and bedding planes still permit subsurface flow

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(Jankowski 2009). The area of active mining, GW3 and GW 4, is still in the compression phase of subsidence with partially re-closed fractures; GW1 and GW2 are in an area yet to be mined and are above the heading at the edge of a mined longwall panel, within the area influenced by the 35° angle of draw (the angle at which the subsidence migrates to the surface subsidence limit) (Jankowski 2009). The river is disconnected-losing because of the likelihood of the development of high-capacity fractures capable of transmitting infiltrated water. Jankowski and Madden (2009) describe the features of an ideal monitoring program for assessing the ecohydrological impacts of longwall mining in hydrologic catchments. The program must be designed to adequately monitor and interpret the changes in groundwater, surface water and water quality in time and space and assess the post-mining recovery of the groundwater systems (Jankowski and Madden 2009).

The overarching principles of sustainable management of groundwater and the preservation of ecosystem services in regions subjected to open-cut and longwall mining is that of comprehensive, long-term monitoring within an effective regulatory framework. Historically, mines in Europe and elsewhere have been active for periods considerably in excess of fifty years with a total time of activity and recovery of centuries. In Australia the cumulative effect of existing mines in the Hunter Valley, NSW, and the Galilee Basin, Queensland, combined with the major proposed expansion of coal mining and coal seam gas production, represents a significant challenge for sustainable management of groundwater.

4.5.2 Sustainable Groundwater Management in Areas of Coal Seam and Shale Gas Development

Coal seam gas (CSG), also known as coal-bed methane (CBM), is the methane generated when the coal was formed and is adsorbed on the surface of the coal under hydrostatic pressure in the fractures and microstructures (cleats) of the coal seam. CSG may also contain trace amounts of carbon dioxide and/or nitrogen. The large internal surface area of a typical coal seam allows the storage of six or seven times the volume of natural gas than exists in the equivalent volume of a conventional natural gas reservoir (U.S. Geological Survey 2000a). When the reservoir pressure is reduced by pumping the groundwater from a well drilled into the coal seam, the methane is desorbed off the coal surfaces and flows into the well. Current drilling and completion technology includes directional drilling laterally into the target seam and hydraulic fracturing ("fracking") – injecting fluid containing additives and sand at high pressure to fracture the coal seam. Palmer (2010) provides an overview of completion methods and their relationship with permeability and well productivity. Water (co-produced water) is pumped from a coal seam as an integral part of the CBM production process. If the well has been fracked the fracking fluid is pumped to the surface via the well and is kept separate from the co-produced formation water. The use of fracking for stimulating CBM and shale gas wells has been the subject of heated debate because of perceived risks to human health and the potential to contaminate groundwater and the environment through the chemicals used. The volumes of water produced and the water quality are highly variable and depend on factors including the length of time the

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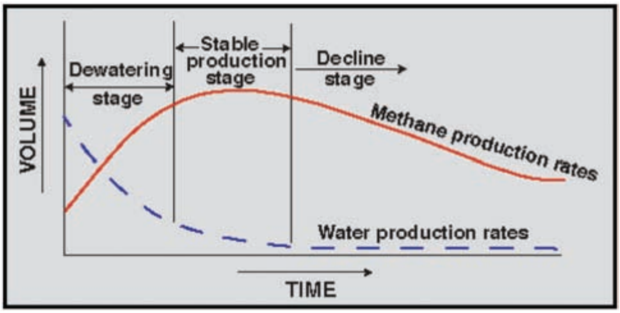

Figure 4.7. Schematic production profile of a typical CSG well
Source: Figure 4.2 in U.S. Geological Survey (2000a)

coal basin has been producing CBM, the coal depositional environment, depth of burial and type of coal (U.S. Geological Survey 2000b). The schematic production profile of a typical CBM (CSG) well, shown in Figure 4.7, illustrates the inverse relationship between CSG and water production rates prior to the peak CSG rate (the dewatering and early stable production stages), and the low yield of water in the later life of the well (the decline stage). The time can range from months to years.

The composition of co-produced water is mainly sodium bicarbonate and sodium chloride type because the presence of methane (CH_4) and carbon dioxide (CO_2 favours the precipitation of magnesium and calcium carbonates; the water is relatively low in sulphates (SO_4) as the reducing conditions tend to convert sulphates to sulphides. The averaged major ion composition of CBM water is consistent with the water quality reported by Van Voast (2003) from the six main producing basins in the USA. A similar composition of major ions was observed by Kinnon et al. (2010) for CSG co-produced waters from the Bowen Basin in Queensland, Australia. Dahm et al. (2011) compiled a geochemical database of 3000 CBM water samples from four basins in the Rocky Mountains region of the USA. The database included physicochemical, organic and inorganic parameters, and radionuclides; although individual constituents were in low to moderate concentrations, the TDS ranged between 150 and 39,260 mg/L and the sodium adsorption ratio (SAR) was between 0.2 and 452.8. The SAR of a water sample is defined as the ratio of sodium ions [Na^+] to the square root of half the ionic concentration of the summed calcium [Ca^{2+}] and magnesium [Mg^{2+}] ions. SAR values >9 pose a severe risk of increasing the sodicity of soils.

The variation in the volumes of co-produced water is illustrated by the observations that CSG wells near Camden in the Sydney Basin southwest of Sydney produced 4.8 megalitres (ML) of water in 2012 out of a maximum of 30 ML/a. In contrast, the range in the Surat basin of Queensland is 7 to 300 ML/a (NSW Department of Primary Industries Office of Water 2013). The CSG industry is more developed in Queensland than in New South Wales–the two major CSG producing States in Australia–and the Coal Seam Gas Water Management Policy 2012, administered by the Queensland Department of

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Environment and Heritage Protection, to sustainably manage the produced water may reflect its longer experience with the industry. The policy is operated under the relevant Acts, e.g. *Environmental Protection Act 1994,* and provides strict guidelines for the conduct of CSG production operations. In New South Wales, CSG co-produced water is managed through the *Petroleum (Onshore) Act 1991* and the *Environmental Planning and Assessment Act 1979*. The NSWAIP governs potential impacts on surface water and groundwater, including the disposal of CSG co-produced water. The use of evaporation ponds or basins is banned by both jurisdictions, and the use of BTEX chemicals (benzene, toluene, ethyl benzene, xylenes) in fracking is also banned by the NSW government. Khan and Kordek (2013) discuss process engineering approaches to beneficial use, risk assessment and risk management of CSG co-produced water as mandated by the regulations.

Unlike coal bed methane which occurs at relatively shallow depths, shale gas is found in deeply buried shale formations hundreds to thousands of metres below ground. Shale gas can be dry, consisting mostly of methane or wet, with small amounts of ethane, propane, butane and other heavier hydrocarbon natural gas liquids. There may also be significant amounts of carbon dioxide, helium, nitrogen and hydrogen sulphide (Schlumberger 2014). The composition of gas from individual shale formations can vary widely due to geological heterogeneity (Bullin and Krouskop 2008). Previously gas-bearing shales had been considered only as a source rock for natural gas and associated oil reservoirs, but the development of fracking technology has made it possible to produce gas from these extremely impermeable formations. Figure 4.8 is a schematic of the various

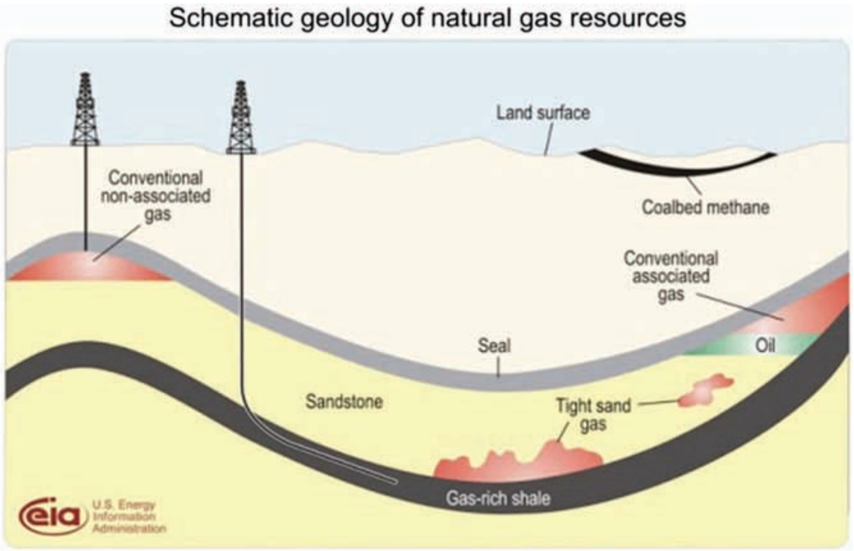

Figure 4.8. Occurrence of natural gas reservoirs
Source: U.S. Energy Information Administration, http://www.eia.gov/oil_gas/special/ngresources/ngresources.html (accessed on February 21, 2014)

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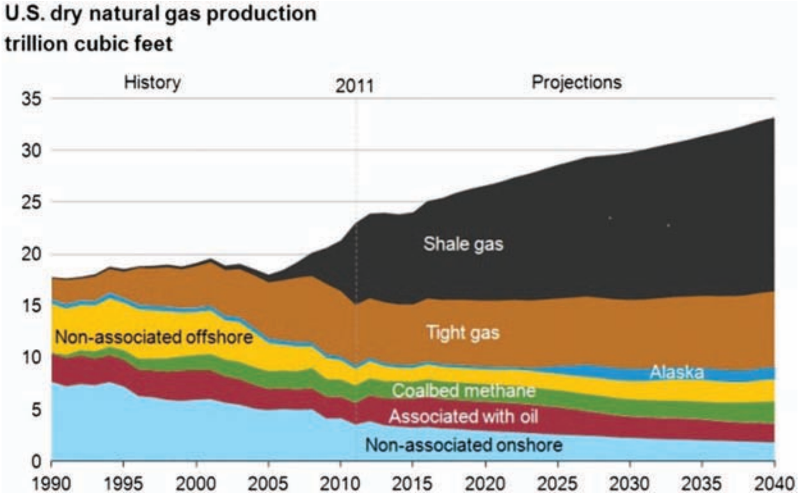

Figure 4.9. Historical trends and projected forecasts of dry natural gas production in the U.S., 1990 to 2040

Source: U.S. Energy Information Administration, *Annual Energy Outlook 2013: Early Release*, http://www.eia.gov/energy_in_brief/article/ about_shale_gas.cfm (accessed on February 20, 2014)

types of natural gas reservoirs and highlights the distinction between coalbed methane and other gas resources. Tight gas refers to gas which is trapped in hard rock formations of very low permeability and porosity.

Shale gas is one of the unconventional gas resources sketched in Figure 4.7, together with tight gas and coalbed methane. The feasibility of producing shale gas from "shale-gas plays" – regionally extensive structural basins in the United States – has increased the proportion of shale gas in the production of dry natural gas in the U.S since 2005 and is forecast to be the major source of supply together with tight gas by 2040 (Figure 4.9). An overview of shale gas resources and plays in the USA has been released by the U.S. Energy Information Administration (EIA 2013).

A recent report commissioned by the U.S. Energy Information Administration outlined the estimated extent of shale oil and shale gas, including wet gas, resources on a world-wide basis (U.S. Energy Information Administration 2013; EIA/ARI 2013). Figure 4.10 indicates the geographic distribution of the survey. With the exception of the United States and Canada, many of the shale gas and shale oil resources identified are either undeveloped or in the initial stages of development. Several countries are exploring their shale gas resources.

Based on the U.S. experience, one of the constraints on the development of shale gas and shale oil is the large volume of water needed for fracking a deep gas well, on the order of 4.5 to 13.2 megalitres with up to 19 megalitres for large operations on a single well (Andrews et al. 2009). Freyman (2014) examined water use data on fracking from almost 40,000 conventional oil and gas and shale gas wells throughout the western United States and Canada and showed that intense

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competition with agricultural, municipal and industrial users for water was highly likely. About half the number of wells were in regions of high water stress where 80% of available surface water and ground water was already allocated. Likewise, shale gas developments in the Barnett Shale in Texas (U.S. Energy Information Administration 2011) have the potential to significantly increase competition for the groundwater contained in the regional Trinity and Woodbine aquifers (Andrews et al. 2009). The cumulative fracking water use by approximately 18,000 Barnett Shale horizontal gas wells from 1981 to 2012 was about 210 Mm^3 (Nicot et al. 2014). The water was sourced equally from surface water and groundwater. An earlier study by Nicot and Scanlon (2012) showed that annual use in the Barnett Shale, Texas-Haynesville Shale and Eagle Ford Shale amounted to some 9% of the consumptive use by the city of Dallas (1.3 million people), but was increasing rapidly. Jiang et al. (2014) analysed data from 500 wells in the Marcellus Shale in Pennsylvania to assess the direct water consumption at each well. They also applied economic input-output life cycle methodology to assess the indirect water consumption and wastewater generation by the wells and showed that an average Marcellus Shale gas well consumes 20,000 m^3 of freshwater over its life cycle and fracking was the largest contributor to the water impacts.

The North American experience with constraints on shale gas development due to unsustainable use of groundwater and surface water may be relevant internationally for application to some of the shale gas and shale oil basins mapped in Figure 4.10. The Neuquén Basin in western Patagonia, Argentina is one of the basins where shale gas is being explored and developed (EIA/ARI 2013). Existing oil and gas industry is one of the users of groundwater in this semi-arid

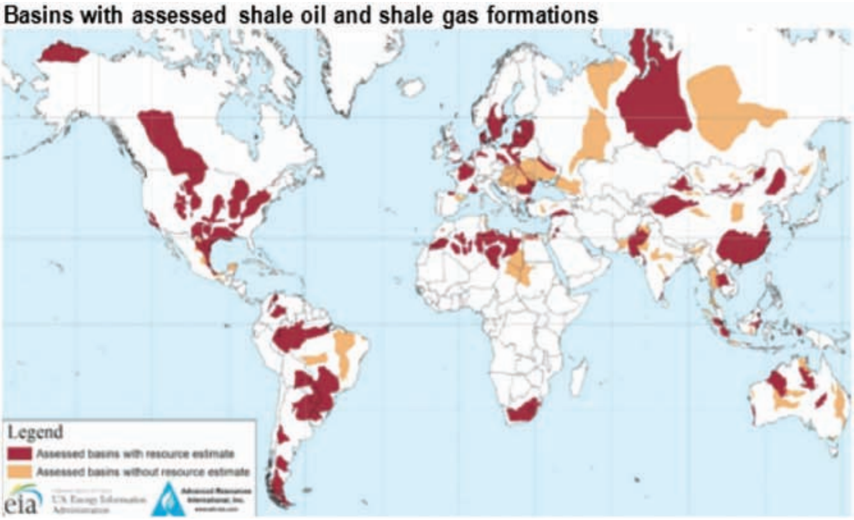

Figure 4.10. Distribution of World Shale Gas and Shale Oil Resource Assessments
Source: U.S. Energy Information Administration (2013)

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region. The Karoo region in South Africa is characterised by an arid climate as are the shale gas prospective basins of Algeria and Libya in North Africa. Although there are very large volumes of fossil and non-renewable groundwater contained in the North African regional aquifer systems the extensive water demands of fracking shale gas wells may lead locally to aquifer overexploitation and ultimately to groundwater mining. Alternative methods of fracking which use recycled frack water, naturally saline groundwater or no water can supplement the single-use, water-based procedures. LeBlanc et al. (2011) describe a fracking operation using gelled propane as the fracking fluid on a tight gas well in New Brunswick, Canada. This waterless frack resulted in better production performance than previous conventional fracks. The elimination of flowback – frack water returned to surface–may also reduce the life cycle water impact of the well. U.S. experience with other concerns about risks to human and animal health (Finkel and Hays 2013; Finkel et al. 2013; Korfmacher et al. 2013; Adgate et al. 2014) and water supply (Fontenot et al. 2013; Jackson et al. 2013) would also need to be considered in shale gas development.

4.6 CASE STUDIES OF AQUIFER MANAGEMENT POLICY AND PRACTICE IN AUSTRALIA

The Great Artesian Basin (GAB) and the Murray-Darling Basin (MDB) are the two major basins of Australia, which contain aquifers with productive groundwater resources. The GAB is located mostly in Queensland but extends across the state borders of New South Wales, South Australia and the Northern Territory, making it a transboundary aquifer system. Its area of 1.7 million square kilometres occupies one-fifth of the Australian continent (Reyenga et al. 1998). The GAB is a confined groundwater basin with multi-layered aquifers recharged mainly from the elevated eastern rim of the basin through the intake beds. The bulk of the surface drainage network of the MDB is located in NSW but extends northwards into Queensland and covers more than 1 million square kilometres, amounting to one-seventh of the Australian mainland in Queensland, NSW, Victoria and South Australia. Tributaries of the Murray River flow northwards from Victoria until the drainage system discharges to the sea at the Coorong in South Australia. Figure 4.11 shows the GAB and MBD groundwater basins.

Both the GAB and the MDB are crucial in the economy of Australia with the GAB producing $3.5 billion worth of output annually (Austin 2010). Agriculture is the major economic activity in the MDB in 80% of the basin and generating 40% of the agricultural production in Australia with 60% of the country's irrigation water (CSIRO 2008). Coal mining and CSG production are significant, especially in the GAB, but there are proposals for new mines and gasfields in the MDB. Although both basins extend beyond the borders of individual States, the management of mining, agriculture and water resources are the responsibility of each State government, and the government of the Northern Territory, with the

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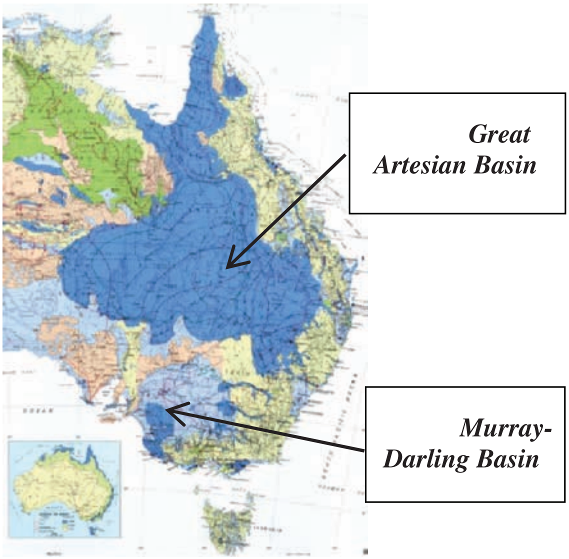

Figure. 4.11. Great Artesian Basin and Murray-Darling Basin
Source: Geoscience Australia (2013); reproduced courtesy of Commonwealth of Australia under Creative Commons License (http://creativecommons.org/licenses/by/3.0/au/)

Australian Commonwealth Government coordinating their activities. In the case of the GAB, the Great Artesian Basin Coordinating Committee (GABCC) undertakes this role, and the Murray-Darling Basin Authority (MDBA) is its counterpart for the MDB. The GABCC and the MDBA are the agencies for the liaison between the State and Commonwealth levels of government in the policy implementation and governance of the two basins.

4.6.1 The Great Artesian Basin

The aquifers of the GAB are the primary or sole source of water for towns, agriculture and pastoral industries in the interior of central Queensland because of the arid climate. The southeastern portion of the GAB, which underlies the MDB in southeastern Queensland New South Wales, is drained by several significant rivers. Natural discharge from numerous springs (mound springs) supports GDEs. The GAB confined sandstone aquifers and shale/mudstone confining layers occur within the Eromanga Basin which is one of the several depositional basins in the folded and faulted sedimentary sequence. Surrounding basins which underly the GAB are hosts to the coal mining and CSG industries in Queensland; also, there is an existing approval and applications for major new mines in the Galilee Basin. Some of these basins have been identified as having shale gas and shale oil potential (EIA/ARI 2013).

Groundwater flows from the intake beds on the eastern margin mainly to the west and southwest but the long travel distance at flow rates of 1 to 5 metres

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per year (Habermehl 1980; Habermehl and Lau 1997) leads to residence and turnover times of up to millions of years (Torgerson et al. 1991). Many flowing artesian and pumped wells (bores) are located in the central parts of the GAB and produce from depths of 1200 to 2500 metres (Reyenga et al. 1998), so that effectively the resource is non-renewable. The cumulative effect of the thousands of bores drilled since 1878 has been to lower the regional piezometric surfaces of the heavily exploited portions of the aquifers by tens of metres (Habermehl 1980; Habermehl and Lau 1997). Bore water is allowed to flow in an uncontrolled manner into open drains (bore drains) to provide water for livestock and it is estimated that up to 90% of this water, amounting annually to 395,000 Ml per year is wasted by evaporation (Austin 2010). A comprehensive study of the GAB, implemented by the Commonwealth Scientific and Industrial Research Organisation (CSIRO) and partners under the *Great Artesian Basin Water Resource Assessment* program has revised earlier conceptual models of the groundwater system and relationship to underlying basins (Ransley and Smerdon 2012). The program also involved the development and review of a thoroughly extensive and detailed 'groundwater and scenario' modelling of the GAB (Smerdon et al. 2012; Welsh et al. 2012). This work and related investigations have provided input to sustainable management policy for the GAB.

It had been realised since the mid-20th century that sustainable management policy for the GAB required a whole-of-basin approach which was not achievable with uncoordinated inputs from the individual States, Northern Territory and the Commonwealth Government. Consequently, the Great Artesian Basin Consultative Council was established in 1997 and developed the *Strategic Management Plan* (SMP) in 2000 which is the guide for the sustainable management of the GAB. The GAB Consultative Council ceased operating in 2002 and was formally replaced by the GABCC in 2004. The overall objective of the SMP is: "*the sustainable use of the GAB groundwater resource and optimum economic, environmental and social benefits*" (GAB Strategic Management Plan Summary, September 2000, GAB Consultative Council). The GABCC has continued implementation of the SMP and has identified the primary issue as declining artesian pressure (GABCC 2008).

The major issue is a continuation of the earlier Great Artesian Basin Bore Rehabilitation Program (GABBRP) started in 1989 with funding from the Commonwealth Government and the State governments of Queensland, New South Wales and South Australia with landholder contributions (Rayenga et al. 1998). Currently the GAB Sustainability Initiative (GABSI) has controlled 1,124 bores, removed 18,756 kilometres of bore drains and installed 18,540 kilometres of piping, saving 293 GL of water per year. The cost of the programs is 450M AUD over 15 years, but groundwater pressures are recovering in many parts of the GAB (Austin 2010). The extraction of coal and CSG from the geological basins surrounding the GAB, especially from the Walloon Coal Measures in the Surat and Clarence-Moreton Basins, poses challenges to the sustainable management of its groundwater and other resources. Existing and proposed developments in Queensland and New South Wales are regulated within the comprehensive

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framework of approval conditions which reflect the risk assessment and adaptive management policy of the respective State governments. The GABCC has emphasised the need to continue the successful GABSI program which should not be put at risk by CSG extraction within the GAB (GABCC 2011a, b). CSG operations and their regulation both utilise regional scale groundwater models, such as MODFLOW. These models may not accurately represent the dual-phase nature of fluid flow as coal seams are dewatered during the initial CSG production phase (Howell et al. 2013; Schmid et al. 2013). The process of upscaling hydraulic properties combined with the use of single-phase, MODFLOW packages to represent the dual-phase regime of gas and water flow can introduce simulation errors (Herckenrath et al. 2013; Moore et al. 2013). Herckenrath and Doherty (2013) describe modifications to the MODFLOW-USG code to include gas desorption resulting in a closer match with the hydrocarbon reservoir simulator ECLIPSE.

4.6.2 The Murray-Darling Basin

The MDB, unlike the GAB to its north, is predominantly characterised by surface water resources, but there are extensive alluvial aquifers comprising interconnected surface water and groundwater systems. Groundwater occurs in fractured rock aquifers around the rim of the Murray geological basin, and there are large volumes of mostly brackish to highly saline groundwater in sedimentary aquifers in the southwestern portion of the basin. Groundwater accounted for 16 percent of the water used in the MDB up to 2008, but the proportion could rise to more than 25 percent by 2030 (CSIRO 2008). The study also showed that groundwater use in seven of the twenty areas of high usage was unsustainable and would result in significant depletion of the resource without changes in management. Extensive water resource development has affected streamflow in the Murray River, so that flow at its mouth in South Australia has been reduced by 61 percent: there is no flow through the mouth 40 percent of the time, contrasting with 1 percent no-flow under pre-development conditions (CSIRO 2008). Water sharing plans are used in New South Wales to reduce entitlements in overallocated groundwater systems; equivalent policy instruments are applied to achieve this objective in the other States within the MDB. Water sharing plans developed by the individual States need to be accredited by the Commonwealth Government to be consistent with the Murray-Darling Basin Plan (the Plan).

The Plan is administered by the Murray-Darling Basin Authority (MDBA) which was established by the Commonwealth *Water Act 2007* and its amendment the Commonwealth *Water Amendment Act 2008.* According to the *Water Act 2007,* the MDBA is required to monitor the Basin's water resources, develop knowledge of the Basin and educate stakeholders. These activities are implemented through Commonwealth agencies and those of the States of Queensland, New South Wales, Victoria and South Australia in which the MDB occurs. Each State has passed legislation to clarify how the *Water Act 2007* is applied along with related State water management policies. The *Memorandum of Understanding on*

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Murray Darling Basin Reform (March 2008) and the *Intergovernmental Agreement on Murray Darling Basin Reform* (July 2008) describe the practical arrangements for governance of the MDB. Major concerns were expressed in stakeholder meetings during the drafting of the Plan that the provisions for environmental water would adversely impact on irrigated agriculture, industries and communities in the MDB. The Plan includes setting long-term average sustainable diversion limits (SDLs) for surface water and groundwater throughout the Basin.

SDLs are defined in terms of the volume of water for consumptive use while retaining adequate amounts for sustaining environmental river flow and GDEs. The procedure for establishing SDLs was to estimate water usage (baseline diversion) and determine the environmentally sustainable level of take or water usage (ESLT). The ESLT was obtained as the optimal balance of hydrologic, socioeconomic and environmental outcomes from the available knowledge base. Crase et al. (2012) provide the background to the policy and suggest that the water buybacks to redistribute water from agriculture to the environment have had positive outcomes. The long-term average Basin SDL was estimated at 10,873 GL per year compared to the baseline of 13,623 GL per year at 2009 (MDBA 2010, 2013). Estimates of the ESLT were reviewed by the CSIRO (Young et al. 2011); findings of the earlier CSIRO Murray-Darling Sustainable Yields Project (CSIRO 2008), surface water and ecosystem modelling (Podger et al. 2010a, b; Saintilan and Overton 2010) and the science policy nexus (Ryder et al. 2010) were incorporated and considered. SDLs will provide a basis for recovering the deficit of 2,750 GL between the baseline and actual usage through water buybacks and improving infrastructure efficiency. SDLs can be modified as information is updated. The SDLs and recovery program will also apply to groundwater as SDLs have been estimated for individual aquifers.

SDLs for aquifers are based on recharge rates, connectivity of the surface and groundwater systems, depth of the aquifers, and water quality and salinity. The distribution of groundwater pumping and the relation with State water sharing plans is also considered. The SDLs were determined from an assessment of the ESLT considering the risks of groundwater extraction (MDBA 2012a, b). The knowledge base of the assessments included previous hydrogeological studies and limited groundwater modelling by State and Commonwealth agencies and universities. Kelly et al. (2013) showed how mapping the hydrogeological framework of the semi-confined alluvial aquifers of the Namoi Valley coupled with analysis of historical groundwater abstraction trends could assist the management of irrigation and environmental demands. Their approach is applicable to similar connected surface and groundwater systems in the MDB. Overall, 66 groundwater SDL resource units were established by the MDBA, the large number reflecting the complexity of the groundwater systems. The long-term average total SDL across the Basin is estimated at 3,334 GL per year, compared with the actual baseline of 2,385 GL per year. Of the 66 units, 34 have an SDL equal to the baseline, 31 are less than the baseline amount, and 1 (the Upper Condamine alluvial aquifer system in southern Queensland) is overallocated. Locally, there may be difference between these classifications and the allocations from State water sharing plans; the

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differences can be negotiated between the MDBA and the State involved using State water legislation and the *Water Act 2007* and the *Water Amendment Act 2008*.

Provisions of the *Water Act 2007* may also be triggered in regard to CSG developments underlying rivers and alluvial aquifers in the Queensland portion of the MDB (Moran and Vink 2010). CSG development in the Walloon Coal Measures which underlie the Central Condamine Alluvium in southern Queensland may create groundwater level drawdowns in the overlying and underlying aquifers as groundwater is pumped from the coals seams to allow the production of CSG. Subsequently, a study undertaken for the Queensland government indicated that there was potential to recharge depleted alluvial aquifers with suitable co-produced CSG water (Arup 2013). Recharge could have a positive impact on MDB system inflows and depleted groundwater resources.

4.7 CONCLUSIONS

This review of groundwater management policy and practice in various parts of the world has shown that many areas are subject to water stress as a consequence of unsustainable management policies. The availability of satellite measurements, such as data from the GRACE and other missions, has facilitated mapping water stress at spatial scales, ranging from local to global. These data are input to models which provide estimates of the impacts of blue and green water depletion on irrigation and rainfed agriculture and assess the groundwater footprints of aquifers. The implications for food security can be assessed with greater precision with these techniques.

The use of GCMs in conjunction with conventional groundwater modelling is a growing trend in the assessment of groundwater resources and adds the precautionary dimension to the formulation of sustainable management policies. Nevertheless, the necessity to feed information to these models from groundwater investigations in the field for estimates of sustainable yield still remains. The classification of groundwater into renewable and non-renewable resources is essential for devising policies for their sustainable management and managing the risks associated with their development.

The extraction of mineral resources, specifically coal and coal seam gas, shale oil and shale gas present significant challenges worldwide for minimising their impact on groundwater and surface water resources. In these respects, the experience of countries like the U.S. and Australia may provide guidelines for future policy development. In particular the Australian examples of collaboration between government agencies and stakeholders in a horizontally and vertically integrated framework for the governance of the Great Artesian Basin and the Murray Darling Basin may be instructive.

Finally, although it is clear that groundwater resources are under considerable stress worldwide, the capability exists for monitoring their status and assessing the

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potential transition to sustainable management. There are the political and socioeconomic considerations which will play a part in determining whether the transition can take place.

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CHAPTER 5

District Water Cycle Management for Wastewater Reuse

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5.1 INTRODUCTION

We are living in a world where freshwater resources are not available everywhere, or the available amount is not sufficient to sustain human lives and economic activities. With climate change apparently induced by global warming and population growth, water scarcity becomes a global problem and is getting more and more serious in many regions (Hanasaki et al. 2012a). By definition, water scarcity refers to the extent to which demand exceeds the available resources (El-Kharraz et al. 2012). Any imbalance between the demand and the resource availability may lead to water scarcity due to demographic, economic and climatic drivers of change (Wiltshire et al. 2013).

The availability of water resources in a country or region can be evaluated using Falkenmark Index (FI) which is defined as the average per capita water available per year (Jury and Vaux 2007; Perveen and James 2011). According to FI, the degree of water scarcity can be evaluated as below (Arnell 2004; Fekete 2010):

- Moderate water stress: IF = 1000–1700 m^3/capita-yr.
- High water stress: IF = 500–1000 m^3/capita-yr.
- Extreme water stress: IF < 500 m^3/capita-yr.

Table 5.1 is a summary of the worldwide renewable freshwater availability and countries experiencing water stress or scarcity according to FI (FAO 2012). It can be seen that of the 27 countries with FI < 500, namely extreme water stress, 14 are in Asia and eight are in Africa, indicating that many countries in these two continents are under serious conditions of physical water shortage. However, the FI data by continent or country may not always reflect the actual condition of water shortage because of the uneven distribution of available water resources and population within a country or a region (Jiang 2009; Fekete 2010; Wu and Tan

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Table 5.1. Worldwide renewable freshwater availability and countries experiencing water stress or scarcity in 2011 according to FI

Area		*World*	*Africa*	*Americas*	*Asia*	*Europe*	*Oceania*
Internal renewable freshwater resources	Volume per year (10^9 m^3)	42370	3931	19104	11865	6578	892
	Per capita in year 2011 (m^3)	6079	3764	20272	2816	8884	30447
Numbers of countries	FI < 500	27	8	3	14	2	0
	500 < FI < 1000	17	9	1	3	4	0
	1000 < FI < 1700	23	11	1	5	6	0
	FI < 1700	67	28	5	22	12	0

Note: Total countries accounted: 175; FI: Falkenmark Index as m^3/capita-yr

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2012; Fekete 2013). There are also the problems of timely scarcity of water resources (Hanasaki et al. 2012b) in many countries and regions.

The worldwide problem of water shortage has much stimulated the requirement for wastewater reuse because many of our water uses may not be necessarily supplied by freshwater resources, and the treated effluent from a wastewater treatment plant can either be used straightforward for irrigation or for other non-potable purposes after further treatment (Levine and Asano 2004; Adewumi et al. 2010; Meneses et al. 2010; Norton-Brandão et al. 2013). The NEWater reclaimed from domestic wastewater in Singapore has already been proved ‘drinkable’ and is now used as one of the ‘National Taps’ for enlargement of the source water for the country’s water supply (Qin et al. 2006; Lee 2010).

It is widely recognized that freshwater resources are maintained by a natural water cycle (Narasimhan 2009), and water resources management should follow the principle of ‘water cycle management’ (Najia and Lustig 2006; Pouget et al. 2012). By definition (Imbe et al. 1997; Kundzewicz 2008a; Amores et al. 2013), the so-called ‘water cycle’ describes the continuous movement of water within a referential domain which can be as large as our earth (the global hydrological cycle), a basin or watershed (the watershed hydrological cycle), or an area where water is supplied and wastewater is discharged through engineering means and related to part of the natural water realm (a water district or district water cycle). The water cycle, no matter large or small, is, in fact, a metabolic system (Tambo 2002). Only when the metabolism, a set of life-sustaining actions, goes on smoothly, can the system be sustained in a healthy condition (Wang 2010; Zhang et al. 2010; Huang et al. 2013). With wastewater being used as a resource in a water district, the movement of water, as well as the substances it carries, will be much altered. Regarding this, Tambo (2006) and Tambo et al. (2012) has proposed the concept of ‘urban water district’ which is a water metabolic space within the hydrological cycle. It stressed the harmony of artificial facilities with water environment in the urban area and drew a clear distinction between the water areas that should be conserved and those to be utilized.

Unfortunately, the conventional water and wastewater systems in cities are not always planned and designed by following the above-mentioned principle of water cycle management. The systems are often managed in a centralized manner with the intent of supply of high-quality drinking water, collection of sewage and storm water and advanced treatment of the collected water prior to discharge into natural water bodies to meet the needs of the public health, industrial growth and prosperity of the society (Wilderer 2001). In such a system, all water to be distributed in the urban area is purified at discrete locations, and the wastewater collected in the area is sent to another discrete plant for treatment and discharge. Therefore, the reuse of treated wastewater by such a system often becomes difficult unless there are potential consumers near the wastewater treatment plant (this may not always be the case), otherwise long distance pipelines and large distribution networks have to be constructed. In contrast, a water and wastewater system managed in a decentralized manner has drawn wide attention (Gaulke et al. 2008; Chen and Wang 2009; Fujiwara 2012). The principle

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of decentralization can mainly be characterized as an independent collection system covering a smaller service area, onsite treatment and onsite reuse to avoid a long haulage distance for both the collected wastewater and the treated effluent (Wang 2007). With the fast urbanization and/or expansion of existing cities, the future tendency of urban water and wastewater system planning will be an optimized combination of centralized and decentralized systems (Wang et al. 2008b). The principle for system optimization is to put water supply, wastewater collection/treatment, wastewater reuse, and the urban water environment into a district water cycle. The system will be designed in a manner that the best management of the water cycle can be easily performed.

5.2 CONCEPTS OF WATER CYCLE MANAGEMENT

5.2.1 Natural Hydrological Cycle

At a global scale, all water is locked into a constant recycling process called the hydrological cycle. The hydrological cycle is initially driven by solar energy (Alavian et al. 2009; Narasimhan 2009). There are two basic processes involved in the cycle, namely evaporation and condensation of water. Evaporation involves adding energy to water molecules so that they become water vapor, while condensation is the reverse process in which molecules of the water vapor give up energy and return to the liquid form. The most intense evaporation occurs on the ocean surface that covers more than 70% of the Earth surface. Moisture is also evaporated from the bodies of freshwater, soil and the surfaces of plants (known as evapotranspiration). The water vapor in the air moves across the surface of the Earth as the atmosphere circulates. As moist air cools, it is condensed into droplets that fall to the Earth as rain or snow. Water, flowing over the Earth as surface water or through the soil as groundwater, returns to the oceans so the cycle starts again. Such a recycling process of water volume is essential for keeping a dynamic equilibrium of water in various water bodies such as rivers, lakes, and groundwater aquifers (Kuchment 2004; Kundzewicz 2008a).

On the other hand, the hydrological cycle is also a process of water purification that ensures the provision of fresh water resources in the cycle by a series of physical, chemical, and biological reactions (Oki and Kanae 2006; Kundzewicz 2008b). In the processes of evaporation and evapotranspiration, only pure water molecules are evaporated so that the water precipitated back to the Earth is ‘freshwater’ in nature though its origin is mostly the ocean where water contains high concentration of salt. Therefore, desalination is the most important function the nature performs for providing freshwater to sustain all flora and fauna on the Earth. In the processes of water flow in rivers and streams and/or storage in lakes and ponds, the impurities in water can be removed physically, chemically, physiochemically, and biologically through what we know as self-purification processes such as sedimentation, adsorption, oxidation, aerobic degradation and so on (Vagnetti et al. 2003; Kuchment 2004). The groundwater

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in the underground aquifers can also be purified as it moves in the porous space by natural filtration process.

5.2.2 Urban and District Water Cycle

The natural hydrological cycle discussed above is the fundamental water cycle everywhere in the world. It can be analyzed at global scale, and also at continental, water basin or sub-basin scale with clear boundary conditions (Tubiello et al. 1999; Vörösmarty and Sahagian 2000; Henderson-Sellers et al. 2004; Molle and Mamanpoush 2012). A water cycle at its primary state, i.e. without large-scale human disturbance, is always under a dynamic equilibrium condition that can be calculated according to water budget and material balance relations (Chikita et al. 2004; Kebede et al. 2006).

From ancient times, people located their homes near water and used water in the simplest manner such as taking freshwater from a nearby clean stream and then disposed the used water arbitrarily. As the scale of water withdrawal and its final disposal was insignificant, it was unnecessary to worry about the water availability and its quality deterioration. The scientific reason behind this, as we know well nowadays, is the carrying capacity of the natural water cycle that could greatly absorb human disturbance and sustain a 'healthy' condition for the water bodies (Feng et al. 2008). People were also able to differentiate 'good water' (palatable water) from 'bad water' (non-palatable water) according to experiences and tried to protect the safe water from being spoiled (Heathwaite 2010).

With population growth and the progress of civilization, individual dwellings grew to villages or communities, villages and communities then grew to towns. Towns became larger and larger and gradually formed cities, all accompanied with growing scale of water applications such as transportation and irrigation in addition to the primary purposes of drinking and washing (Postel et al. 1997; Novotny and Brown 2007; Sobsey et al. 2008). However, it was until the industrial revolution era when people realized the disturbance of human beings on the intact of natural water cycle and began to suffer from the associated water problems (Raskin et al. 1996). In order to protect human health, modern sanitation systems were firstly provided in London and other fast developed European cities for transferring human wastes swiftly out of the urban area and protecting the source water from being polluted (Bracken et al. 2007; Lofrano and Brown 2010). As clean water became less and less available quantitatively and qualitatively within or near the growing cities, longer distance transfer of source water from remote locations to cites and large scale drinking water purification and distribution became indispensible infrastructures for cities (Botkin et al. 1995; Shannon et al. 2008). Meanwhile, as concentrated discharge of human wastes and various wastewaters into receiving waters brought serious deterioration of their quality, large scale wastewater treatments had also provided for reducing the pollutant loading in the waste flows to a level that would not damage the receiving waters (Larsen and Gujer 1997; Gogate and Pandit 2004).

It is not the purpose of this chapter to review the history of urban water and wastewater system development. The message to be given to our readers is that in

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a modern city, there is already an artificial water cycle built by human beings to supply a large amount of water to the city for various uses and then to discharge the used water out of the city (Amores et al. 2013). The artificial water cycle is connecting with the nature at two locations: one at the water intake where source water is withdrawn from a natural water body with sufficient quantity to meet the water demand, and another at the outlet(s) of treated and/or untreated urban discharge where the used water returns to the natural water body. The water body to provide source water and that to receive urban discharge may not be the same one, but they often belong to the same water basin where the city is located. In broad sense, within the water basin, the artificial water cycle is overlaid onto the original natural water cycle (hydrological water cycle) and may strongly disturb the natural water cycle (Bertrand-Krajewski et al. 2000).

For most cities, the available water resource is distant from the city, and if a river basin is referred, it is often at the upstream side. Therefore, long transfer pipelines are usually provided to send the source water (when water purification plant is built within the city) or the purified water (when water purification plant is built near its source) to the city. Likewise, long transfer pipelines may also be required to send the collected wastewater to locations where wastewater treatment plants are built. The locations are near the ultimate discharge point which is also distant from the city and is at the downstream. Long distance water and wastewater transfer may thus be the main characteristic of modern urban water systems built in a centralized manner (Burian et al. 2000). As cities grow larger, larger water systems have to be provided and the water and wastewater transfer pipelines will also become longer and larger (Noll et al. 2000), not to mention the huge water distribution and wastewater collection networks within urban areas. In addition to the current difficulties that large cities face for the operation and maintenance of large centralized water and wastewater systems and the anticipated difficulties for the systems' upgrading and/or replacement, another problem aroused when the reclaimed water produced in wastewater treatment plants outside a city has to be sent back to the city area again. This again needs the construction of another long distance water transfer pipeline unless the consumers of the reclaimed water, such as an industry or an agricultural farm, are near the location of its production.

For these reasons, it is widely recognized that the centralized urban water and wastewater system, though it is still the main type of urban infrastructure and with a long history and rich engineering experiences for its design, construction, operation and maintenance, is only suitable for water supply and wastewater management in a conventional manner characterized by 'end-of-the-pipe' technology without water reuse (Somlyódy 1995). With the needs for recovery of water and other useful materials from wastewater, a decentralized system has shown its advantages over the centralized system in integrated water, wastewater, reclaimed water and even other useful materials' recovery in smaller systems where long distance transfer of any water flow can be left out (Mankad and Tapsuwan 2011; Marlow et al. 2013).

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Although system scale may be an important factor when centralization and decentralization are discussed, the essence of the concept of decentralization is not merely the system scale but the principles of (Gunaratnam et al. 2005; Friedrich et al. 2009; Ray et al. 2009):

- Minimization of fresh water supply and maximization of water recycling.
- Onsite treatment and onsite reuse.
- Harmonic integration of the subsystems of water supply, sewerage, water reuse, and water environment in one framework.

The system designed following such principles can be as small as necessary but as large as possible (Deniz et al. 2010). Terminologically, 'semi-centralization' (Cornel et al. 2007) is proposed to differentiate a system with moderate scale designed following these principles from the conventional centralized system and also from small size systems. In order to get rid of terminological confusions and stress the relation between an engineered water/wastewater system and its related natural waters, 'district water cycle' is used in this chapter to express a water cycle involving both the artificial and natural elements of a water system for a whole or a part of a city irrespective of the system scale.

5.2.3 Conceptual Models

Model of an urban/district water cycle. An urban or district water system usually has four elements or subsystems, namely water resource subsystem, water supply subsystem, water use subsystem, and wastewater subsystem (Mitchell et al. 2001; Fane 2005; Friedrich et al. 2009; Lim et al. 2010). Figure 5.1 outlines the relationships among these subsystems and the formation of an urban/district

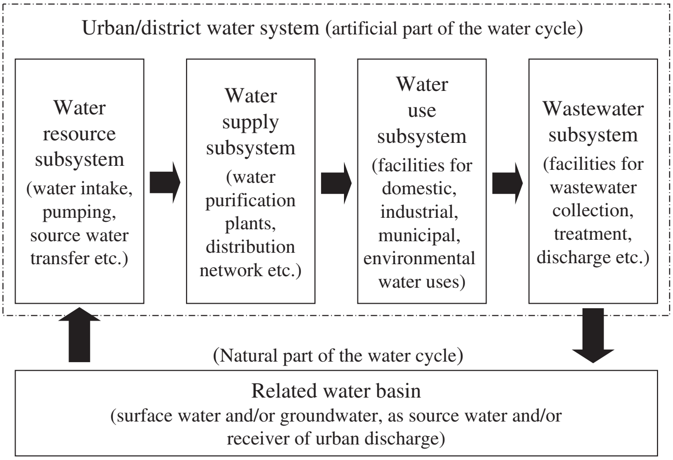

Figure 5.1. Composition of a conventional urban/district water system and the formation of an urban/district water cycle that contains the artificial and natural parts

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water cycle which contains the artificial part (the urban/district water system) and the natural part (the related water basin as source water and/or receiver of urban discharge).

Models of urban wastewater reuse. Through a conventional urban/district water system, water uses are in an 'end-of-the-pipe' manner (Somlyódy 1995) in which freshwater from a natural water body is supplied for various uses and the used water is discharged back to the natural water body thus forming a water cycle as indicated in Figure 5.1. In this case, the basic requirement for water supply is that the total quantity of water withdrawal from the water source should meet the demand of various water uses in the urban district.

As wastewater is to be used as a usable source, the composition of the urban/district water system should be modified in either of the following two ways:

- Addition of an inner cycle to the urban/district water system where part of the discharged water (after quality conversion) returns to the water use subsystem to supply certain amount of the water for certain uses that do not necessarily need freshwater. As a result, the quantity of water withdrawal from the water resource (in the water resource subsystem) and the quantity of water supply (in the subsequent water supply subsystem) are reduced. This can be called a 'water saving model' as shown in Figure 5.2a.
- An enlargement of the water source by adding an amount of the reclaimable wastewater to the source water (in the water resource subsystem). As a result, the capacity of water supply (in the water supply subsystem) to various uses (in the water use subsystem) is increased. This can then be called a 'water source enlargement model' as shown in Figure 5.2b.

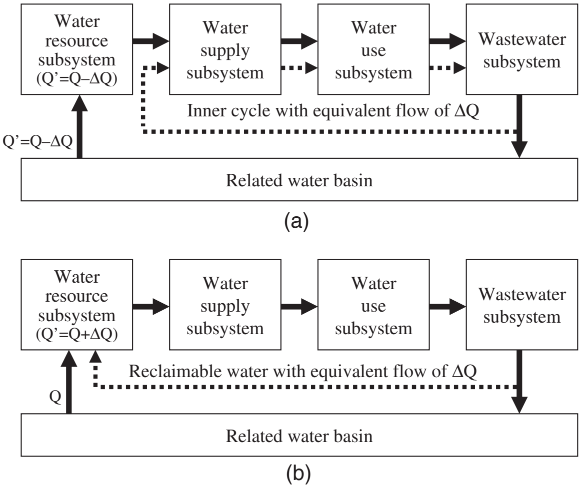

Figure 5.2. Models of wastewater reuse for (a) water saving, and (b) water resource enlargement (ΔQ as the flow rate of the reclaimable water equivalent to that of the source water saved or enlarged)

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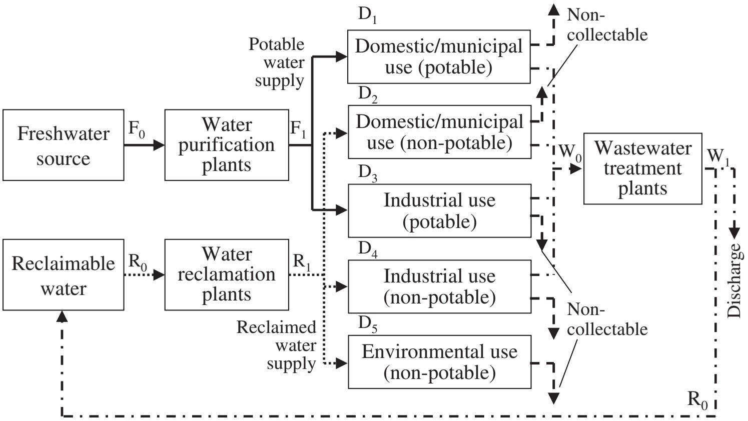

Figure 5.3. Quantitative model of an urban/district water cycle with water reuse (in many cases, a water reclamation plant may be part of the wastewater treatment plant where reclaimed water is directly produced)

A quantitative model of an urban/district water cycle. When wastewater is used as a resource either for water saving or water resource enlargement, a quantitative model can be formulated as shown in Figure 5.3. From the viewpoint of water supply, water from both the freshwater source (surface water and/or groundwater as available) and reclaimable water source (from the urban and/or district wastewater treatment plants), after proper treatment, should be with sufficient quantities to meet the demands for the following potable and non-potable water uses (Bixio et al. 2006; Gikas and Tchobanoglous 2009; Willis et al. 2011):

- Domestic use: household and community water uses for potable and non-potable purposes.
- Municipal use: urban public water uses including those for public service and commercial activities of potable and non-potable purposes.
- Industrial use: water uses in industries for industrial processes and related activities of potable and non-potable purposes.
- Environmental use: water uses for environmental purposes including landscaping, gardening, urban irrigation etc. which can be considered as non-potable water consumptions.

Agricultural irrigation is not put into Figure 5.3 because in most cases, urban reuse is the main objective of water reclamation.

Materials balance model of an urban/district water cycle. In a conventional urban/district water system, water from a freshwater source has to be treated to meet the quality requirement for potable use but in fact it is supplied for various uses. The collectable wastewater is then treated to meet the quality requirement for discharging into a receiving water body (Bouwer 2000; Sarkar et al. 2007). In such a case, the mass balance relationship is simple because the pollutant loading in the collectable

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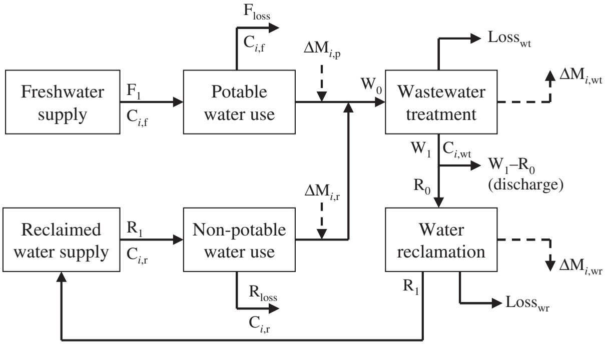

Figure 5.4. Materials balance model of an urban/district water cycle with water reuse regarding pollutant i

wastewater flow is only a factor to be considered in designing the wastewater treatment facilities but not a factor to affect the quality for water supply. However, as wastewater becomes a useful resource, there is an inner water cycle within the water system as shown in Figures 5.2 and 5.3. In this case, in addition to the requirement of reclaimed water quality for reuse purposes, there should be a requirement on prevention of pollutant accumulation in the water system. Therefore, materials balance analysis may become important for rational design of the system.

Figure 5.4 is the materials balance model of an urban/district water cycle with water reuse. Attention is paid to the mass balance of pollutant *i* in the water cycle. In the figure, F_1, W_0, W_1, R_0, R_1, F_{loss}, and R_{loss} are quantities of potable water supply, collected wastewater, treated wastewater, source water for reclamation, reclaimed water supply, water lost during potable water use, and water lost during reclaimed water use, respectively, all as m³/d; $C_{i,f}$, $C_{i,wt}$, and $C_{i,r}$ are concentrations of pollutant *i* in potable water, treated wastewater, and reclaimed water, respectively, all as mg/L or g/m³; F_{loss} and R_{loss} are quantities of water loss during potable and non-potable water uses, respectively, all as m³/d; $Loss_{wt}$ and $Loss_{wr}$ are quantities of water loss in wastewater treatment and water reclamation, respectively, all as m³/d; $\Delta M_{i,p}$, $\Delta M_{i,r}$, $\Delta M_{i,wt}$, and $\Delta M_{i,wr}$ are masses of pollutant *i* entered the water cycle or removed from the water cycle through potable water use, reclaimed water use, wastewater treatment, and water reclamation, respectively, all as g/d.

5.3 METHODS FOR WATER CYCLE ANALYSIS

5.3.1 Water Budget Analysis

Water budget analysis is usually an analysis of the relationship between various water demands and the capacities of water supply which depend on the availability of water resources. As shown in Figure 5.3, water demands for an urban district may mainly include those for domestic/municipal, industrial, and environmental uses. For conventional urban water supplies, where tap water with potable water quality is distributed to the whole service area with high quantity irrespective of the purposes of water use, the water demand is calculated regarding the total quantity based on population (for domestic use), population and/or service scale (for municipal use), type and production capacity of industry (for industrial use) and so on (Berger et al. 2007). However, when reclaimed water is also used for water supply, more detailed analysis is required on both the demands for water quantity and quality because of the qualitative difference between the reclaimed water and ordinary tap water. Table 5.2 summarizes the main water usages and corresponding requirements for potable water and/or reclaimed water as alternatives (Joksimovic et al. 2006; Berger et al. 2007).

Table 5.2. Urban water usages and corresponding requirements for water supply

	Supply requirement		
Water usage	*Potable water*	*Reclaimed water*	*Remarks*[a]
Domestic water use			
Drinking/cooking	××		
Bathing/washing	××		
Toilet flushing	×	×	Dual pipe needed
Gardening	×	××	
Municipal water use			
Drinking/dining services	××		
Swimming pool	××		
Commercial laundries	×	×	High quality required
Toilet flushing	×	××	
Cleaning	×	××	
Fire protection	×	×	High quality required
Urban irrigation	×	××	
Car washing	×	×	High quality required
Construction work	×	××	
Industrial water use[b]			
Cooling water	×	××	
Washing water	×	××	
Boiler water	×	×	Special quality requirement
Process water	×	×	
Environmental water use			
River flow augmentation	×	××	
Recreational lake/pond	×	××	

Note: ××: preferential use; ×: alternative use

[a] Remarks on reclaimed water use

[b] Industrial water use may also include water for drinking and/or dining that requires potable water supply

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For domestic or household water supply, reclaimed water may be preferentially used for gardening. Toilet flushing may also use reclaimed water, but this often needs the provision of dual pipe systems to supply potable and reclaimed waters to each household (Jorgensen et al. 2009). For municipal water supply, reclaimed water may be preferred for toilet flushing in public buildings, street cleaning, urban irrigation, and construction work (Willis et al. 2011). Commercial laundries, fire protection, and car washing may also be potential users of reclaimed water (Kennedy and Tsuchihashi 2005), but higher water quality is often required to ensure that clothes and cars may not be stained or scratched, and water quality deterioration may not easily occur in fire water tanks. Reclaimed water is most popularly used in industries for cooling and washing (Bixio et al. 2006). It can also be used as boiler water and process water, but specific quality requirement often has to be taken into account (Wintgens et al. 2005).

Taking both the quantitative and qualitative requirements into consideration, a water budget analysis can be conducted regarding the relationship between available water resources and various water demands. As shown in Figure 5.3, in an urban/district water cycle with water reuse, the freshwater from surface and/or underground sources is the primary source water with a quantity F_0, and the reclaimable water as part of the effluent from the wastewater treatment plant is the secondary source water with a quantity R_0. 'Secondary' here does not mean it is less important but means it is derived from the primary source water after being used. Another feature of water flow in the water cycle shown in Figure 5.3 is that the reclaimed water, after being used for certain purposes, may also add to the collectable wastewater flow which enters the wastewater treatment plant and thus enlarges the potential for water reclamation. Therefore, the following relationships can be established.

Supply-demand relationship for potable water. If the freshwater source is only used for potable water supply, its quantity should meet the following relationship:

$$F_0 > F_1 \geq D_1 + D_3. \tag{Eq. 5.1}$$

where, F_0 is the quantity from freshwater source, F_1 is the quantity of total potable water supply after water purification, D_1 and D_3 are demands of potable water uses for domestic/municipal consumption and industrial consumption, respectively.

Supply-demand relationship for water reclamation. If all non-potable water uses are supplied by reclaimed water, the relationship between the quantity of reclaimable water and the demands for reclaimed water supply should be as below:

$$W_1 > R_0 > R_1 \geq D_2 + D_4 + D_5. \tag{Eq. 5.2}$$

where, W_1 is the quantity of effluent from wastewater treatment plant, R_0 is the quantity of reclaimable water, R_1 is the quantity of total reclaimed water supply,

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D_2, D_4 and D_5 are demands of reclaimed water uses for domestic/municipal consumption, industrial consumption, and environmental consumption, respectively.

Reclaimable water source. After potable and reclaimed water uses, part of the used water can be collected through the wastewater collection system, while others are not collectable such as those lost due to evaporation into atmosphere or penetration into soil, diverted out of the system, and carried away by consumers. The quantity of the reclaimable water can thus be determined by the following relationship:

$$R_1 < R_0 \leq W_1 < W_0 = \alpha F_1 + \beta R_1. \qquad \text{(Eq. 5.3)}$$

where, W_0 is the quantity of collected wastewater as the influent to wastewater treatment plant, α is the fraction of water collected after potable water use ($\alpha < 1$), β is the fraction of water collected after reclaimed water use ($\beta < 1$).

If the wastewater treatment and water reclamation units shown in Figure 5.3 are combined to one treatment unit as in the case of reclaimed water production directly from collected wastewater and the recovery ratio of reclaimed water production (the quantity ratio of reclaimed water to collected wastewater) is written as γ ($\gamma < 1$), then Eq. 5.3 can be rewritten as

$$W_0 = \frac{R_1}{\gamma} = \alpha F_1 + \beta R_1 \qquad \text{(Eq. 5.4)}$$

The relationship between R_1, the quantity of reclaimed water supply, and F_1, the quantity of potable water supply, can then be written as

$$\frac{R_1}{F_1} = \frac{\alpha\gamma}{1 - \beta\gamma} \qquad \text{(Eq. 5.5)}$$

where, $\frac{\alpha\gamma}{1-\beta\gamma}$ can be called 'recycling ratio' in an urban/district water cycle. If the reclaimed water is only used once but not recycled again, then $\beta = 0$ and the recycling ratio is $\alpha\gamma$ which is the product of α, the fraction of water collected after potable water use, and γ, the recovery ratio of reclaimed water production. The latter is mainly determined by the fraction of the collected wastewater to be used for water reclamation, in addition to the loss of water in the reclaimed water production process.

5.3.2 Materials Balance Analysis

Materials balance analysis principally follows the law of conservation of mass (Chikita et al. 2004) which can be expressed as

$$\text{Inputs} - \text{Reacted} = \text{Outputs} + \text{Accumulated} \qquad \text{(Eq. 5.6)}$$

For materials flow in an urban/district water cycle shown in Figure 5.4, each of the items in Eq. 5.6 can be evaluated regarding pollutant *i* as followings.

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Inputs of pollutant *i* to the water cycle. The inputs of pollutant *i* include those entering the water cycle with freshwater and reclaimed water supplies, and those adding to the water cycle due to freshwater and reclaimed water uses.

$$\text{Inputs} = F_1 C_{i,f} + R_1 C_{i,r} + \Delta M_{i,p} + \Delta M_{i,r} \qquad \text{(Eq. 5.7)}$$

Pollutant *i* reacted (removed). The masses of pollutant *i* reacted include those removed in the processes of wastewater treatment and water reclamation.

$$\text{Reacted} = \Delta M_{i,wt} + \Delta M_{i,wr} \qquad \text{(Eq. 5.8)}$$

Outputs of pollutant *i* from the water cycle. The outputs of pollutant *i* are those contained in the waters which are used and cannot be collected along with potable water use, reclaimed water use and treated wastewater discharge.

$$\text{Outputs} = F_{loss} C_{i,f} + R_{loss} C_{i,r} + (W_1 - R_0) C_{i,wt} \qquad \text{(Eq. 5.9)}$$

Accumulation of pollutant *i* in the water system. As discussed in Section 5.2.3, because there is a closed loop of reclaimed water in the water cycle, pollutant accumulation may occur in the water system. By substituting Eqs. 5.7–5.9 into Eq. 5.6, pollutant accumulation item can be solved as

$$\begin{aligned}\text{Accumulated} = {} & (F_1 - F_{loss}) C_{i,f} + (R_1 - R_{loss}) C_{i,r} - (W_1 - R_0) C_{i,wt} \\ & + (\Delta M_{i,p} + \Delta M_{i,r} - \Delta M_{i,wt} - \Delta M_{i,wr}) \qquad \text{(Eq. 5.10)}\end{aligned}$$

All items on the right sides of Eqs. 5.7–5.10 are those indicated in Figure 5.4.

5.3.3 Requirement for Water Quality Conversion

For water reuse, there is basically a requirement for the reclaimed water quality to meet the needs for various reuse purposes. This often requires considerations on the qualities of the wastewater as the source water for reclamation (Deniz et al. 2010) and the objectives of water reuse. Standards, regulations, and guidelines are put forward by international organizations (WHO 2006) and governmental agencies in many countries (U.S. EPA 2004; UNEP 2005; JISM 2006; Ministry of Water Resources, PRC 2006) to provide criteria for setting targets of water quality conversion for safety use of reclaimed water. This relates to a careful selection of suitable treatment technologies which will be discussed in detail in Section 5.4.

On the other hand, for a water cycle discussed in this chapter, attention should also be paid to the prevention of pollutant accumulation in the water cycle.

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Based on the materials balance relationship discussed in 5.3.2, the limit condition for zero-accumulation of pollutant i can be extrapolated from Eq. 5.10 as

$$\begin{aligned}(F_1 - F_{loss})C_{i,f} + (R_1 - R_{loss})C_{i,r} - (W_1 - R_0)C_{i,wt} \\ + (\Delta M_{i,p} + \Delta M_{i,r} - \Delta M_{i,wt} - \Delta M_{i,wr}) = 0\end{aligned} \qquad \text{(Eq. 5.11)}$$

5.4 WATER CYCLE MANAGEMENT FOR QUALITY CONTROL

5.4.1 Treatment Technologies for Wastewater Reuse

General stages of wastewater treatment. At present time, unit operations and processes are grouped together to provide various levels of treatment known as preliminary, primary, advanced primary, secondary, tertiary, and advanced treatment, each has the following characteristics (Asano et al. 2007).

- Preliminary treatment: mainly by screening for removal of wastewater constituents such as rags, sticks, floatables, grits, and grease.
- Primary treatment: mainly by sedimentation (and flotation sometimes) for removal of a portion of the suspended solids and organic matter from wastewater.
- Enhanced primary treatment: enhanced removal of suspended solids and organic matter from the wastewater, typically accomplished by chemical addition or filtration.
- Secondary treatment: biological and chemical processes for removal of suspended solids, biodegradable organic matter (in solution or suspension), and microorganisms (by disinfection usually as the final step).
- Secondary treatment with nutrients removal: enhanced biological and chemical processes for removal of biodegradable organics, suspended solids, and nutrients (nitrogen, phosphorus, or both nitrogen and phosphorus).
- Tertiary treatment: additional removal of residual suspended solids (after secondary treatment), usually by granular medium filtration, surface filtration, and membranes (nutrients removal is often included).
- Advanced treatment: additional combinations of unit operations and processes for removal of constituents that are not reduced significantly by conventional secondary and tertiary treatment for specific water reuse applications.

Although primary and/or enhanced primary treatments are still used in some countries and regions, secondary treatment (including secondary treatment with nutrients removal) has become the minimum required process before urban wastewater is discharged into receiving water bodies in most cities all over the world (Sonune and Ghate 2004). The quality of the secondary effluent can

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marginally meet the requirement for certain reuse purposes such as gardening and urban irrigation, but in most cases, tertiary and/or advanced treatment are required for reclaimed water production for broader range of purposes including industrial and most domestic/municipal uses (de Koning et al. 2008). The selection of unit processes for tertiary and/or advanced treatments depends on the treatability of various pollutants in wastewater. Table 5.3 summarizes the treatability of a spectrum of pollutants usually encountered by a series of unit operations typically used for water reclamation (Asano et al. 2007; Tansel 2008).

Conventional tertiary treatment. Among the unit operations listed in Table 5.3, coagulation, depth filtration, surface filtration, dissolved flotation, and disinfection belong to the category of conventional tertiary treatment processes because they are the processes conventionally used for drinking water purification (Tansel 2008). By a combination of these unit operations, suspended particles, particulate organic matter, and microorganisms can be well removed. However, most of the dissolved matters (organics and inorganic salts), nutrients, and trace pollutants are not removable by these operations except for coagulation which can effectively remove phosphorus through the action of chemical precipitation (Omoike and Vanloon 1999; Sonune and Ghate 2004).

Advanced treatment. Carbon adsorption, ion exchange, electrodialysis, and advanced oxidation can be taken as unit operations for advanced treatment for water reclamation, because, as shown in Table 5.3, the main target of treatment is to remove dissolved organic matter, trace pollutants, TDS etc. which are hardly removable by conventional tertiary treatment. Of these unit operations, ion exchange and electrodialysis are widely used in industrial water treatment for the reduction of salt content for water supply to boilers, textile industries and pulp/paper processes etc. which often need TDS concentrations as low as 100 mg/L or still lower level (Cavaco et al. 2007). For water reclamation, ion exchange and electrodialysis are also used mainly in industries but not for other reuse purposes. Carbon adsorption and advanced oxidation are widely used for the removal of the dissolved organic substances especially the non-biodegradable fraction. A combination of these two processes is also a common practice in many cases by placing a carbon adsorption unit after oxidation for an effective removal of the oxidized products including the trace oxidation byproducts (Ince and Apikyan 2000). When ozone is used as the oxidant, it can partially oxidize the organic molecules and improve their biodegradability (Ledakowicz et al. 2001). In this case, ozonation is often followed by biofiltration with quartz sand or granular activated carbon as biofilm carriers. The latter treatment is called a biological activated carbon process (Zhang et al. 1991).

Membrane filtration. Although membrane filtration is sometimes regarded as tertiary or advanced treatment, due to its unique properties for pollutant removal all the pressure-driven membranes can be put into one group in Table 5.3. It is noticeable that all pollutants listed in Table 5.3 can be removed by membranes because the cutoffs of MF, UF, NF, and RO range from micrometers to molecule sizes, irrespective of the physical, chemical, and biological properties of the pollutants in the water to be treated (Deniz et al. 2010). Therefore, direct filtration

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Table 5.3. Treatability of pollutants by unit operations/processes for tertiary/advanced treatment

	Unit operation for tertiary/advanced treatment												
	Conventional tertiary treatment					*Advanced treatment*				*Membrane filtration*			
Pollutants	*Coagulation*	*Depth filtration*	*Surface filtration*	*Dissolved air flotation*	*Disinfection*	*Carbon adsorption*	*Ion exchange*	*Electrodialysis*	*Advanced oxidation*	*Microfiltration (MF)*	*Ultrafiltration (UF)*	*Nanofiltration (NF)*	*Reverse osmosis (RO)*
Suspended particles	×	×	×	×						×	×		
Colloidal matter	×			×				×		×	×		
Organic matter (particulate)			×	×					×	×	×	×	
Organic matter (dissolved)					×	×			×			×	×
Nitrogen							×						×
Phosphorus	×												×
Trace pollutants						×	×		×			×	×
Total dissolved solids (TDS)							×	×				×	×
Bacteria		×	×		×				×	×	×	×	×
Protozoan cysts/oocysts		×	×	×	×				×	×	×	×	×
Viruses					×				×		×	×	×

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using one and/or several stages of membranes is considered to be an effective way for water reclamation (de Koning et al. 2008). Taking advantage of physical cutoffs, the low-pressure membranes such as MF or UF can also be combined with other physicochemical operations such as coagulation and adsorption. Specific pollutants which can easily coagulate and/or adsorb onto particle surfaces can attach to the flocs and/or adsorbents and then be removed by membrane filtration even though the pore size of the membrane is not fine enough for direct removal of these pollutants (Asano et al. 2007; Fujioka et al. 2012).

Another combined process for wastewater treatment and reuse is a membrane bioreactor (MBR) which combines biological treatment with an integrated membrane system to provide enhanced organics and suspended solids removal (Alturki et al. 2010). In a MBR system, membranes (usually MF or UF) replace both sedimentation and depth filtration for separating the biomass in the suspended liquor in the biological unit. The biomass concentration in the reactor can be several folds higher than that in conventional activated sludge tanks so that biological degradation can be performed more effectively. Due to the good separation capacity of the membranes, solid/liquid separation can be performed effectively as well. Therefore, the treated water is often of high quality to meet the requirement for various reuse purposes (Santasmasas et al. 2013). MBR is widely recognized as the most promising technology in water reuse systems.

5.4.2 Water Quality Control during Storage

To supply reclaimed water for reuse in an urban district, water storage is often required. Similar to conventional water systems for supplying potable water to a service area, the objective of reclaimed water storage is for providing a storage capacity which can equalise the imbalance between its inflow (supply) and outflow (demands). An optimized design of the storage facilities may require a careful analysis of the supply (usually a constant flow)—demand (usually a varied or even intermittent flow) relationship (Keller et al. 2000). Another simpler but commonly used method is to provide a storage capacity of 25 to 50 percent of the maximum day demand (Majozi 2005, 2006). The storage facilities can be reservoirs (open storage) or tanks (enclosed storage). According to the elevation, water can be sent to the consuming points by gravity (elevated tank) or pumping (ground level tank). In an urban/district water cycle when landscaping lakes or ponds are replenished by reclaimed water, the lakes/ponds can also be utilized as storage facilities.

General water quality problems during storage. Water quality deterioration may occur during storage due to climatic conditions (solar radiation, temperature etc.), microbial actions (microorganisms and algae growth), physical features of storage reservoirs (capacity, open surface, depth etc.), and operation modalities (continuous flow or batch storage) (Cirelli et al. 2008). The issues of concern include physical, chemical, microbiological and aesthetic water quality problems (Asano et al. 2007).

Water temperature, turbidity and suspended solids are typically physical water quality parameters. Water temperature can increase significantly when reclaimed water is stored in open reservoirs or aboveground storage tanks,

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particularly under hot and arid climates. Although water temperature may not directly affect the uses of reclaimed water, an elevated water temperature can accelerate changes in water quality such as bacterial and algae growth, and chlorine residual reduction (Kirmeyer et al. 2001). In open reservoirs, plankton and algae growth and local runoff may also result in significant increases in turbidity and suspended solids concentrations (Geldreich 1996).

Parameters related to chemical water quality include pH, alkalinity, and disinfectant residual (residual chlorine in most cases). As water is stored, biological oxidation of residual organic matter may happen. This releases carbon dioxide as a byproduct and thus lowers the pH of the water stored. On the other hand, biological nitrification of residual ammonia to nitrate may also release hydrogen ions that lower the water pH as well. Residual chlorine concentration may decrease as the residence time of water in the storage facilities increases. Bacterial re-growth can easily occur if residual chlorine drops to low concentrations (Jjemba et al. 2010).

Microbiological problems during storage are mainly caused by algae growth. When sunlight is available as energy source, algae growth consumes CO_2 in water and produces dissolved oxygen (DO), while when sunlight is not available algae use DO in water for respiration and releases more CO_2 to water (Robertson et al. 2003). Excessive algae growth in open storage reservoirs can lead to operation and maintenance problems for irrigation water reuse. The presence of algae in the stored water is also aesthetically unacceptable for many reuse applications.

The physical, chemical, and microbiological problems discussed above may all result in the generation of color and turbidity in the reclaimed water stored. This strongly influences the aesthetic property of water for its uses. Another aesthetic issue is the generation of offensive odor as a result of the accumulation of ammonia and hydrogen sulfide under a condition of low DO concentration (Keller et al. 2000). Loss of oxygen and odor formation often happen in stagnant water in underutilized enclosed storage tanks or in the bottom layer of stratified open reservoirs where anaerobic zones are in existence. Due to depleted DO concentration, nitrification of ammonia cannot proceed smoothly so that ammonia gas can accumulate. When the reclaimed water contains dissolved sulfates, they can be biologically reduced to hydrogen sulfide by facultative bacteria under anaerobic conditions (Wilkie et al. 1995).

Water quality control for open storage reservoirs. The strategic countermeasure for preventing water quality deterioration in open storage reservoirs is to use aeration for providing oxygen and eliminating stratification (Asano et al. 2007). The commonly used aeration facilities include surface aerators with high pumping capacity, brush aerators, static tube aerators, and diffused aeration devices (Gonzalez 1995). In order to prevent planktons from uncontrolled growth, copper sulfate and other selective algaecides can be used. This often needs a careful examination of the number and type of microorganisms to be controlled (Geldreich 1996). It is not recommended to use chlorine for plankton control in open reservoirs because chlorine may combine with odor-causing compounds present in the reservoirs to intensify odors (Robertson et al. 2003).

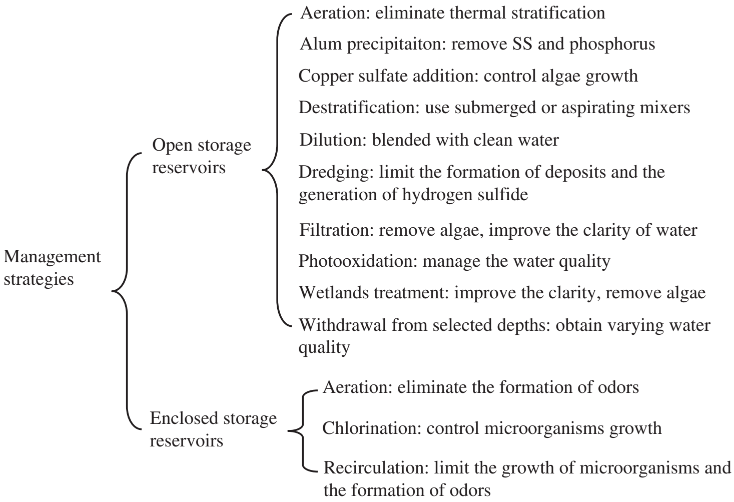

Figure 5.5. Management strategies for open and enclosed reservoirs used for the storage of reclaimed water

Water quality control for enclosed storage reservoirs. For enclosed reservoirs, the main strategic measures include providing facilities to re-circulate the contents of the storage volume and to dose additional chlorine to maintain a residual at sufficient high level (Robertson et al. 2003). Aeration devices or pumps are widely used to circulate the stored water in most cases, while for enclosed storage tanks of smaller scale, the inlet and withdrawal piping can be configured in a manner to secure water circulation without additional device (Singleton and Little 2006). Chlorine addition is usually limited to small off-line storage reservoirs typically used for landscape irrigation and some industrial reuse applications.

The management strategies for open and enclosed storage reservoirs are summarized in Figure 5.5. Regardless of whether open or enclosed storages are used, to ensure that the reclaimed water is produced with good quality is the most effective countermeasure, especially for a system where long-term water storage is required.

5.4.3 Enhancement of Natural Purification

In a broad sense, water reuse is not a new idea but a long-lasting practice since human beings began to withdraw water from natural water bodies for various uses (Raskin et al. 1996). No matter how simple the way of water use is, the used water, if not completely evaporates into the atmosphere, will return to natural water bodies through different routes. Therefore, people living in the downstream side of a river basin will inevitably use the water blended with the treated or untreated wastewater from the upstream (Postel et al. 1997). The larger the scale of water use in the upstream area, the higher percent of wastewater blended in the source water at downstream. However, people do not refuse such a manner of water use because

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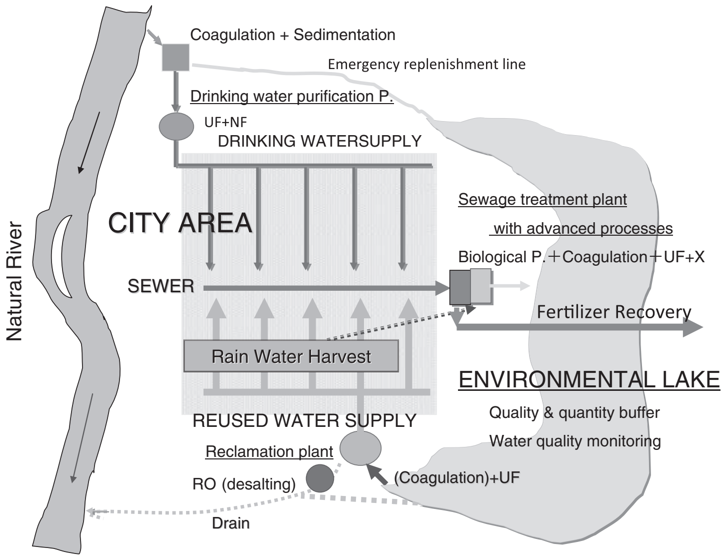

Figure 5.6. A water district with an environmental lake as a quality and quantity buffer

Source: Figure 13 in Tambo et al. (2012); reproduced with permission from *Journal of Water Sustainability*

they perceive that the water, even at the most downstream section of a long river, is from the natural source but not somewhere else. Scientifically, the water is safe for use in most cases because it has been purified naturally while flowing through the river channel, although a part of it has been used many times. The natural purification or self-purification mechanism is well illustrated by Streeter and Phelps (1925) who formulated a model to describe the consumption of oxygen in an idealized river that is proportional to the biochemical oxygen demand (BOD). Numerous studies have indicated that a natural water body can perform the roles of removing organic and inorganic pollutants, and even micro pollutants through physical, chemical, physiochemical, biological, and ecological actions (Gijzen 2006; Karaouzas et al. 2011). The function of natural purification can also be called water metabolism (Tambo 2002; Wang and Chen 2010; Tambo et al. 2012). It is recommended that water reuse can be integrated into a water district as shown in Figure 5.6 where an environmental lake, either natural or artificial, can be utilized as a quality and quantity buffer in the district water cycle.

If water reuse is practiced in such a natural or semi-natural manner, the reclaimed water quality can be controlled or even improved by enhancing natural purification in the water bodies via the following ways (Karaouzas et al. 2011):

- Optimization of hydraulic/hydrological conditions: making water flowing but not stagnating in any part of the water body, usually by rational control of hydraulic retention time (HRT), careful selection of locations for its inflow

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and outflow, modification of flow path etc. For large lakes receiving local runoff, hydrological calculation is needed.

- Enhancement of reaeration: improvement of the reaeration condition in the water body, usually by the installation of aerators or utilization of hydraulic potential to form waterfalls, etc. Water entertainment facilities over a landscaping lake often need water pumping to create water scenes. They can also be utilized for enhancing reaeration.
- Vegetation management: utilizing aquatic plants to improve the ecological condition and assist nutrients removal in the water body. Aquatic planting can often combine with wetland systems adjacent to the water body. Floating beds of the plantation are also used in many cases.

5.5 A CASE STUDY

5.5.1 Case Description

The project site is Xi'an Siyuan University located in the southeast suburban area of Xi'an, a megacity in northwest China where low annual precipitation and dry climate result in serious water shortage problems. The university campus is on a hill with an average elevation about 200 m higher than the surroundings and about 13 km from the central city. As this area is not covered by the centralized urban water supply system, the university has depended on groundwater wells for obtaining water for various uses since it was established in 2001. The maximum capacity of groundwater withdrawal is 3000 m^3/d which could meet the demand for potable and non-potable water uses years ago when the number of students was small. However, with the fast development of higher education in China, the university expanded its scale rapidly and began to face a water shortage problem. Currently, the number of students living in the campus amounts to about 25000, and the campus area covers an area about 80 ha of which about 50 ha are green belts. The university also plans to increase the total number of students to 35000 in five years. By taking into account the limited amount of groundwater as the source for water supply and the students as the main users of water, the available water is merely 120 L/d per capita at present and will be 85–100 L/d in the near future, which can marginally meet the lowest requirement for potable consumption but insufficient at all for non-potable consumptions as irrigating the large green belt in such a dry area often needs large amount of water. In order to solve the water shortage problem, the university had two options: one was to enlarge the water source such as to apply to the municipal government for access to the urban water supply network; another was to practice on campus wastewater treatment and non-potable water reuse. As water reclamation and reuse has been encouraged and supported by local authorities, the university decided to choose the later option. A project was thus implemented for building a wastewater treatment and reuse system to meet the present and future requirements.

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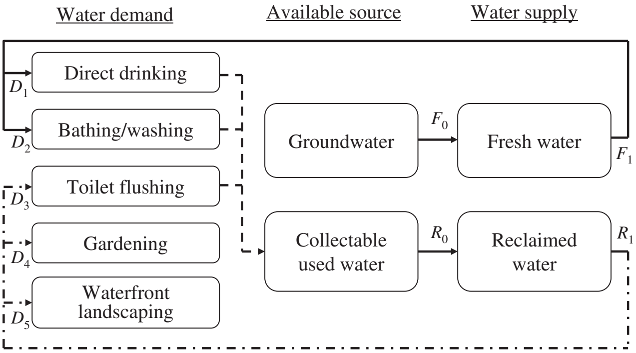

Figure 5.7. Relationship between water demands, available sources, and categories of water supply for water budget analysis

5.5.2 System Design and Implementation

Water demand and availability. Water demand and availability were evaluated by water budget analysis basically following the method described in Section 5.3.1 and taking into account the practical condition as shown in Figure 5.7, where D_1, D_2, D_3, D_4, D_5 are demands for direct drinking, bathing/washing, toilet flushing, gardening, and waterfront landscaping, respectively; F_0 and R_0 are sources from groundwater and collectable used-water, respectively; F_1 and R_1 are quantities of fresh water supply and reclaimed water supply, respectively. All quantities are as m^3/d.

The water budget relationship should meet the following conditions:

$$F_0 \geq F_1 = D_1 + D_2 \tag{Eq. 5.12}$$

$$D_1 + D_2 + D_3 = R_0 + (\text{water loss during water use}) \tag{Eq. 5.13}$$

$$R_0 \geq R_1 + (\text{water loss during wastewater treatment}) \tag{Eq. 5.14}$$

If the currently used groundwater was taken as the sole source for potable water supply at the present time (population as 25,000) and in the near future (population as 35,000), the first question was whether or not the groundwater supply could meet the needs for potable water use. Through a survey on the service level and water consumptions for potable uses at various locations [such as washing at the students dormitories, bathing or showering at the bath center (very common in China for collective life on campus), students canteens, and educational facilities that needed fresh water supply], it was estimated that the per capita water consumption only for potable purposes was between 70 and 80 L/d. By taking 80 L/d as the demand for per capita potable water use, the current total water demand for potable water supply would be 2,000 m^3/d while that for the

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future would be 2,800 m^3/d. The conclusion was that the maximum capacity of groundwater withdrawal of 3,000 m^3/d could meet the current and future needs for potable water supply while all non-potable uses were impossible to be covered by groundwater supply.

The second question was about the non-potable water demand. To answer this question, a projection was conducted as shown in Table 5.4 for various purposes of non-potable water supply. The projection was based on an assumption that in the near future (in 5 years) there would be an increase in the population from 25,000 to 35,000 persons while the campus area would not change. As a result, the total non-potable water demand at current time was projected as 3,450 m^3/d, a value much higher than the demand for potable water supply. With the increase of population in the future, the demand for toilet flushing would increase and the total demand would become 3,750 m^3/d.

For landscaping lakes, the requirement of 20% daily replacement was mainly for controlling the hydraulic retention time so that water stagnation or eutrophication could be easily prevented. This would not physically consume water. In order to improve the efficiency of water utilization, one possible way would be to place the landscaping lakes in mid of a water cycle but not as an end-user of the reclaimed water. As the demand for gardening and toilet flushing was larger than that for lake replenishment, it would be plausible to let water flow through the lake before it was used for other purposes. In this way, the total non-potable water demand would be greatly decreased as shown in the last row of Table 5.4.

System configuration. Following the discussion on the relationship between water demands, available sources, and categories of water supply, the water system was configured in a form as shown in Figure 5.7. Under the assumption of future population as 35000 persons and groundwater supply as 2800 m^3/d, the collectable used-water would be 80% of the total potable water supply as 2240 m^3/d. As the reclaimed water used for toilet flushing would flow into to the collection system, the additional flow to the wastewater treatment and reclamation unit could be estimated as 90% of the used-water as 945 m^3/d so that the total inflow to the treatment unit would become 3185 m^3/d, a much enlarged source for water reclamation. If 90% of the inflow could be reclaimed for non-potable water supply, the potential of reclaimed water production would become 2867 m^3/d which could cover the water demand of toilet flushing, gardening, and evaporation and other losses from the landscaping lakes. According to the distribution of non-potable water users, a part of the reclaimed water would be sent directly to some of the locations for toilet flushing and gardening. However, more than half quantity of the reclaimed water could be injected to the lakes for a replacement of the water stored. As water could be pumped from the lake to various locations for toilet flushing and gardening, a dynamic equilibrium state could be maintained between the inflow (from the treatment unit) and outflow (to downstream reuse) so that the lake water replacement could be realized without additional water consumption. As shown in Figure 5.8, there could be a surplus (117 m^3/d) between the water supply and demand for gardening, indicating that through the system with a partially closed water loop and water regulation by the landscaping lakes, the total

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Table 5.4. Projection of non-potable water demands

	Water use	*Specification*	*Quantity*	*Demand*	*Remarks*
1	Toilet flushing	30 L/d/n[a]	25,000–35,000 persons	750–1,050 m^3/d	
2	Gardening	3 L/m^2/d[b]	500,000 m^2	1,500 m^3/d	For 50 ha green belt
3	Lake replenishment[c]	20% daily replacement	50,000 m^3	1,000 m^3	For lakes of 5000 m^2 and 1 m depth
4	Lake water loss[d]	20% of lake replenishment	1,000 m^3	200 m^3	Evaporation and other loss
5	Total			3,450–3,750 m^3/d	Including item 3
				2,450–2,750 m^3/d	Excluding item 3

Note: [a] According to Chinese specification of 20–40 L/d/person for toilet flushing (Li 2002)

[b] According to Chinese specification of 2.5–3.5 L/m^3/d for gardening (Li 2002)

[c] According to Chinese specification of water replacement per time in 4–5 days interval (Li 2002)

[d] According to local experience

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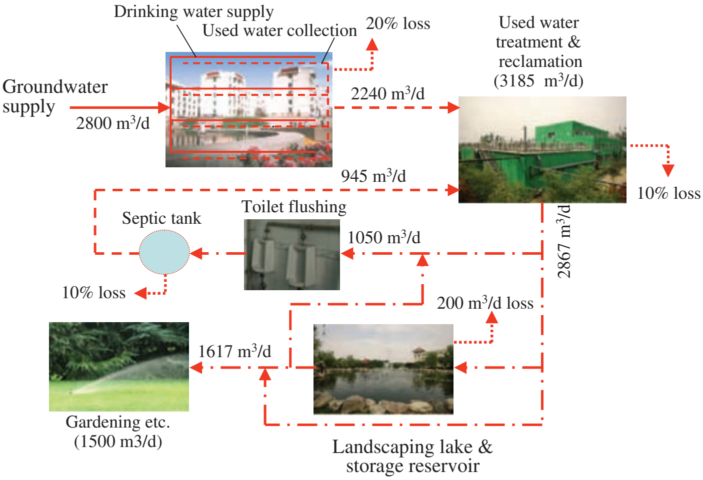

Figure 5.8. Configuration of the on-campus water system

capacity of water supply could be enlarged to more than 5600 m^3/d including that for potable and non-potable water supply which is a doubled scale of the original groundwater supply.

Selection of treatment process for water reclamation. The materials balance relationship for the on campus water system could take a form as shown in Figure 5.9. By utilizing Eq. 5.11 in this case for evaluating the required removal of mass of pollutant *i* by used water treatment and reclamation, the following equation was obtained.

$$\Delta M_{i,2} = F_1 C_{i,1} + \Delta M_{i,1} + \Delta M_{i,3} - \Delta M_{i,4} - (R_1 - D_3) C_{i,2} \qquad \text{(Eq. 5.15)}$$

In Figure 5.9 and Eq. 5.11, F_1, R_1, and D_3 are as indicated in Figure 5.7; $C_{i,1}$ and $C_{i,2}$ are concentrations of pollutant *i* in the groundwater and reclaimed water,

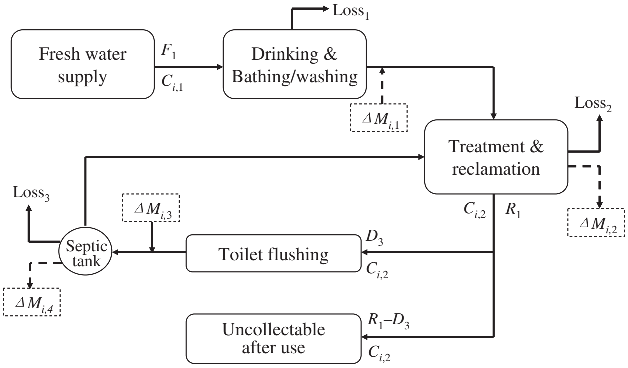

Figure 5.9. Materials balance relationship for pollutant i in the water cycle

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Table 5.5. Chinese water quality criteria for different reuse purposes

		Reuse purpose		
Parameter	*Unit*	*Toilet flushing*	*Landscaping lake*	*Gardening*
BOD	mg/L	10	**6**	
SS (Turbidity*)	mg/L (NTU)	**5***	10	10*
TDS	mg/L	1500	–	1000
TP	mg/L	–	**0.5**	–
TN	mg/L	–	**15**	–
NH_3-N	mg/L	10	**5**	20
Fecal coliform	1/L	**3**	2000	3
Residual chlorine	mg/L	**1.0**	0.5	1.0

*Turbidity values

respectively, as mg/L or g/m^3; $\Delta M_{i,1}$, $\Delta M_{i,2}$, $\Delta M_{i,3}$, and $\Delta M_{i,4}$ are masses of pollutant *i* input due to bathing and washing, removed by treatment, input due to toilet flushing using reclaimed water, and removed by septic tank, respectively, all as g/d; Loss_1, Loss_2, and Loss_3 are uncollectable water after drinking and bathing/washing, water lost in the treatment process, and water lost for desludging the septic tank, respectively, all as m^3/d. Because $C_{i,2}$ is the concentration of substance *i* in the reclaimed water that meets the requirement for reuse purposes, it could be decided according to the Chinese standards on water reuse as shown in Table 5.5 for toilet flushing, landscaping lake and gardening (Standardization Administration of China 2002a, b).

It can be seen that water reuse for lake landscaping demands certain levels of organic and nutrient contents, while toilet flushing requires specific values of turbidity, fecal coliform, and residual chlorine. For gardening, the requirement for salt content (TDS) is high. Therefore, the bold figures in Table 5.5 were taken as the targets for reclaimed water quality control, i.e. $C_{i,2}$ in this case.

On the other hand, the total mass of pollutant *i* entering the wastewater treatment unit would be

$$M_{i,in} = F_1 C_{i,1} + \Delta M_{i,1} + \Delta M_{i,3} - \Delta M_{i,4} + D_3 C_{i,2} \qquad \text{(Eq. 5.16)}$$

and the mass of pollutant *i* remaining in the reclaimed water could be

$$M_{i,out} = R_1 C_{i,2} \qquad \text{(Eq. 5.17)}$$

Then the required removal of pollutant *i* by the wastewater treatment unit equals:

$$Removal\ (\%) = \frac{M_{i,in} - M_{i,out}}{M_{i,in}} \times 100\% \qquad \text{(Eq. 5.18)}$$

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Table 5.6. Estimation of organic and nutrients loading

Parameter	Unit loading[a] (g/d/person)	Population (persons)	Calculated loading (kg/d)[c]		
			Total	Fecal	Miscellaneous
COD	42	35000	1470.0	558.6	911.4
BOD[b]	25.2		882.0	335.2	546.8
TN	14		490.0	401.8	88.2
TP	0.8		28.00	19.04	8.96

Note: [a]Unit loadings were estimated according to experiences in China regarding COD, TN, and TP (Wang et al. 2008a; Feng et al. 2009). [b]BOD/COD ratio as 0.6 in wastewater from domestic source according to experiences in China. [c]Percents of fecal and miscellaneous loadings were estimated as 38% and 62% for COD, 82% and 18% for TN, 68% and 32% for TP (Feng et al. 2009)

Table 5.6 shows the estimated organic and nutrients loading discharged daily to the wastewater flowing to the treatment system. By substituting the calculated miscellaneous loading ΔMi,1, fecal loading ΔMi,3 into Eqs. 5.16–5.18 and taking into account the fecal loading reduction by the septic tank, and the target quality for reclaimed water (bold figures in Table 5.5), the required removals for BOD, TN, and TP by the wastewater treatment unit were evaluated as 97.7%, 89.1%, and 93.7%, respectively. In order to achieve such a high removal for the production of high quality reclaimed water and prevention of organic and nutrients accumulation in the water cycle, a sophisticated treatment process as a combination of anerobic-anoxic-oxic (A^2O) and membrane bioreactor (MBR) as shown in Figure 5.10 was implemented (Hu et al. 2013).

Stepwise water use and enhancement of water quality improvement by the landscaping lakes. As can be seen from Figure 5.11, the landscaping lakes in the water cycle have performed several important roles. Firstly, they act as a receiver of the reclaimed water after being used for a series of on-campus water landscapes from the upstream side and a provider of water for further uses in the downstream side so that stepwise water use was realized. Secondly, with a total storage volume of 5000 m^3, the lakes also perform the role of storage reservoirs in the water cycle

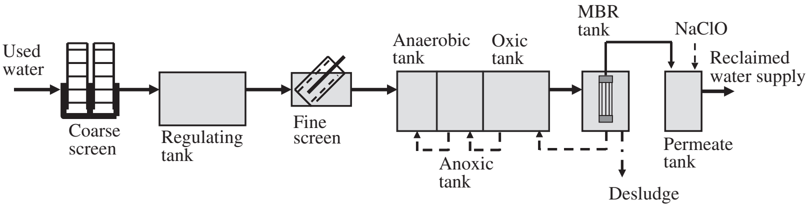

Figure 5.10. Schematic diagram of the anaerobic–anoxic–oxic (A^2O) biological unit followed by a submerged membrane bioreactor (MBR) for reclaimed water production (full capacity of treatment as 4000 m^3/d)

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Figure 5.11. Landscaping lakes in the water cycle for stepwise water use, water storage and water quality improvement

for equalizing quantitative fluctuation between reclaimed water production and consumption. Thirdly, their hydraulic and ecological conditions are favorable for preventing water quality deterioration and even for water quality improvement because the lake water is always circulating and the waterfalls, fountains and water plants in the lakes can assist aeration and natural purification in addition to their landscaping effects (Figure 5.12).

5.5.3 Effects of System Operation

Water source augmentation for various water uses. The system has been put into full operation since April 2011 after the completion of all construction, installation and rehabilitation works. With most of the non-potable water uses shifted from the groundwater supply to the reclaimed water supply, as the groundwater withdrawal was kept at 2000 m^3/d on average. Even in the hottest periods of summer, the groundwater supply did not exceed 2500 m^3/d. The condition of water supply was completely changed and over-pumping of groundwater did not happen again. At the current population level, the daily production of reclaimed water was about 2500 m^3/d which could meet the needs for toilet flushing and gardening in the whole campus area. As the lakes could store a water volume for two days' non-potable water consumption, the contradiction between the constant reclaimed water production rate and timely fluctuation of water use was well solved.

The A^2O-MBR treatment system was partitioned into multiple trains in parallel to cope with the seasonal fluctuation of inflow because there would be a substantial decrease in water users on weekends and school holidays. The lakes could provide a buffer zone in the reclaimed water application system to absorb

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Figure 5.12. Enhancement of natural purification in the lakes utilizing (a) rockwork with falling water, (b) fountains, (c) water falls, and (d) water plants

this variation. In the past two years, the system worked well under a dynamic equilibrium state for effective water use. Lake water overflow only occurred in heavily rainy days. However, as will be discussed later, because the lakes are almost in a mimic natural state and with favorable water quality, the occasional overflow may not result in adverse impacts on the environment.

On the other hand, if Eq. 5.5 is used to evaluate the recycling ratio of water in the water cycle, referring to Figure 5.7 it can be estimated that the fraction of water collected after potable water use is $\alpha = 0.8$, the fraction of water collected after reclaimed water use is $\beta = 0.33$, and the quantity ratio of reclaimed water to collected wastewater is $\gamma = 0.9$. It can then be calculated that under the current condition of water uses, the recycling ratio is

$$\frac{R_1}{F_1} = \frac{\alpha\gamma}{1 - \beta\gamma} = 1.024 \qquad \text{(Eq. 5.19)}$$

indicating that in the on campus system the quantity of total reclaimed water supply (R_1) is over the quantity of total potable water supply (F_1) and maximized water reclamation and reuse is realized.

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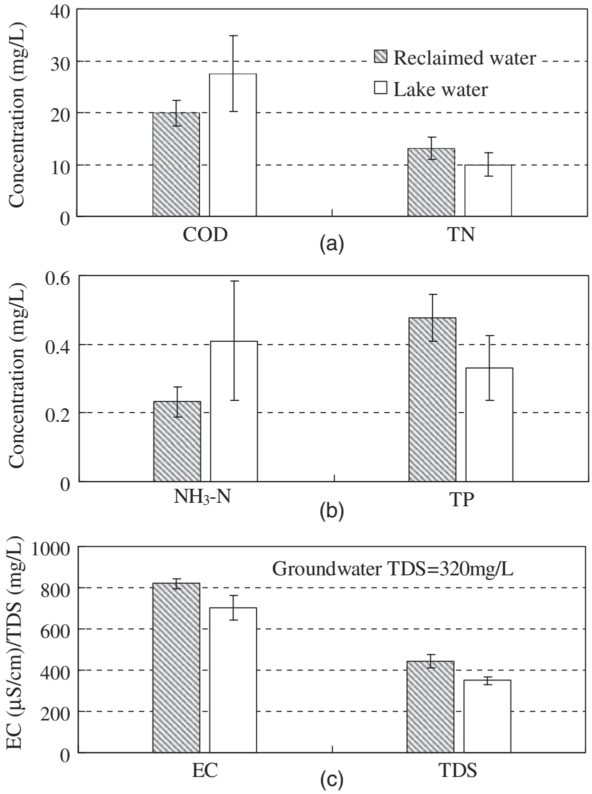

Figure 5.13. Comparison of the reclaimed water and lake water for conventional water quality parameters and salt contents (Error bars are based on weekly water quality monitoring in 2012)

Water quality in the landscaping lakes. The reclaimed water produced by the A_2O-MBR treatment process has provided high-quality water to meet the prescribed requirements (Table 5.5). Although in the process design, attentions were mainly paid to BOD, TN, and TP control, with the high performance of the membrane for effective separation and the provision of final chlorination, the requirements for turbidity, fecal coliform, residual chlorine were also well satisfied. As the lakes are not only used for landscaping purpose but also as a storage reservoir for non-potable water supply, attention should be paid on the variation of water quality during its storage in the lakes.

Figure 5.13 compares the lake water with the reclaimed water from the A^2O-MBR system regarding conventional water quality parameters and salt contents based on the weekly water quality monitoring in 2012. It can be seen from the figures that COD and NH_3-N concentrations became slightly higher in the lakes than the reclaimed water. This is believed to be due to non-point source contamination during water storage because COD and ammonia can be from

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various sources relating to human activities. However, it is noticeable that TN and TP concentrations tended to be lower in the lakes than the reclaimed water, indicating that the lakes can assimilate nutrient salts through natural processes. The similar tendency can also be seen from the total salt contents, because both EC and TDS of the lake water showed lower values than that of the reclaimed water. Salt accumulation is usually a concern for a water cycle through water evaporation and continuous input of salt substances such as through toilet flushing. However, in comparison with the TDS of the groundwater as 320 mg/L, the TDS of the reclaimed water was maintained at a level just about 100 mg/L higher. After storage in the lakes, the TDS almost returned to the original level of the groundwater. Although the mechanism of salt reduction in the lake is a topic for investigation, natural actions such as adsorption, ion exchange, plant absorption, and natural water replacement during rainy days may have played important roles.

Socioeconomic benefits. The social and environmental benefits of the project are obvious. Through its implementation, fresh water resource is only used for potable purposes whereas all non-potable water uses are covered by the reclaimed water. In other words, the efficiency of water utilization has been doubled and the precious freshwater resource is saved. Along with the collection and reclamation of all collectable used waters, wastewater discharge has almost been eliminated, except for the overflow of excess water from the landscaping lakes in rainy days. For a university with a large campus area and high green coverage with water landscapes, water is indispensable for its maintenance. By using the reclaimed water, a green campus has been well sustained without additional freshwater supply. The lakes and the surrounding greenbelts have become the central water landscapes in the university campus (Figure 5.14). The mimic natural beauty has completely changed human perception on wastewater reuse.

Figure 5.14. Central scenery area in front of the university main buildings with lakes and green belts maintained by reclaimed water

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For a partially closed water cycle where black water after toilet flushing returns to the system, sophisticated treatment, such as the A^2O-MBR process, has to be applied for obtaining a high removal of pollutants and production of high quality reclaimed water. This inevitably results in higher unit cost for reclaimed water production than conventional wastewater treatment and reuse (usually by biological treatment + coagulation and sand filtration) due to power consumption (about 1 kWh/m^3) for membrane operation and additional cost for membrane installation, renewal, and maintenance. However, the average unit cost of 2.02 Yuan/m^3 (or 0.22 Euro/m^3 including all direct and indirect costs) is about half of the local water tariff for tap water. If the sewage fee of 0.7 Yuan/m^3 exempted due to the elimination of wastewater discharge into the public sewer system is also counted, the economic benefit is more significant.

5.6 SUMMARY

In this chapter, the concepts of water cycle management were discussed with attentions paid to the relationships between natural hydrological cycle and artificial water cycle of water uses for various purposes which need water supply from freshwater sources and water reclamation. From the beginning of civilization, human beings on one hand have depended on the hydrological cycle to obtain available water sources, and on the other hand have learnt from the nature the ways to purify water when it is deteriorated and to make it qualitatively suitable for use. In the whole world, water reuse has in fact been practiced for long on basin scales with a full utilization of the natural purification capacity so that the discharged wastewater from cities at the upstream can become part of the source water for cities at the downstream without much concern of water quality problems. Nowadays as natural water resources are no longer sufficient, and people have realized that wastewater is a resource, we have to consider how to utilize this resource in a more efficient and environment-friendly way. The best answer to this question, as discussed in this chapter, should be to integrate urban wastewater reuse and other components such as urban water supply, urban sewerage, and urban water environment into one system characterized by a district water cycle of semi-natural features. A series of conceptual models were proposed to describe the urban/district water cycle without or with water reuse, and the related water budget and materials balance relationships. The fundamental methods to analyze a water cycle are water budget and materials balance analyses from which the requirements for water quality conversion through engineering means can be determined. In addition to the integrated design of urban/district water systems following the concepts of water cycle management, control of reclaimed water quality in the water cycle is also important. This needs a careful selection of treatment technologies based on the treatability of target pollutants in the wastewater, technologies for water quality control during reclaimed water storage, and technologies for enhancing natural purification in the water cycle.

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A case study was introduced in this chapter as an example of application of the water cycle management principles. The system implemented in Xi'an Siyuan University, China has integrated water supply, used-water collection and reclamation, water landscaping in one framework characterized by a local water cycle, where maximized water reclamation and reuse was realized and the efficiency of water utilization was more than doubled. With landscaping lakes with sufficient storage capacity but frequent replenishment by reclaimed water inflow and outflow as a buffer zone in the water cycle, remarkable effects were obtained in improving the lake water quality, especially regarding TN, TP, and TDS.

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CHAPTER 6

Green and Sustainable Natural Wastewater Treatment/Disposal Technologies

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6.1 INTRODUCTION

The most critical issues in the world today are water scarcity and water pollution associated with it. An important part of urban development is effective wastewater treatments (WWT). Urban areas of the world face increasing immigration and rapid expansion. As one of the major drawbacks, urbanization creates extensive air, water and solids pollution. Moreover, future demands on potable water in residential areas would lead to increased wastewater reuse (U.S. EPA 1997). On the other hand, half of the populations in the world live in rural areas where a complete sewerage system may never be possible or desirable (NAE 2011). Sewage contamination has reached dangerous levels. “The greatest challenge in the water and sanitation sector over the next two decades will be the implementation of low cost sewage treatment that will at the same time permit selective reuse of treated effluents for agricultural and industrial purposes” (Green Arth 2012). It is imperative for us to transform the situations to a sustainable, close-loop urban wastewater management system that is geared towards the conservation of water and resources (e.g., nutrient, energy).

Historically, the primary focus of wastewater management activities has been on community point-source wastewater discharges. Since 1980s, non-point source pollution control has gained more and more attention. Later, best management practices (BMPs) have been practiced everywhere (e.g., formally introduced in the Clean Water Act amended in the 1999). Meaning while, new technologies and hardware were introduced for small treatment systems (i.e., wastewater flow < 3,785 m^3/d), making the implementation of small and decentralized wastewater management (DWM) be possible. In 1998, Crites and Tchobanoglous (1998)

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published the textbook "*Small and Decentralized Wastewater Management Systems*," symbolizing the significant advance of the movement of DWM. In the 2000s, the concept of low impact development (LID) became popular and is used for 1) land-use planning, 2) stormwater runoff management (e.g., in the US and Canada), and 3) any type of development that either enhances or does not significantly diminish environmental quality (as in the U.K.). All over the world, people are continuously searching for systems that are appropriate in scale, cost, and flexibility, and in harmony with the principles of sustainability. Since the 2010s, Green and Sustainable Natural WWT and Disposal Technologies (GSNWWTDTs) are gradually realized by the public as the key to achieve sustainability in WWT and resource management in the world.

This chapter focuses on GSNWWTDTs. The chapter first introduces the concepts and major categories of GSNWWTDTs, and then focuses on a few selected GSNWWTDTs. Through critical but non-exhausted literature review and analysis of current issues of these technologies, this chapter may reach its purpose of introducing the principles, advantages, applications and considerations of GSNWWTDTs when dealing with sustainable WWT systems. Finally, the chapter describes the strategies to implement these GSNWWTDTs along with future trends and brief conclusions.

6.2 GSNWWTDTS: CONCEPTS AND MAJOR CATEGORIES

Nowadays, funding for large-scale infrastructure systems is difficult to obtain. In addition, the relevance of projects that involve high energy consumption, large pipes, tons of concrete, steel, and other structural impacts is highly questionable. Currently, it is widely accepted that we need to reduce water pollution and implement measures to expand water resources and waste reuse. WWT goals should include the recovery of nutrient and resources for reuse in different sections and reduction of the overall user-demand for water resources. The wastewater management team needs to create a strategy that will recover resources from industrial wastewaters and reduce pollution, thus contributing to improve public health. Wastewater treatment designers should select a suitable technology for site-specific conditions and financial resources of individual communities. In addition to, there should be a particular focus on meeting sustainable treatment. Van Lier et al. (1998) summarized the criteria for sustainable technology that should be considered in the treatment of wastewater as follows:

- Do not dilute high strength wastes with clean water;
- Focus on maximum recovery and reuse of treated water or by-products obtained from the pollutants (e.g., irrigation, fertilization);
- Focus on low-cost technologies that are simple in their construction, operation and maintenance with a long-term efficiency, robustness, and reliability;

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- Pay attention to the degree of applicability on a wider scale;
- Lead to a higher degree of self-sufficiency; and
- Be highly acceptable to the local community.

One approach to sustainability is through the application of "decentralization" in WWT systems (DWM). DWM is defined as the collection, treatment and reuse of wastewater at or near its source of generation. Significant improvements in recent decentralized technologies have led it to integrate seamlessly and efficiently with water-carriage waste removal. Essentially, the core components of DWM are similar to the centralized collection and treatment systems, but the applied technologies are different. Table 6.1 shows some representative technologies used in DWM and non-point source (NSP) pollution control, most of which belong to GSNWWTDTs. Table 6.2 shows a comparison of some major natural WWT technologies.

Decentralized systems currently serve approximately 25% of the U.S. population, and they have been shown to save money and promote a better watershed management. They are suited to a wide variety of site conditions (U.S.EPA 1997). Decentralized systems with GSNWWTDTs offer higher flexibility and can adapt quickly to match the local conditions of the urban area, and they are reported to suit well to the requirements of the local community and its population as it increases with time (Wendland et al. 2003). Usually, DWM with applications of GSNWWTDTs need the participation of the entire community and often requires a strong administrative capability for the community to move forward. For example, Palo Alto, California developed a Water Reclamation Master Plan which intended for a dual distribution system for large turf areas (such as golf courses and parks) that used a blend of treated and reclaimed water. This system saves millions of gallons of treated and reclaimed water per year, and the reclaimed water also helps to serve irrigation needs (SWRCB 2003). New York City's 2004 Comprehensive Water Reuse Program (CWRP) provides a 25 percent reduction in water service rates for property owners who treat and reuse water on-site for non-potable uses (NYCDEP 2004).

There are endless opportunities to optimize our water, wastewater and stormwater management systems for sustainable development. For example, black and gray water can be treated or reused separately from the excreta. Energy in gray or black water can be recovered with heat-pump systems, and treated gray water can be used for water supply sources or industrial water use. Gray/rain water can be treated and stored in retention ponds for fire protection, landscape irrigation, or groundwater recharge, wetlands creation, and urban non-potable uses such as toilet flushing, car washing and decorative lakes and fountains. All these are currently being practiced in Florida (SFWMD 2004). Continued research has improved the operation and management of these GSNWWTDTs and has resulted in innovative and improved on-site treatment technologies, e.g. intermittent and recirculating packed-bed filtration. This has resulted in an increased implementation of GSNWWTDTs in developing urban fringe areas with growing populations.

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Table 6.1. Representative technologies used in DWM and resource recovery systems

Technologies/processes category	*Description of related processes/application/occurrence*
1. WW pretreatment: • Bar racks/screening/communition; gravity separation/filtration/flotation; • Imhoff tank/oil/grease removal/septic tank	Removal of solids of varying size, oil/grease, and condition the WW • Used for the removal of suspended materials; settleable/floatable/fine solids • Used for the removal of suspended materials, oil/grease from individual discharges
2. Biological WWT & N/P removal: • Aerobic and/or anoxic processes • Anaerobic processes • Combined aerobic/anoxic/anaerobic processes for nutrient (N, P) removal	Mainly for BOD removal, nitrification/denitrification and P removal • For BOD removal, nitrification/denitrification, and P removal. Include: suspended-growth (e.g., extended-aeration variations; intermittent decanted extended aeration; sequencing batch reactor; and pre-engineered package plants); biofilm processes (e.g., trickling filters, packed-bed reactors for nitrification/ denitrification); and hybrid (combined processes (e.g., trickling filter + activated sludge; construction wetlands) • For WWT, energy recovery and production of value-added products with different kinds of feedstocks (WW, MSW, WAB, etc.). Include: suspended-growth (e.g., anaerobic contact processes and anaerobic digestion); biofilm processes (e.g., anaerobic fixed bed); and combined processes (e.g., upflow anaerobic sludge blanket (UASB) for high strength wastes stabilization and fixed-bed reactor • These are single- or multi-stage processes various proprietary processes for nitrification/ denitrification and P removal
3. Natural WWT systems • Lagoon (or pond) treatment systems	Mainly for BOD removal, nitrification/denitrification, and P removal • Earthen basins that are most widely used in small communities for WWT, including aerobic, anaerobic, facultative, and maturation (tertiary) lagoons.

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• Wetlands and aquatic treatment systems	• Use aquatic plants and animals for WWT, including constructed wetlands (free-water-surface CWs, subsurface-flow CWs, vertical-flow CWs), floating aquatic plant systems and combinations systems
• Land treatment systems	• The controlled application of WW onto the land surface for WWT, including slow rate, rapid infiltration, and overland flow
• Geo-purification systems	• Treat WW partially and then artificially recharges the aquifers and then withdrawn for future use, including soil aquifer treatment (SAT) systems, rapid infiltration well systems, rapid infiltration underdrain systems, river bank filtration systems
4. Effluent disposal processes:	Mainly for onsite disposal/reuse of WW after pretreatment
• Conventional and modified leachfields	• Include: gravity leachfields (trench or absorption beds) and their modifications (deep or shallow trench). They are most common onsite systems
• Alternative systems	• To overcome the site/soil constraints. Include: mound system, fill systems, At-grade systems, sand-filled trenches, evapotranspiration systems, evaporation ponds, CWs, etc.
• Intermittent/recirculating packed-bed filters	• Low-rate filters are very useful for effluent disposal, including intermittent (single-pass) and recirculating (multi-pass) sand filters and other types of filters (e.g., absorbent plastic-medium filters, textile packed-bed filters, peat filters). System used for nitrification/denitrification include septic tank + attached-growth reactor, RUCK system, sawdust system and sulfur-limestone autotrophic denitrification systems
• Reuse systems	• Include: drip irrigation, spray irrigation, and graywater reuse
• Other systems	• Include: holding tanks as seasonal use alternatives and surface water discharge
5. WW reclamation/reuse systems:	Mainly for providing additional reliable water sources
• Reclamation of WW	• Processes used for DWM include packed-bed filtration, membrane filtration, chemical precipitation for P removal/recovery, and disinfections
• Effluent reuse	• Effluent reuse includes: agricultural/landscape irrigation, industrial reuse, recreational impoundments, groundwater recharge, habitat wetlands, water supply for potable use.

(Continued)

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Table 6.1. Representative technologies used in DWM and resource recovery systems (Continued)

Technologies/processes category	*Description of related processes/application/occurrence*
6. BMPs for NPS pollution control:	Mainly for non-point source pollution control of MS4
• Six minimum BMPs	• Six BMPs were identified by the CWA: 1) public education and outreach; 2) public participation and involvement; 3) illicit discharge; 4) construction site storm water runoff control; 5) post-construction storm water runoff control; and 6) municipal operations pollution prevention and good housekeeping. MS4s' objective is to reduce pollutant effluents to the Maximum Extent Practicable (MEP)
• Structural BMPs/green roofs for stormwater runoff treatment and management	• These are for storm runoff control and treatment of first half-inch stormwater runoff, including: vegetated filter strips, vegetated swales, bioretention, sand filter, horizontal filter, check dams, infiltration trench, detention/retention ponds, etc.
• BMPs for agricultural NPS pollution control	• These include: CWs, ponds, filter strip, stripcropping, grade stabilization structure, terrace, subsurface drain, tile outlet, conservation tillage, and management of different things (e.g., animal waste, pesticides, nutrient, pasture, soil fertility, etc).
7. Other processes	Those used for resource/material recovery and pollution control
• Urban mining technologies	• Any urban mining technologies that involve water and wastewater treatment, including sorption/ desorption processes, biodegradation, bioleaching, etc.
• Carbon capture and sequestration (CCS)	• Any technologies or processes used for CCS that involve sustainable practices and water/wastewater treatment, such as farming practices and conversion to pastureland with good grazing management, placing biochar in soils, or using steel slag/waste concrete to transfer CO_2 to solid carbonates, etc.

Note: WW = wastewater; WWT = WW treatment; N/P = nitrogen/phosphorus; MSW = municipal solid waste; WAB = waste agricultural biomass; CW = constructed wetland; BMPs = best management practices; NPS = non-point source; MS4 = Municipal Separate Storm Sewer System; SAT = soil aquifer treatment; CWA = Clean Water Act

Source: Crites and Tchobnoglous (1998); NAE (2011); Zhang and Surampalli (2013)

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Table 6.2. Comparison of some major natural wastewater treatment technologies

			Design parameters			*Capital costs*					
Natural system type	*Pretreatment requirements*	*Treatment goals*	*Hydraulic loading (cm/d)*	*Specific treatment area (ha/ 1000 m^3-d)*	*Water depth (m)*	*\$1,000/ ha*	*\$/m^3-d*	*O&M costs \$/m^3*	*Disposal to*	*Advantages*	*Disadvantages*
Onsite Infiltration	Primary setting in septic or Imhoff tank	BOD$_5$ and TSS reduction (approximately secondary)	0.5–4.0	2.5–20	N.A.		1000–3000	0.01–0.10	Ground water	Zero discharge; low energy	Requires permeable unsaturated soils; limited to small systems (<−200 m^3/d)
Slow-rate land application	Primary or secondary	BOD$_5$, TSS, and nutrient reductions	0.15–1.6	6–67	N.A.	50–150	800–2000	0.10–0.20	Ground water	Zero discharge	Requires permeable unsaturated soils; high energy cost
High-rate land application	Primary or secondary	BOD$_5$ and TSS reductions	1.6–25	0.4–6	<1	300–600	450–900	0.05–0.10	Ground water	Zero discharge; low energy	Requires highly permeable, unsaturated soils; potential nitrate contamination
Overland flow	Primary or secondary	BOD$_5$ and TSS reductions	1–10	1–10	<0.1	240–400	600–1000	0.08–0.15	Surface water	Aerobic treatment; moderate energy use	Crop maintenance; TSS breakthrough
Facultative ponds	Primary	BOD$_5$ and TSS reductions	0.7–3.4	3–14	1.2–2.5	80–160	500–1000	0.07–0.13	Surface water	Aerobic/anaerobic treatment; low energy use	High algal TSS in outflow; little operational control
Floating aquatic plant systems	Primary or secondary	BOD$_5$, TSS, and nutrient reductions	2–15	0.7–5	0.4–1.8	270	500–1000	0.12–0.14	Surface water	Phosphorus removal through harvesting	Anaerobic treatment plant harvesting and disposal; pests
Wetlands	Primary, secondary, or advanced	BOD$_5$, TSS, and nutrient reductions	0.4–20	0.5–20	<0.6	25–250	500–1000	0.03–0.09	Surface water	Low energy; aerobic/ anaerobic treatment; wildlife habitat	Maintenance of plant population; hydraulics in subsurface-flow systems

N.A. = not available.Source: Data from WEF (1990)

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6.3 SELECTED GSNWWTDTS: APPLICATIONS AND CURRENT ISSUES

There are many options of GSNWWTDTs for one to choose to find the most appropriate technology for a particular site/scenario. Here, we describe a few selected GSNWWTDTs. Instead of providing an exhausted review on the selected technologies, we organize the material as i) types and applicability, ii) removal of pollutants, and iii) current issues related to the technologies to better achieve the purpose of the section. For some technologies, case studies also are introduced to illustrate the applications and concerns related to these technologies.

6.3.1 Lagoon Treatment Systems

Types and Applicability. Lagoon treatment systems are earthen basins or reservoirs that are constructed to use natural forces (chemical, physical, biological and solar) and energy-efficient processes to provide a low-cost WWT. Lagoon systems can consist of a single pond or a series of ponds. In most cases, two or more small lagoons can provide better quality treatment than one large lagoon. In systems that employ more than one lagoon, each lagoon cell has a different function to perform, so different forms of lagoon design may even be used for each cell (pond).

As shown in Table 6.1, there are four major types of lagoons with regards to their dissolved oxygen concentration status (Crites and Tchobnoglous 1998). Anaerobic lagoons are most often used to treat animal wastes from concentrated animal feed operations (CAFOs), commercial or industrial wastes, or as the first treatment step in systems using two or more lagoons in a series. Aerated lagoons are very common in small communities (Piper 1997). Partial-mix aerated lagoons are sometimes called facultative lagoons that have been adapted and upgraded to receive more wastewater.

Lagoons are often used for treating wastewater directly or after pretreatment (category 1 in Table 6.1). Lagoons can provide preliminary treatment or secondary treatment, depending on its design. When used for preliminary treatment of wastewater, a lagoon's effluent needs to be refined by different processes, such as intermittent sand filters, wetlands, aquatic treatment systems, and land treatment systems (category 3 in Table 6.1).

Lagoons are one of the most cost-effective WWT options for many homes and communities. In the U.S., most WWT lagoons are found in small and rural communities. Lagoons are especially well-suited to small communities because they cost less to construct, operate, and maintain than other systems. However, the availability of land becomes a challenge in an urban setting (Van Lier et al. 1998). Lagoon systems use less energy than most wastewater treatment methods, and they are simple to operate and maintain. Lagoons' capability of handling intermittent use and shock loading is much better than many treatment systems. Moreover, they are effective at removing pathogens from wastewater. Due to its high nutrient and low-pathogen content, this effluent can be suitable for irrigation.

Performance and Removal of Pollutants. So far, little has been reported on metal removal from anaerobic lagoons (Mara and Mills 1994). Metal removal has

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been assumed to occur by precipitation and microbiological activity (Reed et al. 1988). An important parameter that affects the solubility of the metal hydroxides and the kinetics of the oxidation and hydrolysis process is the pH of the water. At high pH values, metal ions tend to precipitate as hydroxides (Moshe et al. 1972). The complex relationship between pH and metal removal varies with metal types and process natures (biotic/abiotic). It is also affected by the availability of dissolved oxygen and microbial activities. Surface adsorption through suspended solids may also play a role in the removal of heavy metals.

Pano and Middlebrooks (1982) analyzed results from three pond systems and reported that more than 90 percent of ammonia (NH_3) removal occurs at pH of 7–8. At low temperatures, as biological activities decrease, ammonia volatilization will be the primary nitrogen removal mechanism in a well- mixed lagoon. At temperatures slightly above 20°C, thermal stratification and poor mixing conditions lead to decreased ammonia volatilization. This was in contrast to the earlier reports by other researchers (McKinney 1976; McKinney 1977; Ferrara and Avci 1982) who concluded that volatilization is not the primary pathway for nitrogen removal from lagoons. Ferrara and Avci (1982) applied an entirely mixed flow model and reported the main mechanism of nitrogen removal to be sedimentation of organic nitrogen via biological uptake. Reed (1985) also employed data from the same three pond systems to develop a model for the fate of nitrogen. However, he could not conclude if it was sedimentation or volatilization to be the main route for nitrogen removal due to complex interactions in the biochemical pathways. Volatilization was believed to be the major mechanism for nitrogen removal in summer months and deposition during the winter months.

Toms et al. (1975) reported that about 80 percent of phosphorus removal could be attributed to the precipitation of hydroxyapatite ($Ca_5(PO_4)_3OH$), which will not re-dissolve. The authors found this to occur in communities with very soft water containing very low calcium concentrations. Mara and Pearson (1987) reported that sedimentation of organic phosphorus as algal biomass played an important role in phosphorus removal from lagoons. Houng and Gloyna (1984) found that an increase in the number of tertiary lagoons provided an effective treatment for phosphorus removal and recycling as more phosphorus was immobilized in the oxidized surface layers of sediments in the lagoons. The authors also reported that phosphorus release rates from the sediments of anaerobic and facultative lagoons were 25–50 times faster than that from the tertiary lagoons. Grizzard et al. (1982) stated that aerobic conditions in the sediment decreased the amount of phosphorus released back to the water column. Another study revealed that the amount of soluble phosphorus released into the water from the sediment is governed by the capacity of the sediment to adsorb and desorb inorganic phosphorus from the solution, the mineralization of organic phosphorus and the simple diffusion of phosphate (Reed et al. 1988). These authors also found that the release of phosphorus from the sediment will occur at high pH values under anaerobic conditions when the concentration of phosphorus in the water is lower than that of the sediment. The presence of iron, aluminum and calcium at high concentrations will play a role in enhancing the adsorption of phosphorus.

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Current Issues Related to Pond Systems. One of the problems that pond systems have is its low performance during the winter time. For every 10°F temperature drop, there is a $\log_{10}$ growth decrease in biological activity. Therefore, in the winter, pond systems would even produce more nutrients than they remove. One way to overcome the problem is to supplement with bacterial products (called bioaugmentation). Many studies focused on these microbial products.

Currently, in developing countries where priorities other than environmental conservation exist, older and well-known threats to biodiversity continue to increase, including eutrophication, acidification and contamination by toxic substances (e.g., heavy metals and organochlorines). However, new threats such as global warming, ultraviolet radiation, emerging contaminants (e.g., endocrine disruptors) and, especially, invasion by exotic species including transgenic organisms are most likely increase in importance for the pond systems in developed countries.

One good example is the ammonia issue that link pond systems with air pollution. Nowadays, it is commonly known that ammonia is generated from the breakdown of manure and urine, as well as wasted animal feed. Ammonia becomes volatilized. Ammonia is a precursor to fine particulate matter ($PM_{2.5}$). It reacts with sulfuric acid and nitric acid to form ammonium sulfate and ammonium nitrate. Ammonium sulfate formation is preferential under most conditions, though ammonium nitrate is favored by low temperature and high humidity (Figure 6.1). Mensink and Deutsch (2008) studied the formation and composition of $PM_{2.5}$ using the EUROS model, and reported that ammonia can

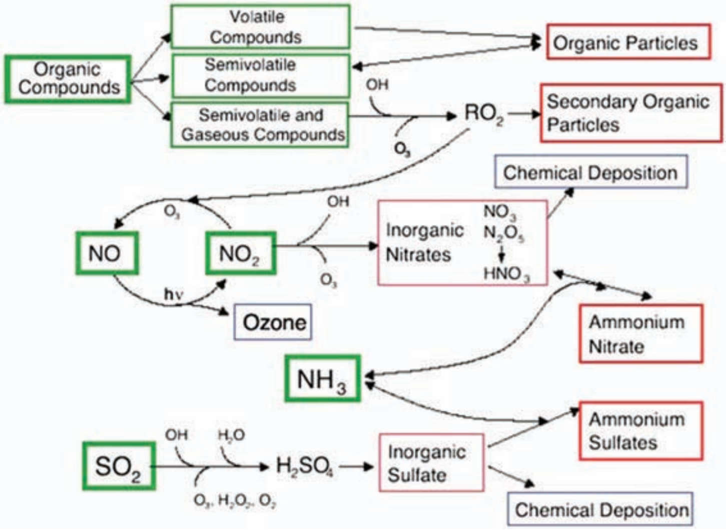

Figure 6.1. Relationships among organic compounds, NOx, ozone, NH_3 and SO_2 in formation of fine particles ($PM_{2.5}$ and PM_{10}) in the atmosphere
Source: Damberg (2007)

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provide an abundant amount of condensation nuclei in the form of ammonium nitrate and ammonium sulfate which, under favorable meteorological conditions, attract hygroscopic water, leading to rapid increase in the $PM_{2.5}$ mass fraction. Agricultural activities, livestock productions in particular, have been reported to be the largest contributor of ammonia emissions into the atmosphere. Therefore, for CAFOs, emission inventories of ammonia contain uncertainties; and, monitoring of ammonia gas and nitric acid from these ponds (or in the nearby environment) is a future trend. In some states in the US, plans for lagoon and sprayfield conversion are implemented. For example, in North Carolina, $\tilde{2}0$% of nitrogen is emitted by Swine CAFOs via NH_3 emission. All swine facilities will be rated to determine their risks to public health and the environment. Facilities that fail to protect public health or the environment will be required to convert to new technologies or close out their lagoon and/or sprayfield systems (HA 2014).

Case Studies. Three case studies are described below to demonstrate how pond systems (simple or complicated) can be used by small communities to solve real world problems.

Located on Flathead Lake in northwest Montana, Polson was incorporated in 1910 and has experienced slow, steady growth over the years. Before 1962, when Polson built its first lagoon system, the city used a series of septic tanks and chlorination to treat its wastewater. The disinfected septic tank effluent was discharged directly into Polson Bay and the Flathead River. Lagoons were an improvement then, and they still work well today. The system built in 1962 consisted of two facultative lagoons. Flows were merely diverted from one lagoon to the other every six months. Recently, the population growth rate has increased to about five percent per year, bringing the current population to about 4,300. To accommodate this population growth, the city built a new system in 1981 with three aerated lagoons and one polishing lagoon. Polson also began to operate its own lab to monitor the system. The system was aerated, based on the recommendations from the engineers, public hearings as well as from the viewpoint of low operation and maintenance costs. They are still using the same system today, with some improvements such as an addition of a wind-powered aerator and mixer, and three floating aerators. The only weak point in the system is the original fine bubble aerators, which lie on the bottom and are very prone to clogging. The residents seem happy with the lack of odor from the system and its low cost. Sewer rates are around $6.50 a month per household, but of that actual treatment costs are only $8.25 per person per year. The system received 1989 U.S. Environmental Protection Agency Region 8 award for operation and maintenance. Since January 1995, effluent biochemical oxygen demand (BOD) levels have an average of 16 mg/L, and total suspended solids (TSS) levels have been 38 mg/L. Currently, Polson is considering ways to upgrade its facilities again, because the system is getting very close to meeting its design flows. Some of the options being considered are replacing the current system with a fully mechanized plant, or expanding the system and adding land application and disinfection. The city will continue to upgrade its collection system. Its goal for the future is to construct the most efficient and long-lasting system (Piper 1997).

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The City of St. Helena, located in the Napa Valley, California installed an integrated wastewater lagoon system in 1966 to treat 1890 m^3/d of municipal wastewater. The system consists of a primary lagoon (with three shallow floating aerators) and a second high-rate aerobic lagoon (algae-laden) for WWT, a third lagoon for settling, and the fourth and fifth lagoons for maturation or storage. The water from lagoon 2 is partially recycled to the primary lagoon, and serves to provide an aerobic cap on the primary lagoon. The advantage of these lagoons systems is that it has little accumulation of sludge in the primary lagoon (Crites and Tchobanoglous 1998).

Denham Springs, Louisiana runs its processed sewage through two shallow 16-hectare (40-acre) ponds that have been lined, carpeted with stones, filled with water and planted with lilies and other plants. Although it looks like a flower farm in summer, the biological sewage treatment facility can treat over 11 million liters (3 million gallons) of sewage per day. Compared with conventional processing, the city saved $1 million in initial construction costs and saved approximately $60,000 per year in operation and maintenance (MacLeish 1990; Marinelli 1990).

6.3.2 Wetlands and Aquatic Treatment Systems

Types and Applicability. Natural wetlands (NWs) act as transitional areas between land and water and are distinguished by the availability of wet soils, plants that are adapted to wet soils and available water depth that enhances these characteristics. On the basis of the dominant plants, wetlands can be classified into three groups: salt and freshwater swamps, marshes and bogs. Swamps are flooded areas dominated by water-tolerant woody plants and trees. Marshes are dominated by soft-stemmed plants, and bogs are dominated by mosses and acid-loving plants (Hammer and Bastian 1989; Kadlec and Knight 1996). Being characterized by high organic matter accumulation, wetlands experience a high rate of primary productivity and a reduced rate of decomposition due to anaerobic conditions (Hammer and Bastian 1989). Many natural and constructed tropical wetlands have a net primary productivity of more than 1000 $g\,C/m^2$-yr, which is greater than most other ecosystems (Neue et al. 1997). Incoming nutrients enhance the growth of vegetation, which converts inorganic chemicals into organic materials, the basis of the wetland food chain.

As shown in Table 6.1, constructed wetlands (CWs) and aquatic treatment systems (ATSs) are those using aquatic plants and animals for WWT. These systems are classified according to the dominant life form of the large aquatic plant or macrophyte in the system. CWs and ATSs present a competitive advantage over conventional treatment systems due to a higher degree of self-sufficiency, ecological balance and economic viability offered by them. A major advantage offered by these treatment systems are that they allow the total resource recovery (Rose 1999). Watson et al. (1989) and Kadlec and Knight (1996) have reported the advantages of using wetland technology for WWT include (1) minimization in fossil fuel requirement, (2) no chemical addition required and (3) multi-purpose sustainable utilization of swamp fisheries, biomass production facilities, and seasonal agriculture (Santer 1989; U.S. EPA 1993; Knight 1997). In addition,

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they are more easily operated and more efficient to maintain. Due to their low-cost and low-technology requirements, wetlands are potential alternative or supplementary systems for WWT in developing countries.

The first experiments on the use of wetland plants to treat wastewaters were carried out in the early 1950s by Dr. Käthe Seidel in Germany. The first full-scale systems were put into operation during the late 1960s. Since then, the subsurface systems have been commonly used in Europe while free water surface systems have been more popular in North America and Australia (Vymazal 2011). However, between the 1970s and 1980s, information on CWs spread very slowly. In the 1990s, CWs and ATSs are widely employed for WWT in Europe and North America (Kadlec and Knight 1996). Vymazal (1998) reviewed various designs for emergent macrophyte CWs and were categorized according to surface (SF) or subsurface (SSF) wastewater flow patterns. Because of the need for more efficient removal of ammonia and total nitrogen, during the 1990s and 2000s, vertical and horizontal flow constructed wetlands were combined to achieve higher treatment efficiency (Vymazal 2011). Meanwhile, ATSs containing free-floating macrophytes with well-developed submerged roots such as water hyacinth (WH), or small surface floating plants with little or no roots such as duckweed have been utilized for WWT (reviewed by Greenway 1997). WH has been extensively experimented due to its higher potential for nutrient removal. The plant has been reported to double its biomass content in 6 days and result in a yield of 88–106 Mg/ha-yr (Reddy and Sutton 1984). More descriptions about CWs and CWs with WH for WWT are as follows.

CWs for WWT. CWs for WWT involve the use of engineered CWs that are designed and constructed to utilize NW processes for the removal of contaminants. These systems are designed to mimic NWs, and they utilize wetland plants, soil and associated microorganisms to remove contaminants from wastewater effluents (U.S. EPA 1993). Most CWs emulate marshes as the soft-stemmed plants in them and require the shortest time compared to plants in bogs and swamps for full development and operational performance (Hammer and Bastian 1989).

CWs have been employed for treating various types of wastewaters in developed countries, e.g. domestic wastewater (Cooper et al. 1997; Schreijer et al. 1997), acid mine drainage (Kleinmann and Girts 1987; Brodie et al. 1989; Howard et al. 1989; Wenerick et al. 1989), agricultural wastewater (DuBowry and Reaves 1994; Rivera et al. 1997), landfill leachate (Dombush 1989; Trautmann et al. 1989; Staubitz et al. 1989), urban storm-water (U.S. EPA 1993), and for polishing advanced treated wastewater effluents for return to freshwater resources (Schwartz et al. 1994; Gschlößl et al. 1998). CWs are also used for treating eutrophic lake waters (D'Angelo and Reddy 1994b) and for the conservation of nature (Worrall et al. 1997). CWs have also been suggested as alternative for treating nitrate-contaminated aquifers, denitrification of nitrified sewage effluents and irrigation return flow (Baker 1998). Denitrification efficiency in CWs for treating high-nitrate waters with low organic carbon has been shown to depend on the C:N ratio, with peak efficiencies occurring at $\mathrm{C{:}N}$ ratios $> 5{:}1$ (Baker 1998).

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In Thailand, CWs have been employed for improving effluents of lagoons treating industrial wastewater (Panswad and Chavalparit 1997). At a retention time of 3 days and a hydraulic loading of 30 cm/d, the copper-rich effluent (5.7 mg/l) and difficult to degrade (COD : BOD = 17) was treated in a Typha latifolia and Ipomes species beds. While BOD removal was inadequate, TN removal was 29%, TP removal of 30% and copper removal of 61%. Since 1994, Mexico has investigated a two-stage system consisting of an anaerobic digester followed by a gravel bed HF wetland system (600 m^2) at a hydraulic retention time (HRT) of 1.7 days with P. australis and T. latifolia is used for abattoir wastewater in Pachuca. The system was reported to obtain 88.5% BOD, 87.4% COD, 89% TSS, 73.6% organic nitrogen and 99% faecal coliforms. Though the system was suitable for irrigation, it started accumulating phosphorus with time (Rivera et al. 1997).

CWs with WH. Application of WH for the purification of wastewater has been well documented (Reddy and Sutton 1984; Reddy and DeBusk 1985; DeBusk et al. 1989; Reddy and D'Angelo 1990; Vymazal 1998). A large surface area for the attachment of microorganisms is provided by an extensive root system, thus increasing the potential for decomposition of organic matter. Major processes for nutrient removal from wastewater systems involve with WH plants. The system performance is closely related to the nutrient loadings, because plant uptake of nutrient is the process control factor (Reddy and Sutton 1984). Nitrogen removal is accomplished through plant uptake (with harvesting), ammonia removal through volatilization and nitrification/ denitrification, and phosphorus removal through plant uptake. CW systems with water hyacinth have been sufficiently developed to be successfully applied in the tropics and sub-tropics (Vymazal 1998) at climatic conditions that favor luxurious and continuous growth of macrophytes for the entire year. Table 6.3 lists recommendations for their applications.

The WH system removed 81% of BOD_5 and 80% of suspended solids at a sewage loading of 440 kg/ha-day and a hydraulic retention time of 3 days. A biomass production of 680 mg/ha-year was achieved from a pond area of 0.75 ha. Methane yield of 0.47 m^3/kg VS was obtained in the anaerobic digester. These systems have been recommended for use in the tropics and subtropics (Vymazal 1998). *E. crassipes*, a WH species was tested in CWs for purification of domestic wastewater for reuse in Morocco under semi-arid conditions (Mandi 1998).

Table 6.3. Recommendations for application of water hyacinth systems

Treatment	*Total detention time (days)*	*Depth (m)*	*Hydraulic load (cm/d)*
Secondary advanced	>40	<1.5	>2
Secondary	6	>0.9	8
Tertiary	6	≪0.9	8

[a] Plant density (loosely packed plants, 80% coverage) 12–22 kg/m^2

Source: Data from Vymazal (1998)

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At a hydraulic retention time of 7 days, a higher reduction of organic load COD, 78%; TSS, 90% and a parasitic load (helminthes eggs 100%) was achieved. The effluent met the WHO (1989) standards for reuse to irrigate cereal crops, fodder crops, pasture, and trees. Application of an integrated rural WWT with WH has also been demonstrated in Brazil for a small community (Roquette et al. 1998). The system has been employed for the treatment of stream water for domestic use, and partly for treating domestic wastewater, piggery, cattle-pen and poultry wastewater. Treated water is returned to the stream. Biogas production (60% methane) was obtained using excess plant biomass. Then, it was used for electricity generation. The excess biomass is used for animal feed and horticulture after composting.

WWT systems with WH produced large amounts of excess biomass due to the rapid growth rate of the plant. For sustaining an efficient treatment system based on WH, a management plan must have provisions for harvesting and use of the excess plant materials. Frequent harvesting for maintaining moderately high plant densities has been recommended for an optimization of productivity of WH wastewater systems which are integrated with methane production or animal feed production. This practice is suitable for the maximum removal of phosphorus but not for the maximum removal of nitrogen (DeBusk and Reddy 1987). Depending on the scale, the cost factor must be considered for harvesting extra biomass. The use of WH on the field scale in developed countries has not been extensively pursued, in spite of its enormous potential for large-scale WWT and biomass production. This may be attributed to the poor performance in Northern Hemisphere winters, given the optimum growing temperature of WH ranging between 20 and 30°C (Reddy and Sutton 1984). Economic feasibility of the system is another likely reason for this.

Hayes et al. (1987) reported the successful integration of WH-systems for WWT into methane/carbon dioxide production projects as means of using excess WH biomass. Three components involved in the cost for the WH systems integrated with energy production included (1) the purchase of land and construction, (2) periodic harvesting and (3) construction, operation and maintenance of integrated methane production system.

Performance and Removal of Pollutants in CWs and ATSs. Wetland systems reduce contaminants including trace metals, organic and inorganic matter and pathogens. Diverse treatment mechanisms such as sedimentation, filtration, chemical precipitation and adsorption, microbial interactions and uptake by vegetation, all act to accomplish contaminant removal (Watson et al. 1989). However, these mechanisms are complex and not yet entirely understood. Main factors influencing the water quality of wetlands include the hydrology of the place, type of vegetation, and soil. Hydrological cycles also affect the type of vegetation, microbial activity and biogeochemical cycling of nutrients in soil (Mitsch and Gosselink 1993). Many authors have documented the role played by wetland plants (macrophytes) in influencing the treatment processes in wetlands (Reddy and DeBusk 1985; DeBusk and Reddy 1987; Brix 1994, 1997; Greenway 1997; Koottatep and Polprasert 1997; Mars et al. 1999; Greenway and Wooley 1999). Table 6.4 summarizes the nutrient uptake capacities of commonly used macrophytes in wetlands.

Table 6.4. Nutrient uptake capacities of some wetland macrophytes

	Uptake Capabilities (kg/ha-yr)	
Macrophyte	*Nitrogen*	*Phosphorus*
Cyperus papyrus	1100	50
Phragmites australis	2500	120
Typha latifolia	1000	180
Eichhornia crassipes	2400	350
Pistia stratiotes	900	40
Potamogeton pectinatus	500	40
Ceratophyllum demersum	100	10

Source: Brix (1994)

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Microorganisms play a central role in the biogeochemical transformation of nutrients (Hoppe et al. 1988; Madigan et al. 1997). Many authors have reported their ability towards the removal of toxic organic compounds in wetlands (Pitter and Chudoba 1990; Kadlec and Knight 1996; Fliermans et al. 1997; Orshanky and Narkis 1997; Reddy and D'Angelo 1990; Suyama et al. 1998; Savin and Amador 1998). A recent report (McLatchey and Reddy 1998) found that organic matter turnover and nutrient cycling appears to be strongly correlated with electron acceptor availability and redox conditions in wetland soil.

Current Issues Related to CWs and ATSs. There are several misconceptions about CMs and ATSs; discussions about them and the reality are as follows (U.S. EPA 2000b):

1. *Wetland design has been well-characterized by the published design equations*. The reality is that it is often a) lack of quality data both temporally and spatially on full-sized CWs; b) lack of paired influent-effluent samples (i.e., taking samples at inlet and outlet at the same time does not provide the paired samples as hydraulic retention time will affect the results); c) lack of reliable information on flow or detention time; d) lack of necessary weathery information (e.g., temperature, precipitation, etc.); and e) limited information on treatability of more concentrated municipal WW.
2. *Significant aerobic micro-sites exist in all wetland systems*. The reality is that the small amount of O_2 leaked from plant roots is insignificant compared with the BOD in the WW. In SFCWs, most parts are in anaerobic conditions. Usually, If 1.0 g of carbon is fixed as cell mass, plants may produce 2.5 g O_2. In CWs, if we assume the carbon fixing rate is 1.0 g C/m^2-d (a high productive condition), still we can only obtain 2.5 g O_2/m^2-d, which is insignificant.
3. *CWs can remove significant amount of N and P*. Nitrification and denitrification are the primary removal mechanisms for N removal (e.g., ~30%), while harvesting removes <20% of influent N (and very limited P) even though plant assimilation may take ~30% of N. This is because when plants

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grow, most of biomass is accumulated in the roots (even 9̃0% for some plants). In addition, in winter, ammonium increases in the effluent.

4) The root areas of SFCWs help to remove suspended solids efficiently. The reality is that the solidification may occur in the root areas of SFCWs after plants are mature (in 5–6 years), which would completely block the WW flow.

One critical issue for subsurface flow CWs (SSFCWs) is medium clogging. Wavy subsurface- and vertical-flow CWs (WSVFCWs) are the modified forms of SFCWs. By adding several baffles in WSVFCWs, the wastewater flow direction changes; the contact between wastewater and wetland media increases; and the short circuiting of wastewater reduces (Ren et al., 2008). Recently, a direct aeration process has been applied in WSVFCWs for enhanced COD removal and nitrification (Nivala et al. 2007; Ren et al., 2008). Ren et al. (2015) evaluated the effects of aeration and wastewater composition on the clogging process in four laboratory-scale WSVFCWs used for secondary and tertiary treatment. They found that the clogging mainly occurred in the upper 0–40 cm layer, and the accumulated material decreased with filter depth (along the flow direction). The dominant particle size contributing to clogging was ~40 μm in the WSVFCWs for secondary treatment and >110 μm in those for tertiary treatment. The accumulated material had 30–40% of organic matter. The clogging mechanisms varied if the composition of influent and aeration conditions are different in WSVFCWs. Aeration promoted the growth of biofilm and mineralization of the accumulated material as well as provided shear force in the WSVFCWs. Aeration has a good effect in extending the operational time in the tertiary WSVFCW, but has a mild effect in the secondary WSVFCWs because of high organic loading rate there. Both the organic and suspended solids (SS) loading rate are important factors and should be controlled to mitigate the clogging problem in WSVFCWs.

Another critical issue is how to use CWs and ATSs for WWT, reducing GHG emissions and simultaneously producing cellulosic biomass as raw material for renewable biofuel or for production of value-added products (e.g., extracting proteins from duckweeds). For example, algae can convert carbon dioxide to biomass and oxygen under sufficient supply of nutrients, photons, and water through photosynthesis (Eq. 6.1):

$$\mathrm{CO_2 + H_2O + Nutrients + Photons \rightarrow Algaebiomass + O_2} \qquad \text{(Eq. 6.1)}$$

If using $CH_{1.8}N_{0.17}O_{0.56}$ (Zhang et al. 2014) to represent the composition of typical algae, every 44 g of CO_2 can produce 25 g of algae biomass through algae photosynthesis, which is a rather efficient way to fix carbon dioxide. As shown in Figure 6.2, CWs and ATSs can be combined with algae or other aquatic vegetation for produce valuable substances. Zhang et al. (2014) provided an overview of these applications.

Liu et al. (2012) reported that the net life-cycle energy output of CWs is higher than that of corn, soybean, switchgrass, low-input high-diversity grassland and

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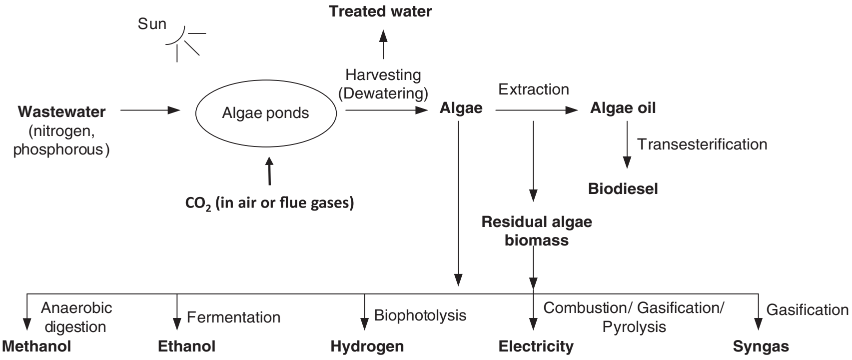

Figure 6.2. CO_2 fixation by algae and possible usage of algae
Source: Adapted from Pilli et al. (2014); copyright ASCE

algae systems. Energy output from existing CWs is ~237% of the input for biofuel production and can be enhanced by optimizing the nitrogen supply, hydrologic flow patterns and plant species selection. Assuming that all waste nitrogen in China could be used by CWs, biofuel production can account for 6.7% of national gasoline consumption. They also reported that CWs have a greater GHG reduction than the existing biofuel production systems in a full life-cycle analysis. This warrants future studies because of CWs' straightforward operation, economic competitiveness, and many ecological benefits.

Case Studies. Jillson et al. (2011) examined the performance of two horizontal SFCWs in the removal of pathogen and pathogen indicators under variable loading and operating conditions. The two CWs are located near Lincoln, NE, USA. Firethorn CW system had four CW cells and a two-cell sand filter. It was used to treat wastewater (pretreated by gravity sedimentation) from a small housing community at a typical flow of 115–125 m^3/d. Rogers Farm CW located at a rural single-family dwelling was used to treat wastewater after septic tank treatment at a typical flow of 1.51 m^3/d. The research focused on pathogenic-related organisms by monitoring fecal coliform and *Salmonella* spp. and their removal effectiveness by the two CWs. Samples at Firethorn were collected at the wetland cell influent and effluent, as well as sand filter effluent (system effluent) from June 1996 through April 2000 and at the influent and effluent points from Rogers Farm from June 1999 through April 2000. The main monitoring parameters were fecal coliform at both sites and *Salmonella spp.* (from August 1999 through January 2000) at Firethorn. Firethorn demonstrated an effective removal of fecal coliforms with 96.3% removal in the wetland cell and 98% by the wetland system, which included a sand filter. Rogers Farm had an average fecal coliform removal of 99.3%. Although *Salmonella spp.* was not detected at Firethorn, reduction of other bacteria was observed through the wetland system. In general, the fecal coliform removal was excellent through the wetland system. No distinct difference in removal efficiency was observed with changes in season and temperature at either facility.

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6.3.3 Anaerobic Digestion

Types and Applicability. Anaerobic digestion is a treatment option when the available land is limited. Anaerobic bacteria degrade organic materials in wastewater in the absence of oxygen and produce methane and carbon dioxide. Methane can be used as an alternative energy source (biogas). Additional benefits include a reduction of total biosolids at a volume of 50–80% and a final waste sludge that is biologically stable to serve as humus for agriculture.

Conventional anaerobic digestion requires longer retention time and produces lower biogas. In the 1960s, the conventional anaerobic digestion process has been extended into two-stage (in some papers, also called two-phase) anaerobic digestion (Ghosh et al. 1974). In two-stage anaerobic digestion, hydrolysis, acidification, and liquefaction are performed in the first stage (i.e., acid-forming phase), and methane production via acetate and hydrogen/carbon dioxide in the second stage (i.e., methane-forming phase) (Pilli et al. 2014). It should be noted that the two-stage anaerobic digestion is different from the temperature-wise two-stage anaerobic digestion, e.g., a mesophilic anaerobic stage (digester) followed by a thermophilic anaerobic stage (digester), which was developed to eradicate the pathogen and to obtain Class A solids. Considerable studies have been conducted to understand the two-stage anaerobic digestion and its applications since 1970s (Chartrain et al. 1987; Zhang and Noike 1991, 1993). While their principles, design, process behavior as well as operation and maintenances (O/M) are well known, the two-stage anaerobic digestion processes have almost never been used for sludge treatment in full-scale WWT plants (WWTPs). Since the 1990s, more and more high rate anaerobic processes have been developed for treatment of not only all kinds of wastewater but also solid waste (e.g., garbage) (Pilli et al. 2014). Table 6.1 shows general types of anaerobic digesters. Table 6.5 summarizes some of the important features of these reactors.

All modern high-rate anaerobic processes are based on the concept of retaining high viable biomass by some modes of bacterial sludge immobilization. Following methods have been recommended by Hulshoff and Lettinga (1996) towards achieving the same: (1) formation of highly settleable sludge aggregates combined with gas separation and sludge settling (e.g. UASB reactor and anaerobic baffled reactor); (2) bacterial attachment to high density particulate carrier materials (e.g. fluidized bed reactors and anaerobic expanded bed reactors); (3) entrapment of sludge aggregates between packing material supplied to the reactor (e.g. downflow anaerobic filter and upflow anaerobic filter). Some of the high rate anaerobic processes are briefly discussed below.

Fixed Film Reactor. In stationary fixed film reactors (Figure 6.3), the reactor has a biofilm support texture (media) such as activated coal, PVC (polyvinyl chloride) reinforces, firm rock fragments or clay circles for biomass immobilization. Fixed film reactors avails of simplicity of structure, elimination of perfunctory mixing, meliorate toughness at superior loading ranks, further skill to withstand huge shock loads (Van den Berg et al. 1985) and organic shock loads

Table 6.5. Characteristics of anaerobic reactors

Reactor type	*Start-up period*	*Channelling effect*	*Effluent recycle*	*Gas solid separation device*	*Carrier packing*	*Loading rate (kg COD/ m^3-d)*	*HRT (d)*
CSTR	–	Not present	Not required	Not required	Not essential	0.25–3	10–60
Contact	–	Non-existent	Not required	Not required	Not essential	0.25–4	12–15
UASB	4–16	Low	Not required	Essential	Not essential	10–30	0.5–7
Anaerobic filter	3–4	High	Not required	Beneficial	Essential	1–40	0.5–12
AAFEB	3–4	Less	Required	Not required	Essential	1–50	0.2–5
AFB	3–4	Non-existent	Required	Beneficial	Essential	1–100	0.2–5

Source: Stronach et al. (1986); Kaul and Nandy (1997)

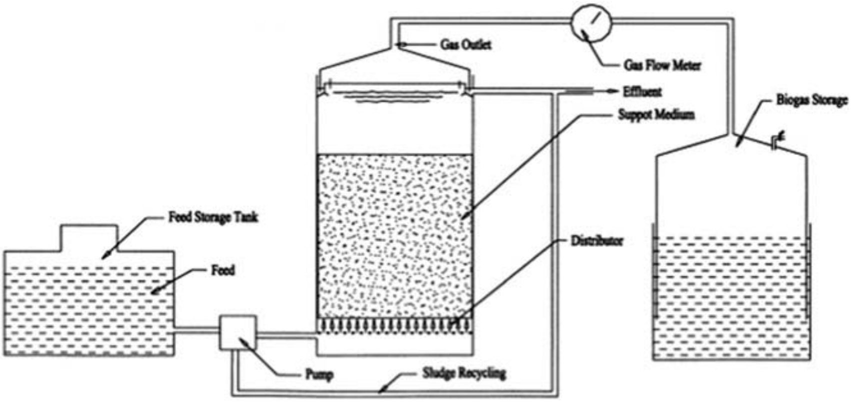

Figure 6.3. Schematic of a fixed film anaerobic reactor

(Droste and Frost 1985). The reactors can redeem quite rapidly later after an interval of starvation (van den Berg et al. 1985). The primary limitation of this design is that the reactor quantity is comparatively high compared to other high rate processes owing to the size busy by the media. Further confinement is clogging of the reactor.

UASB Reactor. An UASB reactor (Figure 6.4) primarily consists of a gas-solids separator (to withhold the anaerobic waste interior the reactor), an influent distribution system, and an effluent collection system. Effluent recycle (to fluidize the sludge bed) is not necessary as sufficient contact between wastewater and

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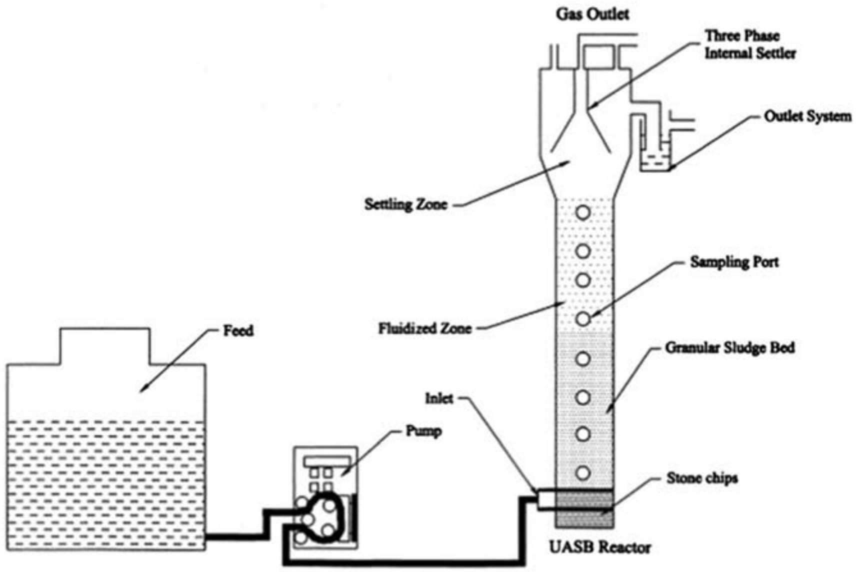

Figure 6.4. Schematic of an UASB reactor

sludge is guaranteed even at low organic loads with the influent distribution system (Lettinga 1982). Furthermore, a noticeably superior loading rate can be accommodated in the granular portion of UASB reactors as compared to flocculent sludge foundation reactors.

UASB technology has been extensively employed for effluents from industries such as distilleries, food processing, tanneries and urban wastewater. A higher quantity of biomass is retained in the reactor by achieving higher mean cell residence time (MCRT) thereby achieving highly cost-efficient designs. An important account is that the technology has relatively less investments compared to an anaerobic filter or a fluidized-bed reactor. Long start-up period along with the requirement for a sufficient amount of granular seed sludge for a faster startup is a notable disadvantage of this system. Also, high sludge wash-out during the start-up process is likely, and the reactor needs skilled operation.

Hybrid UASB Reactor. A modified version of the UASB reactor incorporates an anaerobic filter to make up one-third of the reactor volume. The hybrid UASB has been successful in treating a wide variety of industrial wastewaters. Elmitwalli et al. (1999) compared the performances of a hybrid UASB-filter and a classical UASB reactor at 13°C. The hybrid UASB-filter reactor reached 64% COD removal, a 4% better removal than the classical UASB. A better colloidal fraction removal was attributed to the attached biomass on the filter. The performance of an UASB reactor and an anaerobic hybrid reactor (AHR) was investigated for the treatment of simulated coal wastewater containing toxic phenolics at different hydraulic retention times (0.75–0.33 d) (Ramakrishnan and Gupta 2008). Energy economic estimate shows that for a coal gasification

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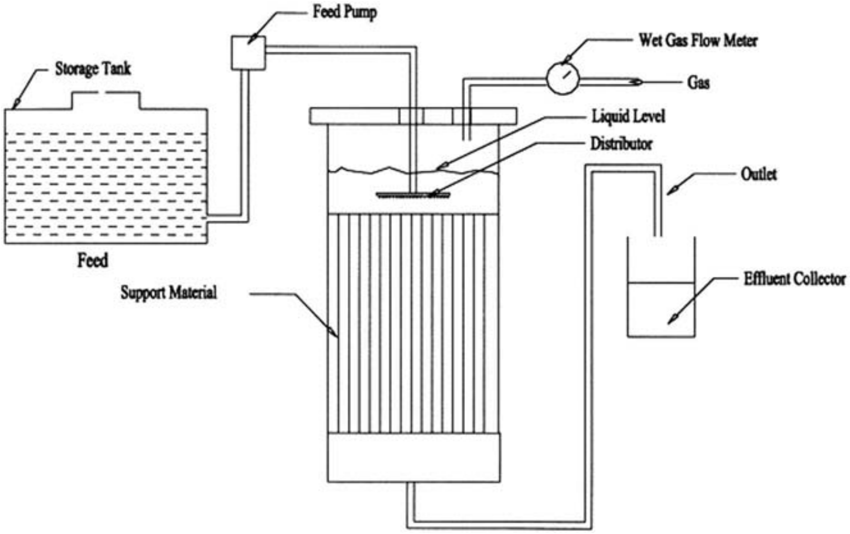

Figure 6.5. Schematic of a fluidized-bed reactor

plant of 50 KLD capacity, AHR can result in an additional COD reduction of 1700 kg and produce a further amount of 30.1 mol of methane per day. Using AHR technology would save 12,159 MJ/d energy compared with the UASB reactor (Ramakrishnan and Surampalli, 2012).

Anaerobic Fluidized-bed Reactor. Anaerobic fluidized bed reactors (Figure 6.5) employ media for bacterial adhesion and development. They are kept in the fluidized state by drag forces exerted by the upflowing wastewater. Different materials (i.e. sand, silica, activated carbon and plastic rings) are used as support for adhesion to facilitate bacterial growth. Under the fluidized state, the media provide a large surface area for biofilm growth and attachment, and thus, enable the attainment of higher reactor biomass and greater system efficiency and stability. This provides higher resistance to inhibition as well as higher organic load attainment. Fluidized bed technology is more effective than anaerobic filter technology as it favors the transport of microbial cells from the bulk to the surface and thus enhances the contact between the microorganisms and the substrate (Peres et al. 1998). In addition, it may eliminate bed clogging whilst provide a low hydraulic head loss, better hydraulic circulation (Collivingnarelli et al. 1991) and a greater surface area per unit of reactor volume. Finally, the capital cost is lower due to the reduction in reactor volumes. However, the recycling of effluent is necessary to achieve bed expansion as in the case of expanded bed reactor. In the expanded bed anaerobic digesters, microorganisms are attached to an inert support medium such as sand, gravel or plastics as in fluidized bed reactor. However, the diameter of the particles is slightly bigger as compared to that used in fluidized beds. The principle used for the expansion is also similar to that for the fluidized bed, i.e. by a high up-flow velocity and recycling.

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So far anaerobic treatment has been successfully employed in many countries (e.g., Colombia, Brazil, India and China) in order to replace the costly activated sludge processes or diminishing the required pond areas. Various cities in Brazil have employed decentralized treatment systems for poor, suburban districts. A wide application range from a subtle to an enormous scale is the advantage of anaerobic treatment technology. This makes it a sustainable option for a growing community.

Performance and Removal of Pollutants. The performance of anaerobic digestion processes is affected by different parameters. As shown in Table 6.6, these parameters are pH, ammonia, VFA/alkalinity ratio, C/N ratio, nutrient, retention time and mixing (Pilli et al. 2014). Increases in ammonia concentration, VFA/alkalinity, C/N ratio, nutrient concentration, mixing and pH will inhibit the growth of methanogens, and thus, decrease the methane production as the concentrations or levels of the parameters are directly related to methanogenic activity.

High-rate anaerobic digesters can handle wastes at a high organic loading rate of ~24 kg COD/m^3 day and high upflow velocity of 2–3 m/h at a low hydraulic retention time (Lettinga 1995). An improvement in the efficiency of anaerobic digestion can be brought about by either suitably modifying the existing digester design or by incorporating advanced techniques. Thus, a plug flow reactor or UASB reactor is superior to the conventional processes due to low concentrations of volatile fatty acids (VFAs) in the effluent, a high degree of sludge retention and stable reactor performance (Van Lier et al. 1994). Another common problem encountered in the industrial anaerobic plants is biomass washout. This can be addressed, for instance, by the use of membranes coupled with the anaerobic digester for biomass retention (Ross and Strogwald 1994).

Current Issues Related to Anaerobic Digestion. All the current issues related to anaerobic digestion are originated from using anaerobic digestion to treat different feedstocks (e.g., WW, biosolids, MSW, WAB) for energy recovery or production of value-added products. For example, it is not fully understood how to design, operate, and optimize different anaerobic digesters according to different feedstock (Table 6.7). Currently, there are still major gaps to be filled, especially due to its "not in sight and not in mind" phenomenon. To manage solid and aqueous wastes and to convert them into a material resource, considerable efforts still are needed. Some of the major current issues are as follows:

- How to enhance pretreatment of different feedstock for anaerobic digestion;
- How to enhance the biogas generation of the different waste materials;
- How to enhance the production of value-added products from different waste materials; and
- How to efficiently collect/separate the biogases for the energy generation and value-added products from anaerobic digesters.

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Table 6.6. Important parameters that affect AD processes

Parameters	*Conc.*	*Effect on AD or co-digestion*
Ammonia	4051–5737 (mg NH_4-N/L)	At this concentration methanogens will not sustain, only *Methanosarcina barkeri, Methanobacterium thermoautotrophicum*, and *Methanobacterium formicicum* can sustain at 10 g NH_3/L. It will change in the intracellular pH, increases maintenance energy requirement, and inhibition of a particular enzyme reaction. The ammonia concentration less than 200 mg/L will enhance the AD process. Total ammonia (free ammonia plus ammonium) concentrations of 1.5–3.0 g-N/L at pH 7.4 and above will cause inhibition but at mesophilic temperature if ammonia is above 3.0 g-N/L, will cause inhibition at all pH levels.
pH	6.5 to 7.2	The hydrolysis and acidogenesis will occur at low pH 5.3 to 6.5. If the pH is less than 6.5 which will result in the toxicity to methanogens and if the pH is greater than 7.5 the ammonia concentration will increase and inhibit the methane production (ammonia toxicity). Methanogenic bacteria are extremely sensitive to pH with the optimum between 6.5 and 7.2.
Temperature	30–37 °C (mesophilic) 49–57 °C (thermophilic)	Growth rates of microbes tend to increase with temperature, within the temperature tolerances of the microorganisms. Too high temperature, however, will cause the metabolic rate to decline due to degradation (denaturing) of enzymes. Waste with a high concentration of ammonia is inhibitory and less stable at thermophilic than at mesophilic temperature during AD. Mesophilic digestion is most commonly employed with the majority of installations operating at ~35°C, and thermophilic digestion has been used on a limited basis.
Alkalinity & VFAs/HCO_3 ratio	$HCO_3^-/VFA = 1.4:1$	Alkalinity is essential for pH control. Alkalinity serves as a buffer that prevents a rapid change in pH. The VFAs produced during AD tend to reduce the pH. A molar ratio of at least 1.4:1 of bicarbonate/VFA should be maintained for a stable and well buffered digestion process. Methane production will be minimised.

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C/N ratio	20–35	The C/N ratio of 20–30 will provide sufficient nitrogen for the AD process. At C/N ratio higher than 30 causes slower microorganisms multiplication and structural material metabolism of microorganisms. This will result in lower substrate degradation. For fruit and vegetable waste, C/N ratio 22 to 25 is the optimum. Co-digestion of algal sludge and waste paper the optimum C/N ratio is 20–25. During the hydrolysis and acidogenesis the required C:N:P:S ratio is 500:15:5:3 and for methogenesis 600:15:5:3 is required.
Nutrients (mg/g of acetate)	Fe = 0.002; Co = 0.004; Ni = 0.003; Zi = 0.02	There is no special nutrient required during the hydrolysis and acidogensis. Nutrient levels should be at least in excess of the optimum concentrations needed by the methanogenic bacteria, since these are the most severely inhibited by slight nutrient deficiencies. For growth of methanogens bacteria the specific metals required are nickel, cobalt, and molybdenum and iron.
Retention time	3–55 days	For solid waste the solids retention time can vary from 3–55 days it varies with types of the organic material. For dry digester it can vary from 14 to 30 days and it can be as low as 3 days. Solid waste from poultry and slaughter house required 50–100 days retention time. A decrease in the SRT decreases the extent of the reactions and vice versa. Each time sludge is withdrawn a fraction of the bacterial population is removed thus implying that the cell growth must at least compensate the cell removal to ensure steady state and avoid process failure.
Mixing	2 min /hr	Proper mixing of waste is one of the most important operating parameters of the AD in achieving optimum performance. It helps in preventing stratification of waste, improves the contact between the micro-organisms and substrate, keeps solid particles in suspension, temperature gradients within the digester, releasing the biogas from the digester content and improves the bacterial population's ability to obtain nutrients.

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Table 6.7. Classification of feedstock and types of digester used

	Feedstock		
Parameters	*Low solids*	*Medium solids*	*High solids*
Classified	<3% total solids by weight, low suspended solids, readily mixed	3 to 12% total solids by weight, slurry phase but can be mixed with traditional methods	Up to 25% total solids by weight, solid processing system requires sophisticated mixing methods.
Feed stocks	Secondary WWT, spent beverages & expired products, hydraulic flush manure systems (swine), commercial WW, whey and cheese wastes.	Dairy manure, fats/oils/grease (FOG), paunch manure, "Scraped" swine manure, industrial DAF sludge, used restaurant cooking oil	Organic fraction of MSW, agriculture residues, food processing waste, food residuals, clarifier sludge (pulp/paper), green and yard waste
Anaerobic digesters used	Completely mixed reactors, filter reactors, sludge blanket reactors, fixed-film packed bed reactors.	Plug flow reactors, CSTR slurry reactors, slurry-loop reactors, acid-phased or temperature phased, contact reactors.	Dry continuous (plug flow, complete mix), dry batch with permeate recycle, sequencing batch reactors.

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Recently, anaerobic digestion facilities have been recognized by the United Nations Development Programme (UNDP) as one of the most useful decentralized sources of energy supply, as they are less capital intensive than large power plants. The energy recovery from anaerobic processes could take the following alternate courses (Banerji et al. 2010):

- **Alternative 1.** Conversion of wastewater organic matter to mostly methane. The energy recovery from methane can have the following options: 1a) methane combusted in an internal combustion engine to produce heat and electricity (cogeneration engines); 1b) methane combusted in a micro-turbine to produce heat and electricity; and 1c) methane after processing used in a fuel cell (FC) system to produce electricity directly.

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- **Alternative 2.** Conversion of wastewater organic compounds to hydrogen using selective environmental conditions, which can be used in a fuel cell to produce electricity directly.
- **Alternative 3.** The wastewater after pretreatment can be used in a microbial fuel cell (MFC) to produce electricity directly.

The methane production from anaerobic processes can be combusted in internal combustion engines or microturbines or fuel cells (FCs) to cogenerate heat and electricity. In many instances, a major portion of energy needs for the wastewater treatment plant can be satisfied from the cogeneration process. Microturbines have been successfully tried at several locations to produce energy from APGs. However, FCs for energy production from APGs are still in the experimental stage and are presently not cost-effective as compared to other options.

Microbial processes to form hydrogen directly from wastewater organic matter are successful but are still in the developmental stage. More applied research needs to be conducted to determine the performance under differing operating conditions with different types of wastewater. The low environmental impact of hydrogen combustion is a significant advantage for the system. Some wastewater, rich in carbohydrates (food processing), have successfully produced hydrogen in dark fermentation reactions, but the rates are slow. The wastewater effluent after the fermentation process still has a high organic content (mainly organic acids). A photo-fermentation process succeeding the dark fermentation process may increase the hydrogen yield. The hydrogen produced can be combusted or used in an FC to produce electricity. Perhaps in the future, wastewater treatment technology will use hydrogen production as an essential goal followed by conversion of the produced hydrogen to electricity using FCs.

The use of microbial FC (MFC) is a promising technology for treating wastewater to produce electricity, but it is still in its infancy and needs more research and development. It can be used in conjunction with an anaerobic treatment process for some industrial wastewater to cogenerate energy and treat the wastewater. It appears that lot of research work needs to be done to manage industrial high strength wastewater in a sustainable way and to make the process energy sufficient.

Case Studies on Anaerobic Digestion Treatment Processes. While this chapter focused on using anaerobic digestion for WWT, the current trend of using anaerobic digestion for municipal solid waste (MSW) treatment should not be ignored. In fact, feasibility of using anaerobic digestion for garbage treatment was studied as early as the 1930s, with different digesters (e.g., bench-scale batch digester, standard Imhoff digester, large continuous stirred-tank digesters or even medium-scale two-stage anaerobic digesters) (CIWMB 2008). Pilot-scale tests were conducted between the 1970s and 1990s in the U.S. and Europe to experiment the feasibility of using anaerobic processes for solid waste treatment, particularly to i) reduce the amount of material being landfilled, ii) stabilize organic material before disposal in order to reduce future environmental impacts

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from air and water emissions, and iii) recover energy (CIWMB 2008). Today, AD and aerobic composting of MSW have been well established in Europe, largely due to waste and energy policies in Europe (e.g., The Landfill Directive). By the end of 2006, there were some 124 anaerobic digester plants with capacity greater than 3,000 MT/y (3,300 tons/y) treating feedstock composed of at least 10% MSW (CIWMB 2008). Therefore, as case studies, we introduced several different anaerobic digestion treatment processes as follows.

Wassa Process. The main reactor in the Waasa Process is divided into various zones in a simple way. The first zone is made up of a pre-chamber inside the main reactor. The mixing in the reactor is by pneumatic stirring, where biogas is pumped through the base of the reactor. A small part of the digestate is mixed into the recycled to the influent to speed up the process by inoculation (Angelidaki et al. 2003). The Waasa plant in the city of Vaasa, Finland has tested the following types of wastes since its start-up in 1989: mechanically or source-separated municipal solid wastes (MSW), sewage sludge, slaughterhouse waste, fish waste, and animal manure. At the Waasa plant, both mesophilic and thermophilic treatment methods are operated in two parallel reactors with a total solids content of 10–15%. Waasa process is also in operation in Kil, Sweden and outside Tokyo, Japan today. Another plant in Groningen, the Netherlands is under construction.

The Dranco Process. The Dranco (Dry Anaerobic Composting) process is a true dry-process for the treatment of organic fraction of MSW (Figure 6.6). This process requires high solids content in the reactor in order to reach an optimal performance. Therefore, it is highly recommended to mix non-recyclable paper or garden waste to enhance the solids content into the MSW in order to achieve high total solids content. The Dranco process is a thermophilic process. Treatment occurs after the waste is pretreated, screened and mixed with recirculating material from the reactor. About three-fourths of the reactor content is recyclable. Mixing of the waste with a large amount of digested material provides an environment for a higher degree of inoculation of incoming material. The biomass paste is conveyed using piston pumps. The reactor is a downward plug-flow type reactor. No significant mixing occurs in this reactor. Today, there are several DRANCO plants in operation, such as the one in Brecht, Belgium (12,000 ton/year);

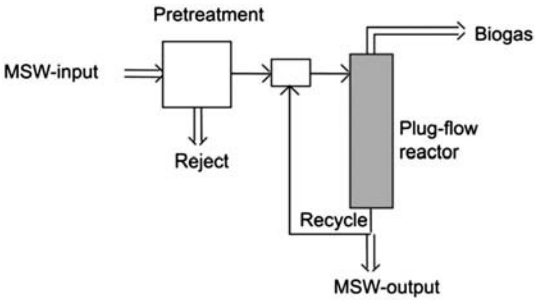

Figure 6.6. Schematic of a Dranco process

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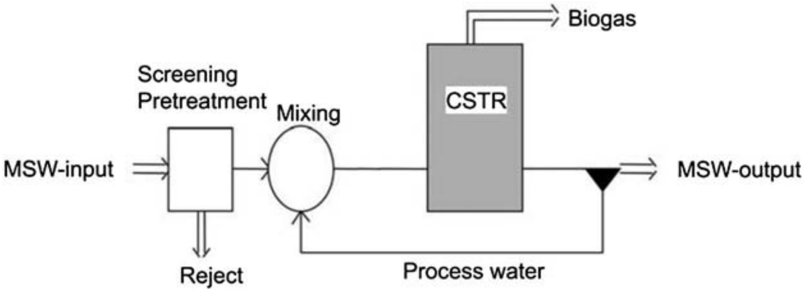

Figure 6.7. Schematic of a Valorga process

Salzburg, Austria (20,000 ton/year); Bassum, Germany (13,500 ton/year), and Kaiserslautern, Germany (20,000 ton/year) (Angelidaki et al. 2003).

The Valorga Process. The Valorga process was developed in France and is a semi-dry process (Figure 6.7). It is a mesophilic process and treatment occurs after the pretreatment of the waste by mixing with recycled process water. Process water is obtained from the separation of reactor effluent by centrifugation, filtration or other types of separation. The influent is pumped into the reactor after mixing with the process water. It is a fully mixed reactor type. Mixing occurs by pneumatic stirring of the biogas produced by the process and recycled to the reactor. Only a small amount of water is recirculated, and a high total solids content is maintained in the reactor. The Valorga process is a relatively widely used process. There are several full-scale plants worldwide, such as in Amiens, France (85,000 ton/year); Grenoble, France (16,000 ton/year); Tilburg, Netherlands (52,000 ton/year); Papeete, Tahiti (90,000 tons/year); and Tamara in French Polynesia (92,000 tons/year) (Angelidaki et al. 2003).

The Kompogas Process. The Kompogas process is a dry process developed in Switzerland. The process operates in the thermophilic range with a hydraulic retention time of ~15 days. The reactor is a horizontal cylinder and the flow through the reactor is plug flow. In the reactor, a stirrer provides some mixing of the waste. Recirculation of a part of the effluent to the incoming substrate ensures inoculation (Angelidaki et al. 2003).

6.3.4 Geo-purification Systems

Types and Applications. Table 6.1 shows the types of geo-purification systems, which depend on soil/aquifer/riverbank (called SAT hereafter) for WWT. The SAT systems are different from rapid and slow-rate land treatment systems because in a SAT system, partially treated sewage effluent artificially recharges the aquifers and is then withdrawn for future use, while land treatment systems usually only focus on WWT without more consideration of WW reuse in the future. The SAT system is a reliable, low-cost and easily operated system for water storage and reuse. Recharge through unsaturated soil layers provides additional purification for the effluent before it is mixed with natural ground water. This treated effluent becomes a considerable resource for improved ground water

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resource. The Gaza Coastal Aquifer management program incorporates treated effluent to the influent to strengthen the groundwater both in terms of quantity and quality (Jhansi and Mishra 2013). The recharged effluent has the potential to eliminate and reduce the concentration of nitrates in the aquifer. This treatment has become a valuable asset in water scarce areas such as in the Middle East and parts of Southern Africa, where wastewater after appropriate treatment is a valuable resource that becomes commercially realistic alternative for groundwater recharge, agriculture and urban use. The SAT can be used efficiently as a WWT plant. It should be recognized as a modern approach to the old method of WWT and reuse. Wherever feasible, SAT should be adopted and regarded as the core of the WWT plant and reuse scheme to be complemented when necessary by suitable pretreatment and post-treatment.

The most well-known SAT systems have been thoroughly investigated since the late 1960s include the Flushing Meadows and the 23rd Avenue projects in Phoenix, Arizona (Bouwer et al. 1980; Bouwer et al. 1983). In these systems, the recharge basins are located in two parallel rows along the river bank, and the recovery wells are drilled in the riverbed. Observation wells are at the outer side of the recharge basin, permitting the monitoring of the recharge basins that are not rising above the general groundwater level (Figure 6.8, top left).

In other rapid infiltration SAT systems, where the groundwater table is shallow, the effluent is collected by underdrains (Carlson et al. 1982). Under this

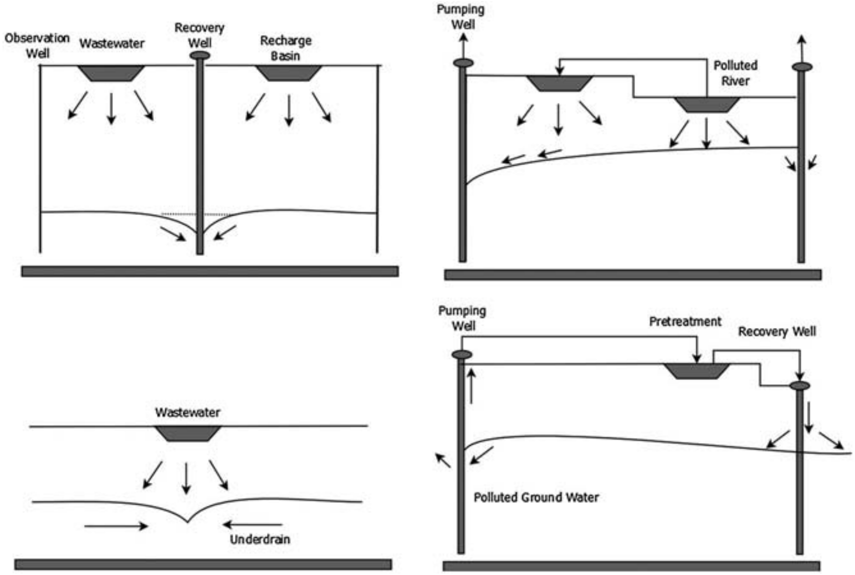

Figure 6.8. Other SAT Systems. Top Left: Rapid Infiltration Wells (Phoenix, Arizona), Bottom left: Rapid infiltration Underdrains (Boulder, Colorado); Top right: River bank Filtration (Germany, Holland); Bottom right: Treatment of polluted ground water (Germany)

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situation, the depth of the unsaturated zone and the thickness of the groundwater layer for the treatment process are much smaller (Figure 6.8, bottom left). In Germany and Holland, the water source for many cities is polluted river water after bank filtration–a concept similar to that of SAT systems (Sontheimer 1980). Advanced water treatment is usually provided after bank filtration (Figure 6.8, top right).

In Germany, the SAT systems are used to remove pollutants from groundwater, especially for the removal of organics from groundwater contaminated by oil spills as well as for iron and manganese removal (Figure 6.8, bottom right). Pretreatment methods applied to enhance the purification in the soil-aquifer treatment system include (1) ozonation for oxidation of iron and manganese, and (2) the addition of organic carbon for denitrification.

Performance and Removal of Pollutants. SAT systems are efficient for pathogen removal whilst are not highly technical to operate. SAT treatment has capacity to remove >99.5% of suspended soilds, 98.5% of phosphorus, >67% cadmium, >70% chromium, >72% copper, >67% Molybdenum, 74% Nickel and >75% Selenium. A majority of the cost associated with SAT system is diverted towards the pumping of water from recovery wells, which is approximately \$20–\$50 USD per cubic meter. SAT typically removes all BOD, TSS and pathogenic organisms from the waste, and the wastewater is treated to a standard that would permit unrestricted irrigation. The most important advantage associated with the SAT system is that it breaks the pipe-to-pipe connection of directly reusing the treated wastewater from the treatment plant (Jhansi and Mishra 2013).

Current Issues Related to SAT Technologies. The major problem with the implementation of SAT technologies is the high cost of wastewater treatment and management associated with the SAT projects. The requirement of a large area for the infiltration basin for surface soil-aquifer treatment adds to the cost of the project. Reclaimed water needs to be sufficiently pre-treated. Insufficient pretreatment will lead to the discharge of nutrient and micropollutants in natural water bodies and in drinking water. The budget also needs to be allocated for periodic cleaning of the top soil surface of the SAT plant as filtration of suspended and colloidal matter in SAT takes place in the top soil layer similar to slow sand filters. Clogging is a problem that affects the treatment capacity of these systems. To achieve maximum efficiency even with the most state-of-the-art technology, proper institutional support and suitably enforced legislations are required. Though financial funding can be organized with the support of international organizations, local conditions need to be favorable for the successful implementation of any SAT technology. Failure to take into consideration of the local conditions of the targeted community would result in a failed project. It is often perceived as the lack of technical knowledge and financial resources. The capacity and efficiency of SAT to remove pollutants from the effluent is governed by the maintenance of the conditions necessary for the development and survival of bacterial populations. Biological processes (e.g., breakdown of organic substances, nitrification and denitrification) occur both in the unsaturated zone and in the aquifer, while recarbonation of high-pH effluent by bacterial activity occurs

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mainly in the upper soil, but can break down if optimal operating conditions do not persist. Also, there is a long term negative impact that might occur in groundwater due to the discharge of pollutants to aquifers. While millions of dollars are spent on construction, few dollars are allocated for gathering reliable design and operation data. Though, replication of successful projects is possible, each system should be adjusted to the local environmental conditions, especially the climate and hydrology. Choice of SAT without pre-thought on environmental and climatic conditions would lead to the alteration of soil and groundwater hydrological properties (Surampalli et al. 2013).

Case Studies. Two case studies are presented here to illustrate the technologies.

SAT System in Dan Region Project, Israel. Data gathered during the 7 years of operation of the Dan Region Project provide information on the SAT system adopted based on the actual field experience (Idelovitch 1980). The partially treated effluent percolates and travels through the unsaturated soil zone until it reaches the ground water and moves in the radial direction in the aquifer until it reaches the recovery wells that are specially designed to pump the recharged water supply (Figure 6.9).

The recharged effluent gradually displaces the natural groundwater toward the recovery wells. Thus, at the initial stage of operation, the wells pump native groundwater; later they pump a mixture of native groundwater toward and increasing amounts of recharged water. At the steady state, the wells pump mostly recharged water from the inner basin where groundwater flow gradients are higher and small amounts of native groundwater from the outer basin. The reclaimed water can be traced and monitored by means of observation wells between the recharge basins and the recovery wells, and is usually of high quality.

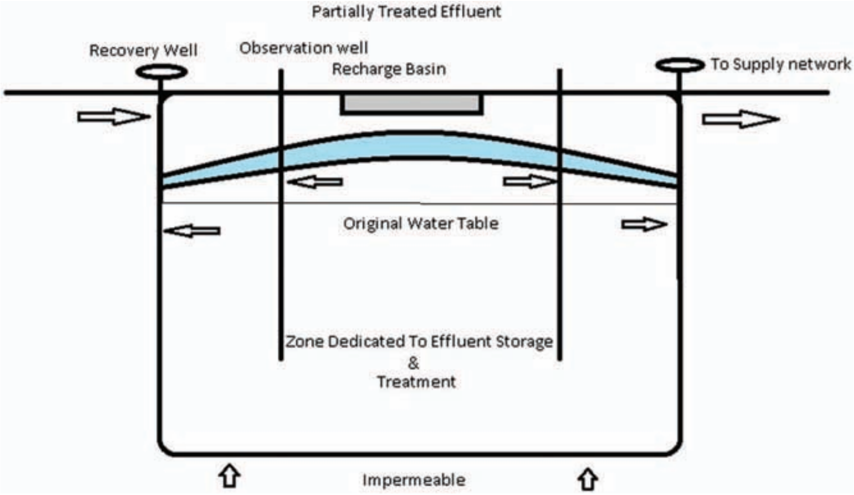

Figure 6.9. SAT System in the Dan Region Project, Israel

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Hence it is most appropriate for industrial uses, unrestricted agricultural uses and non-potable municipal use (lawn irrigation and toilet flushing) and recreational use. The reclaimed water could also be used as a raw source for drinking water supply (Idelovitch 1980). The effluent recharge must be done with spreading basins in order to take advantage of the purification capability of both the unsaturated zone and the aquifer. Continuous flooding of recharge basins should be avoided to obtain steady infiltration rates. Otherwise, the infiltration rates would reach low levels such that the operation of the system at the same capacity would require increasing amounts of land. Although significant purification of the effluent takes place during vertical flow through the upper soil layer and the whole unsaturated zone, it is important to allow the recharged water to flow horizontally in the aquifer for additional purification and for regaining aerobic properties in the areas where anoxic conditions prevail below the recharge basins.

Land Treatment Systems in Muskegon, MI, USA. The Muskegon County wastewater land treatment system is one of the largest land treatment systems in the U.S and has been operated since 1974. The system consists of 5200 acres slow rate SATs and 150 acres rapid infiltration SATs (see Table 6.8). The wastewater consists of paper mills (50%), other industrial WW (25%) and domestic WW (25%) with flowrate being about 34 million gallon/d (MGD) in 1974 and 25 MGD in 2003. The pretreatment has two phases: Phase 1 has 2 aeration tanks (each 42 million gallon in volume with an HRT = 1.5 d), and Phase 2 has 2 settling tanks (HRT = 3 d). The system has two storage lagoons (each 850 acres, HRT = 187 d).

Table 6.8. Some parameters of the Muskegon system

Soil types	Rubicon, Roscommon, AuGres, and Granby
Avg. wastewater (WW) flow	Q = 98 410 m^3/d (26 MGD) in 2004 (design capacity = 158 970 m^3/d, 42 MGD)
WW applied in 1974–2001 (cm)	Rubicon soil = 12055; Roscommon = 8666; AuGres = 9601; Granby = not available
P loading (kg/m^2)	Rubicon soil = 0.12; Roscommon = 0.03; AuGres = 0.09; Granby = not available
Crop type corn	Corn, soybean, and alfalfa, rotated yearly in each irrigation field
Irrigation systems	Sprinkler (center pivot), time on/off varies; usually, the sprinkler will rotate one circle per day
WW application rate	Rubicon soil (best) and Roscommon (2nd best)) 2.5 cm/d for ∼180 d; AuGres) 0.8–1.5 cm/d for 180 d; whole site avg. weekly rate = 7.6 cm for ∼180 d
Annual precipitation/ evaporation	Avg. rainfall in 1974–2001 = 85.1 cm; annual evaporation = 76.2 cm

Source: Data from Hu et al. (2005)

After disinfection, the WW is spread via sprinklers, infiltrates into the land (sandy soils), and then collected by perforated pipes at ~6 ft underneath the ground surface. The finished WW is discharged into Lake Michigan via two creeks.

The build-up of phosphorus (P) in soil is a major factor limiting the operating life of a wastewater land treatment system. In 2003–2005, studies were conducted to evaluate 1) the remaining useful life of the land treatment system and 2) the performance of P removal in a long-term operation period. The performance of the system during the operation period of 1973–2001 was evaluated. The records show that the land treatment system has been successful in generating high-quality effluent, with total P and 5-day biochemical oxygen demand (BOD_5) consistently lower than 0.03 mg/L and 5 mg/L, respectively. The fate of P was evaluated by profiling the P distribution in the soil and conducting mass balance on soil adsorption and crop assimilation. Changes in chemical properties, P profiles, and adsorption isotherms in the soils of the system also were determined. While P removal by plant assimilation accounts for less than 25% of total P applied, much of the P have been retained on the top layer of the soil. It was found that the pH in the 15-cm topsoil increased from ~5–6 in 1973 to ~7.4–7.8 in 2003; a large amount of salt (e.g., Ca, Mg) in wastewater was adsorbed by the soil; the soil Al content (either exchangeable or oxalate extractable) decreased, while the oxalate-extractable Fe content remained at the same level. Ca-bound P accounted for $\geq$ 70% of the total P adsorbed in the soil. The soil P adsorption capacity increased and was positively correlated with the concentration of exchangeable Ca in the soil. A higher concentration of exchangeable Ca was found in the 15-cm topsoil, where a higher total organic carbon was present. More P was accumulated in the upper soil than in the deeper soil (Hu et al. 2005). Later, Zhang et al. (2007) did column tests by using soil sampled from Muskegon site to evaluate phosphorus fate and transport in soil. The results indicated that the height of the mass transfer zone, solvent pore velocity, and soil's life expectancy for phosphorus removal increased with depth, while the retained phosphorus per kilogram of soil and the linear adsorption equilibrium coefficient, R, decreased with depth. The results of X-ray diffraction and washout tests indicate that calcium-phosphorus precipitation and/or crystal growth occurred in the columns. Therefore, the adsorption of Ca in wastewater by the soil has extended the life expectancy of the Muskegon land treatment system (Hu et al. 2005; Zhang et al. 2007).

6.4 IMPLEMENTATION STRATEGIES AND FUTURE PERSPECTIVES

Management strategies for sustainable GSNWWTDTS and DWM systems should be site-specific, considering the local social, cultural, environmental and economic conditions. Choice of the "most appropriate technology" for the local conditions is an important management strategy. The technology should be economically affordable, environmentally sustainable and socially acceptable for the local community. Sufficient funds should be available in the community to finance

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Table 6.9. Force analysis for implementation of advanced integrated urban water and wastewater management systems

Advancing forces	*Restraining forces*
Water scarcity	Stove-piped professional thinking
Resource constraints	Institutional constraints
Population growth/aging and extended life span	Existing practices
A myriad of inventions/innovations	Lack of public acceptance
Increased demand/standard of living	Economic evaluation procedures
Global climate change	Efficient communications among planners/politicians/the public
Multi-purpose and functional Unban	Lack of tools for day-to-day multiple criteria decision making
A rapid change in social paradigms*	Differences and unbalance between different countries and regions

*such as networking, flatter organizations, decentralization, conservation, and less authoritarianism
Source: Daigger (2009); NAE (2011)

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the implementation of the system, including the operation and maintenance, as well as additional capital improvement costs, long term repairs, and replacement costs. There should be a comprehensive site evaluation and a detailed research/development plan for the selection of a suitable technology for understanding the receiving environment.

Suitable guidelines need to be developed for the selection of small community wastewater treatment systems, and it needs to facilitate a decision. Centralized management of the decentralized wastewater treatment plants needs to be planned to ensure proper inspection and regular maintenance. Educating the local community by providing them with access to resource and information for decision-making is a crucial step towards the sustainable management of wastewater.

Daigger (2009) analyzed the driving- and restraining- forces for implementation of advanced integrated urban water and wastewater management systems. To implement GSNWWTDTs and DWM, one should consider promoting the driving forces and depressing the restraining forces (Table 6.9), such as:

- Providing thorough analysis of the economics of alternative GSNWWTDTs and DWM systems. Usually, life-cycle assessment of the is desired;
- Addressing institutional barriers, such as overcoming the key barrier of the water management profession;
- Developing new communities and retrofitting the existing communities with higher performing DWM systems and/or GSNWWTDTs–to create more efficient and effective models for demonstration; and

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- Communicating effectively with the public and coupling people with measures that can help individuals to change their behavior concerning water consumption and resource recovery.

It is difficult to predict how our society will be evolving in the future. However, security, economic, environmental, health, and quality of life are essential for evaluating the sustainability of our society. While the optimization of technological systems can have profound biosocial implications, it is more important for our society to shift from the traditional liner "take, make, waste" approach to the more closed-loop water and resource management approach (Daigger 2009). To this end, the future trends are anticipated as follows:

- A more sophisticated toolkit consisting of storm/rain water management, water conservation, water reclamation/reuse, and energy/resource recovery/management will be developed;
- Hybrid modern alternative systems that can incorporate both centralized and decentralized elements to water and resource management systems will be developed;
- Proper approaches to economic analysis and decision making for selecting alternative modern systems and utilizing the toolkit will be developed; and
- More projects will be conducted to demonstrate the practicality, economics, and sustainability of different modern systems.

The knowledge base of environmental problems related to the sustainable wastewater treatment systems need to be strengthened, and solutions for the problems need to be derived from scientific thought and empirical experience of the local conditions. Training programs need to be devised for the municipality employees for the proper operation and maintenance of equipment and facilities including monitoring of wastewater quality. Institutional strengthening and administrative reforms through reduced government involvement and bureaucratic control along with user participation should be in place to ensure the sustainable management of wastewater.

6.5 CONCLUSIONS

There is a demand to make drastic changes in how we manage storm and wastewater utilizing sustainable technologies. DWM promote better watershed management and suited to a wide variety of site conditions. GSNWWTDTs like lagoons and wetlands can be utilized in areas where land is not scarce. For areas of limited land availability, anaerobic reactor technologies could be implemented. For agricultural areas and small communities, SAT technologies can be implemented to treat and utilize treated wastewater (e.g., for irrigation and recreational purposes).

There is a need for consistent, institutional, legislative, economic and social arrangements to apply for sustainable wastewater treatment and management.

Choice of the "most appropriate technology" for the local conditions is imperative, and it should be economically affordable, environmentally sustainable and socially acceptable for the local community. Centralized management of the decentralized wastewater treatment plants needs to be planned to ensure proper inspection and regular maintenance. Also, knowledge of local community needs to be enhanced by providing them with access to resource and information for decision making on environmental planning, including site selection. Also, a comprehensive site evaluation and a detailed research/development plan for the selection of a suitable technology for understanding the receiving environment need to be in place. Usually, life-cycle assessment of the technology and system are encouraged. In addition, the recommendation of new highly performing DWM systems and/or GSNWWTDTs needs to be strengthened i to create more efficient and effective models for demonstration. Moreover, effective communication with the public can help individuals to change their behavior concerning water consumption and resource recovery. Effective programs for wastewater management and reclamation, including education and information programs, laws and standards, wastewater reclamation and reuse programs coupled with public involvement in decision-making, would ensure sustainable urban wastewater management for communities.

6.6 ABBREVIATIONS

AAFEB	Anaerobic Attached Microbial Expanded Bed Reactor
AFB	Anaerobic Fluidized Bed Reactor
AHR	Anaerobic Hybrid Reactor
ATS	Aquatic Treatment Systems
BOD	Biochemical oxygen Demand
BUD	Bellevue Utilities Department
COD	Chemical Oxygen Demand
CSTR	Continuous Stirred Tank Reactor
CW	Constructed Wetlands
CWA	Clean Water Act
CWRP	Comprehensive Water Reuse Program
DWM	Decentralized wastewater management
FC	Fuel Cell
GSNWWTDT	Green and Sustainable Wastewater Treatment and Disposal Technologies
GVS & DD	Greater Vancouver Sewerage & Drainage District
HF	Hybrid Filter
HRT	Hydraulic Retention Time
LID	Low Impact Development
MCR	TMean cell residence time
MGD	Million Gallon/Day

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MFC	Microbial Fuel Cell
MSW	Municipal Solid Waste
MS4	Municipal Separate Storm Sewer System
MT	Matric Ton
NPS	Non-point Source
NYCDCP	New York City DUSEPArtment of City Planning
NWs	Natural Wetlands
PVC	Polyvinyl chloride
SAT	Soil Aquifer Treatment
SFCW	Subsurface-flow Constructed Wetland
SFWMD	South Florida Water Management District
SWRCB	California Water Resources Council
TN	Total Nitrogen
TSS	Total Suspended Solids
UASB	Up–flow Anaerobic Sludge Blanket
US USEPA	United States Environmental Protection Agency
VFA	Volatile Fatty Acid
VSS	Volatile Suspended Solids
WAB	Waste Agricultural Biomass
WH	Water Hyacinth
WSUD	Water Sensitive Urban Design
WSVFCW	Wavy subsurface- and vertical-flow Constructed Wetland
WW	Wastewater
WWT	Wastewater Treatment

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CHAPTER 7

Green Technologies for Industrial Wastewater Treatment: Sustainable Attributes and Prospects of Anaerobic Granulation

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7.1 INTRODUCTION

As the world's population has reached over seven billion people, sustainable wastewater treatment is critical to ensuring clean water and energy availability for future generations. Anaerobic granular sludge technology is now perceived to be the most promising and favorable wastewater treatment process as it fulfills the desired criteria for future technology in sustainable green development. Achieving an effective prevention and control of pollution requires an integrated management of emissions to air, water and land, as well as the efficient use of energy and raw materials. Anaerobic granular sludge technology appears to meet these criteria well. The main reason is that treatment through anaerobic granular sludge is an efficient natural process in which a variety of microbial species work together to convert organic wastes into an excellent source of energy in the form of methane gas. Methane can be used to heat the waste stream for a higher rate of stabilization or to supplement in-plant power requirements. Pathogenic microorganisms are reduced, and the objectionable organic matter is eliminated through anaerobic decomposition. The nutrient-rich digestate after anaerobic digestion can be used as fertilizer. The net result is the production of biosolids that are also widely used

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as soil conditioner. Additionally, with industrial wastewater treatment, the amount of biosolids produced is far less than that with aerobic treatment while the biosolids are already anaerobically stabilized for the final land application. Moreover, nutrient requirements for anaerobic treatment are much lower than that of aerobic treatment.

Biosolids agglomeration in which microbial cells are organized into dense and compact granules has been extensively investigated in biological wastewater treatment. In light of the development in biogranulation work, advanced anaerobic processes integrating granular biomass as predominant waste degraders appear to be desirable technologies for industrial wastewater treatment. As a result of increasing acceptance towards the anaerobic granular processes, a growing interest in the technology has resulted in a remarkable increase of full-scale plants installed worldwide over the last three decades.

An anaerobic granule is composed of diverse bacterial populations striving upon a microbial syntrophic relationship. Complete degradation of industrial xenobiotic compounds involves complex interactions between the syntrophic species thrived within the granule matrix. There are likelihoods for microorganisms to form granules in the process of microbial evolution (Fitzpatrick et al. 1989). In a microbiological sense, granulation is able to support heterogeneous ordered populations of syntrophic communities in the form of a multi-cellular association under favorable physiological conditions. While syntrophic interactions between adjacent organisms can facilitate genetic exchange, granulation may protect cells from predators such as anaerobic ciliates. In consideration of thermodynamics, the diffusion distance for fermentation intermediates is minimized within closely structured granules, which is a very efficient means to conserve energy available in the degradation system. Moreover, for microbes to thrive under adverse environment that is not favorable for microbial growth (e.g. extreme pH and/or toxicity), a more favorable micro-environment can be maintained within the granules so that metabolism can be sustained.

In view of the current granulation R&D, processes based on anaerobic granular sludge are emerging as the most promising technologies. Dense and sturdy granules lead to rapid settling of biomass, thereby enhancing separation of purified liquid from the mixed liquor in granular sludge reactors (Noyola and Mereno 1994; Batstone and Keller 2001). Because of the effective retention of fast settling granules leading to high biomass inventory and rich microbial diversity, these reactor systems provide efficient and stable plant operation with remarkable performance. Two most popular granular reactor systems, namely the upflow anaerobic sludge blanket (UASB) and the expanded granular sludge blanket (EGSB) technologies, have respectively acquired predominant shares of full-scale industrial applications. They have been used in treating high organic strength industrial wastewaters from brewery, food processing, distillations and fermentation, sugar processing, chemical industry, and so forth (Frankin 2001).

A major problem associated with granular sludge systems is the prolonged startup required for successful development of granules. In cases where inoculation is seeded with flocculent sludge, it usually takes several months or longer

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before the sludge develops into granules. In order to reduce the long startup of granular sludge systems, technologies for enhanced and rapid production of anaerobic granules are desirable. This chapter reviews current research work encompassing salient features, which include merits and limitations of anaerobic granulation. In comparison with aerobic processes, outstanding advantages of treatment by anaerobic granular sludge systems are discussed. Energy production and assessment associated with anaerobic granulation are delineated in the perspective of the water-energy nexus. Lastly, anaerobic reactor systems integrating granular sludge for waste degradation and the prospects of anaerobic granulation are also outlined.

7.2 MERITS AND LIMITATIONS OF ANAEROBIC GRANULATION

Biosolids agglomeration in which microbial cells are structured into dense and rapid settling granular biomass has been extensively studied due to its practical significance in biological wastewater treatment. As shown in Figure 7.1, an anaerobic granule is consisting of closely aggregated microbial cells thriving within the granule matrix. This enhances complex interactions between the syntrophic bacterial species leading to efficient degradation of pollutants. This section discusses principal advantages and limitations of anaerobic granular sludge and its comparison with aerobic and/or conventional anaerobic treatment.

It was calculated that the distance between acetogenic and hydrogenotrophic microorganisms ranged between 5 and 11 μm at a hydrogen turnover rate of

Figure 7.1. Anaerobic granules developed in a full-scale bioreactor treating chemical wastewater

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320 $\sec^{-1}$ (McCarty and Smith 1986). Subsequently, maximum distances of 4, 9.3 and 660 μm for propionate, butyrate and ethanol turnover, respectively were deliberated (Stams et al. 1989). These results indicated that it is favorable for the microorganisms to be very close to each other in order to achieve high substrate conversion rate. On the other hand, it was found that syntrophic relations in flocs or granules are not only of significance for interspecies hydrogen transfer, but also for interspecies transfer of formate (Thiele and Zeikus 1988).

Significant limitations of non-granular anaerobic processes encompass a better understanding of refractory contaminant degradation and process reliability, as loose and fluffy biomass is susceptible to environmental factors such as pH, temperatures, changing organic loadings and toxicity in the feed. Successful cultivation and retention of biomass in a bioreactor appeared to be the key to developing a more reliable treatment. Such operational requirements are achieved via cell immobilization or granulation, and proper attention to satisfying trace metal requirements for granule formation.

There are several advantages of granules over other forms of biomass growth (Wiegant 1988; Fitzpatrick et al. 1989), which are summarized in Table 7.1:

In granular sludge reactors, development of cells into larger and dense granules results in rapid settling of the biomass thus improving separation of treated effluent from mixed liquor (Noyola and Mereno 1994; Batstone and Keller 2001). As good liquid-solid separation leads to better effluent quality, it also increases biomass concentration and enriches microbial diversity in the system. In applications of cell-immobilization technology, anaerobic granular sludge reactor systems appear to be the most promising in terms of treatment and plant operation. These reactor systems provide efficient waste degradation and stable operational performance, attributable to its effective retention of the biomass in the form of granules. Two popular granular reactor systems, namely the sludge-based upflow anaerobic sludge blanket (UASB) and expanded granular sludge

Table 7.1. Advantages of granules over other forms of biomass growth

1. Development of heterogeneous ordered populations of syntrophic microorganisms in the form of multi-cellular association under favorable physiological conditions
2. Symbiosis interactions between adjacent organisms and facilitation of microbial genetic exchange
3. Increase in nutrient uptake to support microbial growth within granules
4. Protection of cells from predators such as anaerobic ciliates
5. Minimization of diffusion distance for fermentation intermediates in enhancing syntrophic biochemical reaction within a granule.
6. Maintaining a favorable micro-environment within the granules to sustain metabolism under adverse conditions for growth such as extreme pH and toxic feed

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blanket (EGSB) technologies dominate a predominant share of industrial applications so far. They have been used in treating high organic strength industrial wastewaters from brewery, chemicals, food processing, distillations and fermentation, sugar processing, and so forth (Frankin 2001).

Nonetheless, there are some drawbacks of the anaerobic granular processes. A large shortfall associated with the granular sludge systems is the low cell-yield and long doubling times of the methane-producing microbes, which results in long operating time for a complete development of anaerobic granules. The time required depends primarily on the source and type of seed sludge used to start up the bioreactor. In cases where inoculation is seeded with flocculant sludge obtained from municipal wastewater sludge digesters, it usually takes several months or much longer before the bioreactor can be operated.

In order to reduce the lengthy startup of granular sludge systems, technologies for enhanced and rapid production of anaerobic granules are desirable. One effective way for a fast startup is by using granular sludge from operating reactors as the seed inoculum. The availability of granular seed sludge, however, is often limited, and the costs for purchase and transportation of the inoculum can be high. Other possible ways of rapid startup are by dosing coagulant polymer (Show et al. 2004a; Wang et al. 2004) or stressing the volumetric loading rate (Show et al. 2004b) during the startup. These studies indicated that the startup times were significantly reduced by as much as 46%.

7.3 ADVANTAGES OVER AEROBIC TREATMENT

Increasing restrictions on sludge landfill, air pollution, hazardous waste disposal, odor control, energy use and other limitations have exerted a considerable impact on applicability of aerobic wastewater treatment. In order to manage a successful and sustainable scheme for wastewater treatment, development of technologies combining high waste removal efficiency, low construction and maintenance costs, low energy use and greenhouse gas emissions has become a major priority. In this respect, anaerobic granular sludge treatment processes are becoming increasingly popular worldwide. In comparison with conventional aerobic treatment, main advantages of anaerobic granular sludge systems include high loading, smaller footprint, high flexibility in applications, lower treatment costs and lower sludge production.

It should be noted that a comparison between aerobic and anaerobic processes should be made with caution, as each individual case has peculiarities that may make only certain processes feasible. In many cases especially in treating high strength industrial effluents, both anaerobic and aerobic processes should be used in stages for best possible performance. Key aspects of the comparison, such as sludge production, feed loading rate, process stability, degradation of recalcitrant and toxic xenobiotics, VOC emissions, surfactant foaming, chemical requirements, and energy efficiency are discussed in the following subsections.

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7.3.1 Sludge Production

Life cycle analysis of wastewater treatment systems has been used as a holistic approach to the evaluation of competing technologies and consistently identifying the strong influence that energy consumption and emissions has on the overall environmental impact. It follows that the strong influence that sludge handling and disposal process have on the overall environmental impact arising from wastewater treatment has to be considered. One of the intrinsic features of aerobic processes is that, the growth rate of the aerobes is considerably faster as much energy can be derived from the oxidation of organic contaminants. Consequently, a large portion of the organic matter is used in the synthesis of new cells. The organics converted to biomass have not actually been stabilized, but are just changed in form. The vast bulk of biological solids generated in the aerobic process requires further sludge treatment for ultimate waste stabilization.

More free energy is available to the organisms when oxygen is the electron acceptor. Abundant free energy in aerobic processes is reflected in the greater amount of excess biomass produced, which must be removed from the system to prevent clarifier failure and excess oxygen consumption. A crucial attribute of anaerobic granular sludge technology is the markedly reduced production of excess sludge (typically 5–15%) comparing with aerobic-based counterparts. Under anaerobic conditions, more than 90% of the wastewater COD is converted to methane gas as an end product. The combustible end product of methane represents an additional source of energy for other operations such as heating and generating electricity. Reuse of methane can also warrant claim of carbon credits in the form of Certified Emission Reductions (CERs) as incentives awarded to countries or businesses for reducing emissions of greenhouses gases (GHG) under the Kyoto Protocol (Show and Lee 2008; Show et al. 2011; Show and Wong 2013). In addition, there is notable saving in the energy needed for aeration. This energy equivalent is not available for biomass synthesis, thereby considerably lessening both financial and waste biomass disposal site requirements. Presently, landfills for organic wastes are near the point of closure due to land scarcity and pricing, technologies such as anaerobic biogranulation producing smaller amounts of waste sludges will put landfills in a better situation.

With anaerobic biogranulation innovation and the combined advantages of significant energy production and decreased excess sludge production, anaerobic granular sludge processes have gained in credibility among industrial management and consulting engineers.

7.3.2 Feed Loading Rate

As the rates of anaerobic reaction are not limited by oxygen transfer, it does not require oxygen in anaerobic waste decomposition. Anaerobic granular-sludge systems are also characterized by higher loading rates commonly varying from 5 to 20 kg chemical oxygen demand (COD)/m^3•d, whereas the usual loads to aerobic systems are much lower at 0.5–3 kg/m^3•d (Hu et al. 1999). This implies a substantial reduction in the reactor volume and the land space required for the

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treatment plant, and, therefore, lower construction and overall investment costs can be derived.

On the other hand, more and more industries are practicing reuse of process water because of escalating water pricing, which results in reduced flow of concentrated wastewaters of high pollutant concentrations. And, treatment processes based on anaerobic granulation are preferred as they can handle high-strength wastewaters with satisfactory performance. The robust granular sludge systems can offer an efficient treatment for a wide range of industrial effluents including concentrated industrial wastewater feedstocks from chemical plants, food processing, palm oil mills, pharmaceutical, pulp and paper industry, distillery, brewery and industries producing high strength organic effluents (Hu et al. 1999).

It has been a notion that a wastewater must be of high BOD concentration in order to be a viable candidate for anaerobic treatment. While anaerobic treatment can accommodate very strong industrial wastewaters, primarily because there are no limitations on oxygen transfer and solids flux thickening, the minimum feed strength is not controlled by BOD concentration but rather by a number of very important design considerations. These include the provisions of the following requirements:

1. Biomass accumulation by means of settling, granulation, adhesion to biofilm, entrapment within the system, or recirculation for longer mean cell retention time;
2. Good contact between biomass and wastewater in overcoming problems of diffusion of substrates and products from the liquid to biofilm or granules; and
3. Maintenance of an environment suitable for bacterial growth.

7.3.3 Process Stability

Biomass washout and sludge bulking of many aerobic processes based on suspended biomass are common operational issues faced by wastewater treatment plants. However, anaerobic processes based on cell-immobilization such as granulation would minimize these problems. Successful cultivation and retention of biomass via granulation or other forms of immobilization appeared to be the key to developing a more reliable system. Process stability, which reflects the capacity to achieve efficient pollutant reduction under varying environmental conditions, is enhanced when an anaerobic facility is designed for efficient biomass retention.

7.3.4 Degradation of Recalcitrant and Toxic Xenobiotics

Recent research indicates that certain organic compounds which cannot be degraded under aerobic conditions can be anaerobically decomposed. For instance, anaerobic processes can successfully dehalogenate highly chlorinated organic compounds from the pulp and paper industry (Parker et al. 1993). Dehalogenation was demonstrated in a non-methanogenic anaerobic granular

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process for pulp and paper mill wastewaters containing organic substances which were chlorinated during the chlorine-bleaching operations. The similar demonstration has since often been repeatedly observed in methanogenic systems. Surprisingly, even certain anaerobes derive energy for cell growth from the dehalogenation process (Mohn and Tiedje 1992).

Scientific findings have reviewed that anaerobic granular sludge process is capable of removing most chlorinated hazardous compounds, including pesticides and chlorinated solvents, and converting polychlorobiphenyls (PCBs) to less detrimental substances. As chlorinated organics are transformed anaerobically, their toxicity is dramatically dampened or nullified. Aerobic processes that have been so widely used do not possess this nullifying capability (Macarie 1999). Wastewaters with high levels of formaldehyde can be effectively detoxified in an anaerobic granular bioreactor through conversion into methanol and then into methane. An operational condition must be fulfilled such that an adequate hydraulic residence time is maintained for stable operation (Omil et al. 1999).

Such detoxifying capability offers a vital consideration for many industries to select anaerobic biogranulation technology. Moreover, granular sludge anaerobic wastewater treatment has successfully achieved complete mineralization of different anthropogenic compounds. Aromatic compounds such as phenols and methylated phenols (cresols) are commonly encountered pollutants in complex effluents, such as those generated by petrochemical industries, which have been reported to be degraded anaerobically (Charest et al. 1999; Kennes et al. 1997).

A review of the development and applications of anaerobic granular sludge technologies for complex industrial effluents containing terephthalic acid, synthetic resins, carboxymethylcellulose, maleic acid, etc., has been reported by Macarie (1999). In many cases, these effluents lack of nutrients required to enhance the growth of anaerobic granules. The small quantity of nutrients makes the economic impact of such nutrients addition negligible.

7.3.5 VOC Emissions

Increasingly stringent controls are now being legislated on air emissions of volatile organic compounds (VOCs) from industrial production, including fugitive emissions from aerobic treatment plants. Many volatile organic contaminants such as acrylic acid and chlorinated solvents tend to be air stripped from the wastewater during aeration. The fact that they are stripped before being degraded would contribute to VOC air pollution (Speece 1996). This environmental drawback cannot be omitted from the design of aerobic systems but is eliminated in anaerobic treatment. Emissions of hazardous volatile organic compounds are not a concern of aeration-free anaerobic granular sludge process, as there is no stripping of air from the reactor liquid.

7.3.6 Surfactant Foaming

Foaming in the aerobic treatment process is a common operational problem in many wastewater treatment plants. Sticky, viscous and brown foam floats and accumulates on top of the tanks, and can take up a large fraction of solids

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inventory and reactor volume, thus decreasing the effluent quality and control of solids retention time (SRT). The foam can also overflow onto walkways and surrounding areas, posting severe difficulties and risk to operation and environment.

Air bubbles provided in an aeration tank is often a primary factor associated with foaming. The issue of foaming of surfactant wastewaters caused by the hydraulic turbulence and/or bubbling of air attributed to the aeration in the aerobic treatment may actually preclude the use of air as the basis of the treatment. Biodegradation free of foaming is possible via anaerobic granular sludge processes and is thus seen to be of advantage in tackling operational problems due to foaming. In comparison, approximately 70 volumes of air are added per volume of wastewater having 2,000 mg/L of BOD for aerobic processes, while only about 1.6 volumes of biogas produced per volume of 2,000 mg/L wastewater treated anaerobically.

7.3.7 Chemical Requirements

Alkalinity or acidity for pH adjustment and buffer capacity and nutrient addition to satisfying synthesis needs of the microorganisms are usual chemical inputs for any biological process. Alkalinity is the most common requirement for pH control. Alkalinity addition is quite often the most expensive operation cost of anaerobic granular sludge systems. In anaerobic degradation, the volatile acids to alkalinity ratio should be in the range of 0.3–0.4. The most economical way of minimizing alkalinity additions may be to install a pH control system to avoid adding excess alkalinity to the influent. Anaerobic granular processes treating industrial wastes or sludges commonly produce 200–500 mg/L of volatile acids. For the range given, 570–1430 mg/L of alkalinity as $CaCO_3$ is required. Aerobic processes do not generally require pH adjustment unless they are designed to convert ammonia to nitrate (nitrification).

As discussed earlier, the nutrient requirement for a given amount of substrate is greater for an aerobic process than for an anaerobic process. Many wastes will contain an adequate amount of nutrients for treatment in either the anaerobic or aerobic mode. The ratio of carbohydrates and fats to protein is the primary controlling factor. The latter contains significant amounts of nitrogen and phosphorus.

7.3.8 Energy Efficiency

Aeration is a tremendous operating cost for most treatment plants adopting aerobic processes. Aerobic treatment generally requires the energy of 0.5–2 $\mathrm{kWh/kg\,O_2}$ for the aerobic microorganisms to thrive (Speece 1996). On the other hand, anaerobic treatment produces as much as 12.7 MJ of biogas energy per kg of COD removed. The biogas can be used to heat the reactor up to a mesophilic operating temperature. Some countries implement feed-in tariffs incentive scheme whereby electricity derived from biogas can be fed onto the grid. This electricity supply offers additional revenues while promoting green energy production. It can be deduced that energy conservation and consequent ecological and economic benefits are possible with the energy-efficient anaerobic granular processes. Further assessment of energy is discussed in the following Section 7.4.

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7.4 ENERGY GENERATION

7.4.1 Generation of Bioenergy

Most studies on anaerobic granulation were conducted whereby methane is produced as the major gaseous product. Not only is anaerobic treatment of value for wastewater treatment, but it is also the process used in solid waste landfills that results in the stabilization of organic wastes, converting them to methane gas, which is increasingly valued as an energy source. Some opponents would cap landfills to prevent water from infiltrating and the natural anaerobic bioconversion into methane to occur, but this practice is questionable. Methane is undoubtedly a powerful greenhouse gas, but if designed and captured for use, it serves instead as a good renewable biomass energy source.

Anaerobic degradation of wastewater produces 1.27×10^7 J of energy in the form of biogas with every kg COD degraded by microbes. This methane-producing feature leads to energy conservation and the concomitant ecological and economic benefits. Part of the energy may be used to heat up the digester to enable a higher rate of anaerobic degradation, while surplus energy can be converted into electricity to supplement in-plant power requirements, or feed into the power grid earning additional revenues from feed-in tariffs. With every kWh of electricity generated from biogas, approximately 1.05×10^7 J of energy can be saved that would be otherwise used to generate the same amount of electricity from fossil fuel. With global concerns over energy shortages and greenhouse gas emissions through combustion of fossil fuels, effort towards renewable energy supply from anaerobic waste treatment clearly fits into the much sought after sustainable development.

Potential of hydrogen as an ideal replacement energy has attracted worldwide attention in the last two decades. Use of hydrogen energy was mooted out of the concerns of energy sustainability and environmental impact such as global warming arising from the combustion of depleting fossil fuels. Hydrogen derived from renewable resources is considered one of the promising alternatives to fossil fuels in the future, since hydrogen releases energy explosively to produce water as the only byproduct. Biological means such as anaerobic fermentation, biophotosynthesis and photo-decomposition to harness hydrogen from renewable sources like water or organic compounds have been gaining considerable interest (Das and Veziroglu 2001).

Biohydrogen production via fermentative, photosynthetic bacteria or algae is an environmentally-friendly and energy-saving development, which appears to be a promising alternative to the conventional (fossil-fuels based) hydrogen production processes. Among the biological processes, anaerobic hydrogen fermentation

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appears favorable, as hydrogen can be generated at higher rates from renewable organic materials with a concomitant reduction in environmental organic pollutants. Feasibility of anaerobic hydrogen production from organic wastes has been demonstrated by some research groups in different countries all over the world (Fang and Liu 2002; Chang and Lin 2004; Wu et al. 2006; Zhang et al. 2006). Nevertheless, application of granular sludge processes for anaerobic hydrogen production has began only in recent years. The formation mechanism of hydrogen-producing granules is yet to be established. While the process is still being developed, it has shown a good potential in hydrogen production as compared to the suspended sludge systems (Liu and Fang 2003; Kotsopoulos et al. 2006).

The physical, physicochemical and hydraulic characteristics of hydrogen-producing granules, such as bioparticle morphology, extracellular polymeric (ECP) substances, and settling velocity, have been investigated by several research groups (Fang et al. 2002; Zhang et al. 2004; Mu and Yu 2006). A novel approach to the rapidly initiate granulation of hydrogen-producing sludge was developed in an anaerobic continuous stirred tank reactor (Zhang et al. 2007a). By applying acidification in culture incubation, granulation was initiated within 5 days which was much shorter than that usually required 2 to 4.5 months (Fang et al. 2002). Formation of granular sludge significantly increased the reactor biomass, which in turn improved the hydrogen production rate.

Although the role of ECP bonding in initiating microbial aggregation remains unclear, associated increases in ECP production with the development of granules indicate that the function of ECP is more likely to maintain structural integrity of microbial granules. Notably, besides the microbial surface physicochemical properties, the hydrodynamic, biological and other forces may also influence or contribute to microbial adhesion and aggregation. It has been reported that microbial aggregation could be initiated and accelerated via different approaches to altering bacterial surface charges. Reducing electrical repulsion between cell and solid surface could improve the microbial adhesion performance (Bonet et al. 1993; Tsuneda et al. 2003). Moreover, microbial granulation is accelerated by introducing multi-valence positive ions and cationic polymers to reduce electrostatic repulsion between negatively charged bacteria (Mahoney et al. 1987; Show et al. 2004a, b; Wang et al. 2004).

7.4.2 Energy Assessment

An energy assessment is important since energy comprises one of the major operating expenses of wastewater treatment plants. Temperature has a significant effect on the rate of reaction by anaerobic microbes. The systems perform better at elevated temperatures in the thermophilic range from 45 to 65°C. Heating the influent, when required, is usually the significant energy input into an anaerobic reactor. Although waste degradation proceeds more rapidly at elevated temperatures, the costs associated with maintaining such temperatures may offset the benefits of higher reaction rates. Treatment by anaerobic granular sludge can be performed at temperature below 20°C in the psychrophilic range. However, operation of the system in this low temperature range is disadvantageous, owing

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to the extremely lethargic microbial degradation and the resulting longer solids retention times. Therefore, most anaerobic granular sludge systems are designed to operate in the mesophilic range from 20°C to 45°C with the most optimum temperatures of around 33–40°C. For a reactor operating at 35°C, degradable wastes typically produce 1 cubic meter of methane for every cubic meter of wastewater treated daily. Methane derived from anaerobic digestion usually satisfies heating requirements of the feed. Non-granular sludge reactors such as the conventional and contact reactors also require energy for mixing the reactor content.

The need to recycle, which requires pumping energy, is dependent on the aerobic or anaerobic process. Granular sludge EGSB reactors undoubtedly need recycle and incur a more significant energy penalty to keep the bed fluidized. Other granular sludge reactors such as UASB typically do not require recycling. All aerobic processes require recycling of sludge or liquid to activate the biomass.

The other significant energy input into a treatment process is for sludge processing. Less energy is consumed for sludge processing in anaerobic granular systems compared to aerobic systems because of lower sludge production in anaerobic granular sludge systems.

Aerobic treatment, except in the case of trickling filters, always requires energy input to pump air or oxygen into the system. Trickling filters use more energy for pumping but, in general, require less energy input than suspended growth aerobic processes. Trickling filters can provide little treatment during winter if they are not enclosed and heated.

The net energy available from an anaerobic granular sludge process is equal to the chemical energy (methane) produced by the process minus the thermal energy required to heat the wastewater to digester operating temperature. The methane yield depends on a number of factors, including waste composition, temperature, hydraulic retention time, and solids retention time. These factors also dictate the organic and volatile solids loadings.

Calculation of energy consumption and the influent COD concentrations needed for energy self-sufficient for several anaerobic processes has been reported (Speece 1996). The study indicated that granular sludge reactor (UASB) exhibits the lowest feed COD concentration for energy self-sufficiency because of its least energy consumption for heat, mixing and pumping. It should be noted that the data for this assessment are derived from an influent temperature of 15°C and a reactor operating temperature of 30°C. It was assumed that the methane yield has been $0.25\ \mathrm{m}^3/\mathrm{kg}\,\mathrm{COD}$ removed and that COD removals of 80% have been attained for each process. Use of heat exchangers was not considered for heating energy consumption. They could significantly reduce energy consumption in some circumstances.

It is observed that energy consumption of anaerobic treatment is dependent on the type of process used and therefore on the type of waste treated. Mixing and pumping energy is the most variable item. Heating energy is directly related to the temperature difference between the reactor and the influent. In addition to the energy consumption factors given, there will be energy costs associated with sludge dewatering and transport to the ultimate disposal site.

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Substantial energy cost benefits can be accrued when proper design criteria of anaerobic granular sludge system are met. The methane production is a positive cost benefit. The anaerobic treatment produces 12×10^6 BTU as CH_4 per tonne of COD converted to CH_4. In many smaller installations, the methane production is merely flared off because it is uneconomical to invest for its utilization. Because no oxygen transfer is required, the need for the 500–2,000 kWh of energy per tonne of oxygen transfer frequently required for aerobic treatment is negated, making energy conservation possible with its concomitant ecological and economic benefits. Since approximately 10,000 BTU are consumed in the generation of 1 kWh of electricity, the expenses incurred in generating the 5 to 20×10^6 BTU/tonne of COD treated which is necessary for oxygen transfer are eliminated, providing even further energy saving.

7.5 GRANULAR SLUDGE REACTORS

For anaerobic treatment to compete with alternative technologies such as aerobic or physicochemical treatment, not only it has to be efficient and reliable but also cost-effective in terms of investment and operating costs. Extensive full-scale applications indicated that overall economic benefits derived from the granulation technology include low operating costs, compact reactor construction, production of energy in the form of biogas, low waste sludge production, which translate into overall economic benefits.

Extensive effort is now being made in exploring broader applications of anaerobic granulation technology for conversion of high strength and recalcitrant organic wastewaters into a renewable energy source. The key to successful use of the anaerobic treatment is to separate the liquid and the solids (biomass) retention times in the reactor system. To achieve high feed-loading rates, short hydraulic retention times are essential whilst maintaining positive net biomass retention. A variety of reactor designs in retaining biomass within the reactor system have been developed over the past two decades. Anaerobic reactor systems integrating granular sludge such as the Upflow Anaerobic Sludge Blanket (UASB) reactor, Expanded Granular Sludge Bed (EGSB) reactor, Hybrid Reactor (HR), Anaerobic Continuous Stirred Tank Reactor (CSTR), Anaerobic Baffled Reactor (ABR), Internal Circulation (IC) reactor, Anaerobic Sequencing Batch Reactor (ASBR), and Anaerobic Migrating Blanket Reactor (AMBR) are briefly discussed in the following section.

7.5.1 Upflow Anaerobic Sludge Blanket Reactor

Upflow Anaerobic Sludge Blanket (UASB) was developed with a remarkable design of a 3-phase separator which serves two key functions using just one single reactor, namely maximizing biomass retention without the need of an external clarifier. The unique gas-solid-liquid separator was designed for the separation of biogas from sludge granules and treated effluent. The UASB technology is well

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accepted because of its high organic removal efficiency, simplicity, low capital and operating costs and low footprint requirement.

UASB has been used in treating food industry wastewaters and a variety of wastewaters including those from piggery, alcohols, fatty acids, slaughterhouse, milk fat, distillery and fermentation, pulp and paper wastes, brewery, food processing, chemicals, pharmaceuticals and so on. Recent studies showed that UASB can be applied in treating wastewaters containing concentrated proteins (Fang 1994) and aromatic compounds such as phenol (Wen et al. 1995). Effluent recirculation is widely used to avoid toxic impact to the microorganisms.

Supplement glucose improves the anaerobic degradation of phenol (Tay et al. 2001). Phenol can be degraded to methane and carbon dioxide through phenol degraders and hydrogen utilizing and acetotrophic methanogens. The phenol removal efficiency was also the best at 98%, compared with 88% without glucose supplement. Moreover, it also exhibited better resistance to adverse environmental conditions and the system recovered faster than the other system without glucose supplement.

Removal of chlorinated phenols is possible in UASB reactors (Droste et al. 1998). Halogenated organic pollutants are labeled as toxic and recalcitrant in the environment. Effluents containing chlorinated phenols and related compounds are especially problematic to treat due to their persistence and their high solubility in fat. Chlorinated phenolic compounds were able to be metabolized to mineral end products, to a large extent of loading rates where the reactor's performance was not hindered. There was no accumulation of phenol in any of the reactors in the experimental conditions.

Treatment of polyethylene terephthalate wastewater with UASB is proven feasible in a full-scale application (Fdz-Polanco et al. 1999). The wastewater from the esterification process consists of mainly unreacted raw material, largely ethylene glycol, and products of the secondary or degradation reactions, such as terephthalic acid esters, methanol, acetaldehyde and crotonaldehyde being the major part. There is also another wastewater stream, viz., the second stream, from the melt spinning process where a bath of chemicals is showered to improve the physical characteristics of the fibre. It was reported that the anaerobic biodegradability was 90% and 75% for esterification wastewater and second stream wastewater respectively.

A main problem associated with the granular sludge UASB systems is the inherent long startup required for the development of anaerobic granules. In cases where inoculation is seeded with flocculant sludge obtained from municipal wastewater sludge digesters, it usually takes several months or even a much longer period before the system can be fully functional. In order to reduce the prolonged startup of granular sludge-based UASB systems, technologies for enhanced and rapid production of anaerobic granules are highly sought after. Much research work has been carried out to address these issues.

An unconventional approach to accelerate startup and granulation processes in UASB reactors by stressing the organic loading rate (OLR) had been developed (Show et al. 2004a). The results indicated that the startup of reactors could be

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significantly accelerated under stressed loading conditions. Startup times of the moderately and severely stressed reactors for operating at OLRs of 1 to 16 g COD/L.d ranged from 10 to 80 days and 13 to 90 days, respectively. In comparison with 17 to 120 days needed for the control reactor to reach the same OLRs, the startup times were shortened by 25–41%. Applying stress did not seem to reduce the reactor loading capacity, as all the reactors reached a similar maximum OLR of 16 g/L.d.

Show et al. (2004a) also explored the possibility of accelerating biogranulation process with stressed loadings. The researchers found that under stressed loading conditions, the sludge particles formed granules earlier in both the stressed reactors after 24 and 30 days of startup. The times taken to form granule were reduced by 45% and 32% in the severely and moderately stressed units, respectively, in comparison with the control reactor without applying stress. The granule formation occurred earlier in the severely stressed reactor than the moderately stressed unit. Characterisation of bioparticles revealed that the granules developed in the moderately stressed reactor exhibited superior characteristics in terms of settleability, strength, microbial activity and morphology, and granular sludge growth, as compared with both the control reactor (without stress) and the over-stressed unit (Show et al. 2004a). The results indicated that the unconventional startup approach could offer a practical solution for the inherent long startup in UASB systems with concomitant saving in time and cost.

A different approach to rapid startup is to adjust the Microbial Load Index (MLI) values (Tay and Yan 1997). Research findings show that under high MLIs of 0.8 and 0.6, granulation developed well in 3 to 4 months of operation, enabling a fast startup. With low MLIs of 0.3 and 0.2, no granulation was observed after 6 months.

Polymers have been used in enhancing anaerobic granulation process (El-Mamouni et al. 1998). Chitosan, a natural polymer, out-performed a synthetic polymer Percol 763 in terms of granules formation rate. Chitosan yielded a granulation rate as high as 56 μm/d as comparing with a lower rate of 35 μm/d with Percol 763 in acidic pH. It has been reported that adding polymer in the seeding stage markedly accelerated the startup time by as much as 50% and the granule formation by 30% (Show et al. 2004b). Granules developed in polymer-assisted reactor exhibited better settleability, strength and methanogenic activity at all organic loading rates tested. Organic loading capacities of the polymer-assisted reactor were also increased significantly from 24 to 40 g COD/L-d. It was hypothesized that the cationic polymer was able to form bridges between the negatively charged bacterial cells, thus enables greater interaction between biosolids resulting in preferential development and enhancement of biogranulation in UASB reactors.

7.5.2 Expanded Granular Sludge Bed Reactor

Developed based on the UASB reactor, the Expanded Granular Sludge Bed (EGSB) reactor is able to overcome shortcomings of the UASB reactor in treating chemical wastewaters (Zoutberg and de Been 1997). The EGSB is able to promote

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the growth of biomass in a granular form similar to the UASB granules. The process is especially suitable to treat wastewater containing compounds that are toxic in high concentrations and that only can be degraded in low concentrations (chemical industry). It is also possible to operate the reactor as an ultra-high loaded anaerobic reactor (to 30 kg COD/m^3-d) for applications in other sectors of industry (e.g. brewery, distillery, yeast, sugar, corn ethanol production, etc.).

Mesophilic conditions at 35°C to treat slaughterhouse wastewater in an EGSB system appear to be a feasible option (Nunez and Martinez 1999). The average removal efficiency was 67% for COD, 90% for total suspended solids, and 85% for fats with no accumulation of fats on the sludge being observed. The specific methanogenic activity of the sludge was about 3 times higher than that of the sludge inoculated into the reactor. The sludge activity did not change significantly after one year of operation.

Thermophilic sulfite and sulfate reduction offers good prospects as part of an alternative technology to conventional off-gas desulfurization technologies (Weijma et al. 2000). Methanol can be efficiently used as electron and carbon source to obtain high sulfite and sulfate elimination rates in thermophilic bioreactors.

A comparison of the behaviour of EGSB and UASB reactors in diluted (e.g. ethanol, diluted beer) and concentrated (e.g. coffee) wastewater treatment has been made. There were no major differences in the removal rates during the operation with coffee wastewater. It was likely that for this effluent, the process is limited by the reaction kinetics instead of by the mass transfer due to the complex nature of the waste. With diluted beer, the EGSB reactor indicated a better performance than the UASB (Jeison and Chamy 1999). The granular sludge-based UASB and EGSB processes gradually take a significant portion of commercial applications. Although UASB remains as the predominant technology in use, ESGB type processes are increasingly gaining more popularity (Frankin 2001).

7.5.3 Hybrid Reactor

A Hybrid Reactor (HR) is mainly designed with a combination of an UASB and a biofilter. The designs include either randomly-packed or corrugated sheet media in the upper portion of the reactor to trap biomass and support biofilm growth. This results in a hybrid sludge blanket-fixed film reactor. The HR has both suspended granular biomass and immobilized biofilm. Evaluation of the respective roles of these two types of biomass with a mathematical model was developed and experimentally verified. It was found that the granular biomass plays a key role in removing both substances in the substrate. This was due to complete coexistence of both trichlorfon-degrading and glucose-removing bacteria in each type of the granules. Such a system is applicable to the treatment of complex industrial wastewaters that contain readily biodegradable organics, as well as refractory pollutants. Simultaneous removal of trichlorfon, with glucose added as a carbon source for degradation requirement of trichlorfon in a hybrid bioreactor, was reported (Chen et al. 1998).

Anaerobic thermophilic (55°C) treatment of thermomechanical pulping whitewater in reactors based on biomass attachment (biofilm) and entrapment

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(granules) was studied (Jahren et al. 1999). Up to 70% COD removals were achieved in all HRs. Degradation rates of up to 10 kg COD/m^3-d were reported. The anaerobic multi-stage reactor (consisting of three compartments, each packed with granular sludge and carrier elements) showed degradation rates up to 9 kg COD/m^3.d. Clogging and short-circuiting eventually became a problem in the multi-stage reactor, probably caused by too high packing of the carriers.

Pentachlorophenol (PCP) was efficiently degraded in a HR supplied treating a mixture of volatile fatty acids (VFAs) and methanol (Montenegro et al. 2001). A COD reduction of 97% was achieved and biogas composition was found to contain 86% of methane. The removal of VFAs was 93%, 64%, and 74%, respectively for butyric, propionic and acetic. More than 99% of the PCP was removed by granular sludge activities throughout the 21 months of reactor operation. Specific removal rate was 1.07 mg PCP/g volatile solids (VS)-d during the highest PCP concentration dosing.

7.5.4 Anaerobic Continuous Stirred Tank Reactor

Anaerobic Continuous Stirred Tank Reactor (CSTR) is a conventional bioreactor used for anaerobic digestion of sludge. It was found that anaerobic granules cultivated in a CSTR disappeared within three weeks when the reactors were incubated statically instead of being shaken (Vanderhaegen et al. 1992). Hydrodynamic shear force appeared to be necessary for maintaining the integrity of granules, and that anaerobic granulation may not be reactor type-dependent but associate with the way the reactor is operated. It should be pointed out that the hydrodynamics in UASB and CSTR are quite different. In CSTR, the bacteria move in a stochastic way, i.e. there is no regular liquid upflow pattern unlike that of the UASB. The study challenged the general belief that liquid upflow pattern is essential for the development of granular sludge.

It is generally believed that spontaneous granulation of hydrogen-producing bacteria can occur with shortened HRT in CSTRs (Fang et al. 2002). Zhang and his co-workers (Zhang et al. 2007a) reported that formation of granules in an anaerobic CSTR was accomplished within a very short cultivation (3–5 days) after the acclimated sludge was subject to 24 hours acid incubation by reducing the culture pH from 5.5 to 2.0. Granules were formed much faster than other studies with several months under normal conditions (Fang et al. 2002). Formation of hydrogen-producing granules was not observed without acid incubation.

Subsequently it was found that microbial granulation is attributed to improvement in surface physicochemical properties such as reduced electrostatic repulsion, improved hydrophobic surface, more ECP secretion and a higher ratio of proteins/polysaccharides (Zhang et al. 2007a, b, 2008a, b). It was reported that changing the culture pH would result in improvement in surface physicochemical properties.

Show et al. (2007) and Zhang et al. (2007b) investigated the influence of HRT, substrate concentration and OLR on hydrogen production of granular sludge in a CSTR. The study revealed that reducing the OLR at a given amount of biomass, i.e. reducing the sludge loading rate (SLR) might result in the culture underfed and

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hence metabolic shift. It was deduced that relatively low hydrogen yield obtained at an OLR of 2.5 g glucose/L·h was possibly attributed to the metabolic shift induced by the reduced SLR. Formation of granular sludge significantly increased the overall reactor biomass concentration to as much as 16.0 g VSS/L, enabling the CSTR to operate at an OLR of up to 20 g glucose/L·h thus enhancing the hydrogen production.

7.5.5 Anaerobic Baffled Reactor

Split-feed Anaerobic Baffled Reactor (ABR) was introduced to shorten the startup and to achieve higher process performance for the treatment of ice-cream wastewater (Uyanik et al. 2002). A scanning electron microscopy analysis revealed that granulation progressed rapidly in the ABR compared with other reactor configurations and that the reactor contained a highly mixed population of methanogens in all compartments. The use of polymer-conditioned anaerobic sludge and granular sludge as the inocula proved to be advantageous over the use of suspended anaerobic sludge. The improved ABR consequently performed more efficiently and also showed greater stability than the conventional ABR.

7.5.6 Internal Circulation Reactor

Internal Circulation (IC) reactor was designed to overcome operational problems due to biomass washout in conventional UASB process (Pereboom and Vereijken 1994). The IC reactor consists of two inter-connected UASB compartments on top of each other. It seems that the high turbulence and adequate mixing characteristics make the IC reactor more attractive for reducing clogging and handling high strength organic wastewater. It was reported that the added external circulation could enhance biomass granulation, accelerate granule development and improve sludge characteristics in the IC reactor (Ding and Wang 2005).

7.5.7 Anaerobic Sequencing Batch Reactor

Anaerobic Sequencing Batch Reactor (ASBR) was developed with a much simpler configuration than UASB. The major differences of ASBR comparing with the UASB are that there is no 3-phase separator and upflow hydraulic pattern. It does not require feed distribution with a modified design of batch feeding mode. However, the non-continuous operation mode of ASBR poses to be a major disadvantage from the viewpoint of investment, as storage of influent feed might be needed if receiving large-flow wastewater.

Granular sludge blanket was successfully cultivated in an ASBR in 5 months after seeding the reactor with non-granular primary digester sludge (Wirtz and Dague 1996). It was found that MLVSS retained in ASBR was 2.5-fold higher than that in UASB, and the COD removal in ASBR is comparable to that of UASB (Angenent and Sung 2001). In a separate study, it was reported that at low OLRs, the performance of continuous UASB and anaerobic SBR were quite similar, but continuous UASB reactors performed better than the anaerobic SBR at high OLRs (Kennedy and Lentz 2000).

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7.5.8 Anaerobic Migrating Blanket Reactor

Anaerobic Migrating Blanket Reactor (AMBR) was designed with a continuous feed and compartmentalized reactor without the requirement of elaborate gas-solid-separation and feed-distribution systems (Angenent and Sung 2001). Operated under identical conditions, granules developed in an AMBR tended to be darker in color, smaller and denser than that in an UASB reactor. The internal structure of AMBR is more complex than that of UASB, especially the multiple-point mechanic mixing to overcome sludge clogging as well as to improve feed distribution. As compared to an UASB system, the possible advantages of an AMBR with more than three compartments include smaller biomass migration rates, less chance of short-circuiting, operation in a step feed mode for high-strength wastewater during shock loads, and difficult-to-degrade compounds would be degraded more efficiently.

7.6 PROSPECTS

Global concerns over energy shortages and greenhouse gas formation arising from the combustion of fossil fuels have prompted more efforts in the conversion of wastes into renewable energy. While anaerobic granular systems have been known for its unique ability to treat high strength wastewaters, greater efforts are needed for broader applications of anaerobic granulation system for ridding the unwanted pollutants by converting them into biogas—a renewable energy source. Research towards efficient methane and hydrogen production from wastewaters converted by anaerobic granular sludge is extensively carried out. Problems that need addressing are a long startup, process reliability, toxicity causes and effects, odor production and control, and better understanding of refractory organic degradation.

Anaerobic granulation has become an established technology for a variety of industrial applications. The technology is accepted in the developed nations as well as in less developed countries. Granular sludge-based anaerobic processes such as the UASB and EGSB systems are gradually commanding a large share of full-scale industrial applications. Although UASB still is the predominant technology in use, ESGB type processes are gaining more popularity driven by economics (Frankin 2001). Development of EGSB and Staged Multi-Phase Anaerobic (SMPA) reactor systems could lead to very promising new generations of the anaerobic treatment system (Lettinga et al. 1997).

New insights into the anaerobic degradation of very different categories of compounds such as fine and specialty chemicals from the chemical industry, coal and petrochemicals, textile and dyeing stuff, and into process and reactor technology will lead to very promising new generations of anaerobic treatment systems (Lettinga et al. 1997). These concepts will provide a better efficiency at higher loading rates, are applicable to extreme environmental conditions (e.g. low and high temperatures) and to inhibitory or toxic compounds. Moreover, by integrating the anaerobic process with other biological methods (effluent polishing

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by aerobic activated sludge and/or biofilm, sulphate reduction, microaerophilic organisms) and with physical-chemical methods, a complete treatment of the wastewater can be accomplished at very low costs, while at the same time valuable resources can be recovered for reuse.

In the fields of psychrophilic and thermophilic anaerobic treatment, a particular reactor development may contribute to further enhancement of volumetric conversion capacities. Due to reduced water usage, both COD and salt concentrations tend to increase for industrial effluents. As a consequence, there is a need for the development of anaerobic reactors retaining flocculant or granular biomass. The membrane bioreactors (MBR) offer a solution for certain niches in wastewater treatment (Mulder et al. 2001). However, poor oxygen transfer economy and membrane fouling are major operating problems of MBR. Membrane bioreactors coupled with granular-based anaerobic processes are worth exploring into.

A promising application of anaerobic granular sludge processes lies with its markedly reduced production of excess sludge. Increasingly stricter environmental regulations have called for a more stringent sludge disposal in many municipalities; some even has implemented drastic measure such as zero sludge discharge policy to tackle dwindling landfills and rampant illegal sludge dumping. With the significant advantage of decreased excess sludge production, applications of anaerobic granular sludge processes will be further boosted.

An emerging application of anaerobic granular systems is associated with Certified Emission Reduction or Carbon Credit set under the Kyoto Protocol. In addition to the contribution to sustainable development with energy recovery in the form of methane, carbon credits can be claimed by application of advanced anaerobic processes in wastewater treatment for mitigating emissions of greenhouse gases. As anaerobic granular systems are capable of handling high organic loadings concomitant with high-strength wastewater and short hydraulic retention time, they could render much more Carbon Credits than other conventional anaerobic systems. Looking at the prospects of carbon trading, it may not be an unreasonable expectation that, in the future, wastewater treatment will experience a global shift towards employment of highly efficient granular sludge-based anaerobic processes in maximising energy production and minimizing greenhouse gas emissions.

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CHAPTER 8

Value-Added Products from Sludge

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8.1 INTRODUCTION

Biodegradation of organic compounds in wastewater is a key process in both natural and engineered systems. Microorganisms are the mainstay for organic pollutant removal in a typical engineered biological wastewater treatment system. While conventional aerobic treatment (e.g., activated sludge process) mineralizes organic compounds in wastewater, it generates a huge amount of biosolids (sludge) at the same time. On average, the activated sludge process produces about 0.4 g biomass per gram chemical oxygen demand (COD) removed (Metcalf and Eddy 2003). Anaerobic treatment is usually used for reducing excess sludge volumes in wastewater treatment plants (WWTPs). This treatment process is energy efficient with lower biomass production and partially converts wastewater organics into methane, which can be used as a gaseous fuel. However, conventional anaerobic processes do not produce high-value by-products and are capital intensive. Therefore, sludge processing, treatment, and disposal constitute one of the major challenges in many WWTPs (Weemaes and Verstraete 1998). In fact, the cost associated with treatment and disposal of excess sludge accounts for up to 60% of the total costs in conventional WWTPs (Canales et al. 1994).

From the sustainability perspective, sludge management must explore the options of recovering or reuse of valuable products from the sludge. Sludge is a very complex mixture of different chemicals, biological components and varying percentages of moisture content. The composition of sewage sludge makes it a potential source for the recovery or production of value-added products. Recently, a large number of value-added products are being investigated extensively at the lab- and/or pilot-scale or commercialized in a large scale, such as construction aggregates,

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adsorbents, fuels and particularly biotechnological products (e.g., bioplastics, biopesticides, bioflocculants and enzymes). This chapter concentrates on the recent advances in the use of activated sludge for 1) polyhydroxyalkanoates (PHA) production 2) *Bacillus thuringiensis* (Bt) based bio-pesticides production/ formulations, 3) vermicomposting biotechnology, and 4) production of different enzymes.

8.2 PHA PRODUCTION

Population growth has led to the accumulation of a massive volume of nondegradable waste materials across our planet. The accumulation of plastic waste has become a major concern in terms of the environment (Saharan and Badoni 2007). Conventional plastics not only take many decades for decomposition, but also produce toxins while in degradation. Hence, there is a need to produce plastics from materials that can be readily eliminated from our biosphere in an “eco-friendly” fashion (Gross and Kalra 2002). Bioplastics are natural biopolymers synthesized and catabolized by various organisms (Saharan et al. 2007). These get accumulated as storage materials in microbial cells under stress conditions (Berlanga et al. 2006). However, the high production cost and the availability of low-cost petrochemical-derived plastics led to bioplastics being ignored for a long time. Currently, different types of biodegradable polymers are being studied for various applications including PHAs, polylactide (PLA), poly(ε-caprolactone) (PCL), poly(p-dioxanone) (PPDO) and poly(butylene succinate) (PBS). The most extensively produced microbial bioplastics are PHAs and their derivatives (Witholt and Kessler 2002). PHAs are one of the relatively newer families of biodegradable polymers that have great potential in the future due to their properties. Currently, intensive research has been conducted on bacterial production of PHAs and improvement of the related technologies (Khanna and Srivastava 2005). However, the PHA production price is still far above the price of conventional plastics (Salehizadeh and Van Loosdrecht 2004).

The new approach involves the use of renewable carbon resources derived from agricultural and industrial waste and/or excess activated sludge from WWTPs as a substrate for PHA accumulation (Chua et al. 2003). These approaches have the advantages of saving cost on PHA production and volume reduction of wastewater sludge. The objectives of this section are to: 1) introduce various types of microorganisms that produce bioplastics; 2) describe the fermentation technology and processes and systems for bioplastics production; and 3) evaluate feasibility of using genetically engineered microorganisms for the production of bioplastics.

8.2.1 Microorganisms Involved

PHAs are produced by many different bacterial cultures. *Cupriavidus necator* (formerly known as *Ralstonia eutropha* or *Alcaligenes eutrophus*) is the one that has been most extensively studied (Vaneechoutte et al. 2004). Other important

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strains that were recently studied included *Bacillus sp., Alcaligenes sp., Pseudomonas spp, Aeromonas hydrophila, Rhodopseudomonas palustris, Escherichia coli, Burkholderia sacchari* and *Halomonas boliviensis*. Table 8.1 summarized the bioplastics produced by microorganisms along with their substrate.

Many species of bacteria, which are members of the family Halobactericeae of the Archaea, synthesize PHAs. The list of such microorganisms is increasing and currently contains more than 300 organisms (Berlanga et al. 2006). The chemical diversity of PHAs is large, of which the most well-known and widely produced form is Poly-3-hydroxybutyrate (PHB) (Kim and Lenz 2001). Synthesis of PHB is considered through the simplest biosynthetic pathway. The process involves three

Table 8.1. List of bioplastics produced by various organisms along with their substrates

Polymer(s)/Bcateria	*Carbon source*	*Reference*
PHB		
Alcaligenes eutrophus	Gluconate Propionate Octanoate	Liebergesell et al. (1994)
Bacillus megaterium	Glucose	Mirtha et al. (1995)
Klebsiella aerogenes recombinants	Molasses	
Methylobacterium rhodesianum	Fructose/ Methanol	Borque et al. (1995)
M. extorquens	Methanol P. putida Octanoate	Liebergesell et al. (1994)
Sphaerotilus natans	Glucose	Takeda et al. (1995)
PHA		
Psuedomonas aeruginosa	Euphorbia Castor Oil	Eggink et al. (1995)
P. putida	Palm kernel oil Lauric acid Myristic acid Oleic acid	Tan et al. (1997)
P(3HV)		
P. denitrificans	Methanol Pentanol	Yamane et al. (1996)
P. oleovorans	Gluconoate Octanoate	Liebergesell et al. (1994)
5POHV		
P. putida	11-Phenoxyundecanoic acid	Song and Yoon (1996)

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enzymes and their encoding genes (Reddy et al. 2003). All these genes are clustered and organised in one operon phbCAB. phaA gene encodes β-ketothiolase, the first enzyme for the condensation of two acetyl-CoA molecules to form acetoacetyl-CoA to (R)-3-hydroxybutyryl-CoA catalyzed by the acetoacetyl-CoA reductase (Steinbuchel and Schlegel 1991). The enzyme is encoded by the phaB gene and is NADPH-dependent. The last reaction is the polymerization of (R)-3-hydroxybutyryl-CoA monomers catalyzed by PHA synthase encoded by the phaC gene (Rehm 2003).

8.2.2 Media Used

The choice of media is critical not only to supply optimal conditions for production but also to do so with high volumetric productivity so that a final product is economically competitive with the traditional plastics. As the major cost in production of PHAs is the medium (Saharan and Badoni 2007), efforts are focused on finding cheap media (Ojumu et al. 2004). Cheap sources for fermentation include media containing molasses (Solaiman et al. 2006), corn steep liquor (Nikel et al. 2006), whey (Koller et al. 2008), wheat and rice bran (Van-Thouc et al. 2008) starch and starchy wastewaters (Halami 2008;), effluents from olive mill and palm oil mill (Bhubalan et al. 2007), activated sludge (Jiang et al. 2009) and swine waste (Cho et al. 1997). The choice of media, partly, depends on whether the microorganism is wild-type or recombinant and whether it needs nutrient limiting conditions (Reddy et al. 2003). Production of homopolymer or copolymer is another factor in the choice of media ingredients.

8.2.3 Fermentation Processes

Widespread and comprehensive studies have been carried out to develop efficient fermentations for the desired PHAs. Batch and particularly fed-batch (Kim et al. 1997) and continuous fermentations have been investigated (Zinn and Hany 2005). Most PHAs fermentations are operated as a two-stage process (Tsuge 2002). The main aim is to produce a high cell density culture in the first stage (growth) and then to increase PHAs concentration during the second stage which is usually a nutrient limited fermentation (Madison and Huisman 1999). Fermentation conditions depend on the demands of the microbes. A typical temperature range of 30 to 37°C along with low stirrer speeds, resulting in low dissolved oxygen tension, is adopted. pH is either left uncontrolled or is regulated linking to substrate (e.g. glucose) addition (Chung et al. 1997). PHAs production in pure cultures is limited by an external nutrient whereas production in mixed cultures is induced by an intracellular limitation. The use of open mixed cultures, such as activated sludge (Lemos et al. 2006) assist in the decrease of PHAs cost, thus enhancing their market potential (Patnaik 2005). It also increases the efficiency of fermentation (Tanaka et al. 1995). When cells are exposed to a medium with very little amounts of nutrient for a long time, the bacteria are altered physiologically (Daigger and Grady 1982). A sudden increase in carbon substrate concentrations causes the cell to change their physiology

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again. As PHA-synthesis requires less adaptation than growth, the culture starts producing polymer. This kind of fermentation is referred to as "feast and famine" (Lemos et al. 2006).

8.2.4 Various Systems for Production of Bioplastics

Individual Bacterial System for Production of Bioplastics. PHAs producing bacteria can be divided into two groups according to the culture conditions required for PHA synthesis. The first group requires the limitation of an essential nutrient(s) for the production of PHAs. Bacteria in this group include *Cupriavidus necator*, *Rhodopseudomonas palustris* and *Methylobacterium organophilum.* The second group synthesises PHAs alongside growth in the cultivation medium. Bacteria in this group include *Alcaligenes latus* and recombinant *E. coli* containing the PHA biosynthetic genes.

Due to the high production cost of PHA, much effort has been made in reduction of the production cost, such as development of fermentation strategies for high PHA productivity and isolation and development of microbial strains which overproduce PHAs from cheap carbon source.

Cupriavidus necator has been widely studied because of its potential for producing significant amounts of PHB from simple carbon substrates such as glucose, lactic acid and acetic acid (Ryu et al. 1997). Olive oil, corn oil and palm oil also have been used to produce approximately 80% dry cell weight (dcw) PHB of dry cell mass from the organism (Futui and Doi 1998). *Methylobacterium organophilum* uses only methanol as cheap carbon source to produce PHAs whereas *Rhodopseudomonas palustris*, a non-sulphur photosynthetic bacterium, has potential to produce PHB and poly(hydroxybutyrate-hydroxyvalerate) [P(3HB-co-3HV)] using different carbon and nitrogen sources. *Rhodospirilium* and *Rhodobacter* are two other non-sulphur photosynthetic bacterial genera that have been found to be particularly versatile in the production of the copolymer, P(3HB-co-3HV), using various carbon sources such as malate, acetic acid and n-alkanoic acid (Carlozzi and Sacchi 2001).

Alcaligenes latus is another organism that produces PHAs using carbon sources such as glucose, molasses and sucrose with good yields. Investigations with different nitrogen sources have proven that *A. latus* is able to grow and produce PHAs with ammonium chloride and ammonium sulphate as nitrogen sources. Ammonium nitrate and urea could not support PHA production in the organism (Grothe et al. 1999). It requires a temperature of 35°C, which makes PHB production from the organism economical by lowering the demand for cooling during fermentation. Optimum biomass and PHA accumulation can be further enhanced by feeding the organism with enriched medium.

Despite these efforts, the current cost of PHA is still much higher than that of conventional plastics. For this reason, many researchers have demonstrated that high PHA production cost can be possibly lowered by using unpurified, low-cost organic wastes from agriculture and food processing. *Azobacter vinelandii* UUWD, a new bacterial strain for PHA production was reported to produce PHA without nutrient limitation and appears to be the best strain for PHA

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production from unpurified substrate (Page 1992). Production of PHA from swine waste liquor by employing *A. vinelandii* has been demonstrated (Cho et al. 1997). When swine waste liquor medium was diluted twofold with distilled water, *A vinlandii* UWD grew to 2 g dry cell weight/L with 34wt% of copolymer p(3HB-co-3HV) containing 7.9 mol% of 3 HV units. When 30 g/L glucose was supplemented, dry cell weight and P(3HB-co-3HV) content reached 9.4 g/l and 58.3%, respectively.

Waste edible oils generated by the food industry and the food service industry are largely destroyed by incineration or lost into the environment – both routes being unacceptable from a green chemistry perspectives. PHA production was conducted by *Ralstonia eutropha* with waste edible oils and fats being carbon sources (Taniguchi et al. 2003). The efficiency of this fascinating process is high, and the polymer can be easily extracted. Thus, a waste is converted by an environmentally benign method to a valuable product (Taniguchi et al. 2003).

Plant oils and fats are renewable and inexpensive agricultural co-products, and thus, they would be one of the most suitable candidates for microbial production of PHAs. Several pseudomonades produce PHA from plant oils and tallow, and *Aeromonas caviae* also accumulates (3hydroxybutyrate-co-3-hydroxyhexanoate) (PHBHHx) from olive oil, although their productivities are quite low in all the cases (Doi et al. 1995). By using *R. eutrophia*, renewable and inexpensive agricultural fats/oils and their potentially useful feedstocks can be used for the PHA fermentation processes.

Agro-industrial oily wastes were also used for the production of poly (3-hydroxyalkaonates) by *Pseudomona aeroginesae* 42A2 (Fernandez et al. 2005). A 54.6% of cell dry weight PHA accumulation was obtained when technical oleic acid (TOA) was used as a carbon source. PHA accumulation was 66.1% of the cell dry weight when waste free fatty acids (WFFA) from soybean oil were used as carbon substrate, 29.4% of that when waste frying oil (WFO) was used, and 16.8% of that when glucose was used. Depending on the substrate supplied, a wide range of components was observed (Fernandez et al. 2005). It was found that the residual waste frying and other oily wastes are suitable substrates for PHA production (Fernandez et al. 2005). Production of PHAs by strain H23 using alpechin looks promising, as the use of a cheap substrate for the production of these materials is essential if bioplastics are to become competitive products (Pozo et al. 2002). The polymer content (88.6% of dry cell mass) reported in this study is the highest one obtained from organic wastes and is comparable with the PHA content from pure sucrose fermentation (Wang and Lee 1997).

Khardenavis et al. (2007) evaluated the waste activated sludge generated from a combined dairy and food processing industry WWTP for its potential to produce biodegradable plastics, PHB. Deproteinized jowar grain-based distillery spentwash yielded 42.3% (w/w) PHB production, followed by filtered rice grain-based distillery spentwash (40% PHB) when used as substrates. The addition of di-ammonium hydrogen phosphate (DAHP) resulted in an increase in PHB production to 67% when raw rice grain-based spentwash was used. Sae wastewater, after removal of suspended solids by filtration and with DAHP,

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supplementation resulted in lower PHB production (57.9% for cell dry weight). However, supplementing other waste with DAHP led to a substantial decrease in the PHB content in comparison to what was observed in the absence of DAHP.

Yu et al. (2001) studied the production of PHA from starchy wastewater in a two-step process of microbial acidogenesis and acid polymerization. The starchy organic waste was first digested in a thermophilic upflow anaerobic sludge blanket (UASB) reactor to form acetic (60–80%), propionic (10–30%) and butyric (5–40%) acids. The acid effluent, after microfiltration, was introduced to a second reactor where bacterium *A. eutrophus* used the acid to form PHA. PHB was formed from butyric acid and P(3HB-co-3HV) formed from propionic acid with 38% hydroxyvalerate (Yu et al. 2001). In further studies by Lee et al. (1997), PHA were produced from municipal sludge in a two-stage bioprocess (i.e., anaerobic digestion of sludge by thermophilic bacteria in the first stage and production of PHAs from soluble organic compounds in the supernatant of digested sludge by *A eutrophus*) accounted for 34% of cell mass, comparable to the amount of PHAs produced from pure volatile fatty acids (33% of cell mass). About 78% of the total organics carbon in the supernatant was consumed by *A. eutrophus*. The conversions of four major acids in the supernatant by *A. eutrophus* were found to be 87.6% (acetic acid), 62.6% (propionic acid), 56.8% (butyric acid) and 32.0% (valeric acid), respectively.

Mixed or Co-culture Systems. Mixed or co-culture systems have also been shown to be effective for PHA production (Tanaka et al. 1995). *Cupriavidus necator* is unable to metabolize sugars, molasses, whey or starchy waste. Consequently, mixed cultures of lactic acid producing bacteria such as *Lactobacillus lactis* (Tanaka et al. 1995), *Propionibacterium* (Tohyama et al. 2002) and *L. delbrueckii* (Patnaik 2005) and *C. necator* have been used in a single-stage fermentation system. The original sugar substrates are converted into lactic acid first, which is later taken up by *C. necator* to produce PHAs (Patnaik 2005). In a two-stage system, xylose is first converted to lactate using *Lacticoccus lactis*. The lactate is further converted to PHB by *C. necator*. *Lactobacillus delbrueckii* can also be used to convert glucose to lactate which is later converted to PHB by *C. necator* (Tohyama et al. 2000).

Use of an anaerobic–aerobic sludge system could enhance PHA production (Satoh et al. 1992). It can be further enhanced by microaerophilic-aerobic conditions, by introducing a limited amount of oxygen into the anaerobic zone of the anaerobic–aerobic system. Hence, it is concluded that the cost of PHA production can be reduced by using open or mixed cultures along with the activated sludge system (Liu et al. 2008). In this case, many researchers have shown that the activated sludge could produce bioplastics using a novel PHA production strategy which is to utilize the mixed bacterial culture. Acetate is one of the well-studied substrates for PHA production by mixed cultures or activated sludge. When acetate is the only carbon source available in the anaerobic phase, the 3-hydroxybutyrate unit is the major unit in the PHA formed (Satoh et al. 1992). 3 hydroxyvalerate (PHV) is formed by conversion of glycogen to propionyl COA via the succinate propionate pathway and subsequent reaction with acety

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CoA (Pereira et al. 1996). Activated sludge from a full scale pulp-paper industry wastewater treatment plant was used as a source of microorganisms to produce biodegradable plastics, PHA at 25°C, pH 7 and with different initial sludge suspended solids (SS) concentration (5 10 15, or 20 g/L) in computer controlled fermenters (Yan et al. 2008). Acetate was used as the sole carbon source at varying concentrations (5 to 20 g/L). The freshly-sampled sewage sludge was found to contain PHA and the amount varied with the sampling date. The PHA productivity and concentration varied with the initial sludge SS and acetate concentrations. Maximum accumulation of PHA (39% w/w of dry sludge SS) was observed at 15 g/L SS and 10 g/L acetate concentration. The sludge biomass increased during the process; however the net amount of the sludge residual solids after extraction of PHA was decreased to varying degrees, depending on the sludge SS and acetate concentration (5.5% to 36.9% w/w). An acetate concentration above 10 g/L was found to be inhibitory to PHA accumulation and biomass growth. Copolymers (PHB and PHV) were produced by the sludge whose molar composition varied with the batch process time (Yan et al. 2008). Furthermore, Takabatake et al. (2002) conducted the studies with activated sludge from the municipal WWTPs in Tokyo, Japan in batch experiments using acetate as the carbon source to evaluate their potential for PHA production at pH 7 to 7.2. The activate sludge samples tested had the capability to accumulate PHA up to 18.8% w/w of dry cell weight on average, with the range of 6 to 29.5%. The results showed that the maximum PHA content was more dependent on the influent of wastewater than on the operational conditions of the activated sludge process, and that conventional activated sludge produced PHA as much as anaerobic-aerobic activated sludge did.

In the other case, Md Din et al. (2006) studied the production of PHA by using single fed-batch mixed cultures and renewable resources. An SBR was used in the study. The initial mixed culture was developed using 10% activated sludge from a WWTP and 90% from palm oil mill effluent (POME). The cultivation was maintained in a single fed-batch reactor and operated in two steps: the growth and accumulation stage. First, the system will allow for an extensive growth (using a nutrient medium), and then a feed with limited nutrients (no nutrient medium adaptation) will be inoculated in the weight. The average production of PHA could only reach up to 44% of cell dry weight. However, the favourable factors (temperature and harvesting time) have been made in the next stage to induce the PHA production (Md Din et al. 2006).

8.2.5 Genetically Engineered Bacteria

Recombinant organisms have been developed for enhancing PHA production. *E. coli* has been one of the most favoured hosts since growth-related PHA production is possible. Also, the ability to grow fast, to achieve high cell density from several inexpensive carbon sources (molasses and whey), and easy purification of the polymer from *E. coli* contribute to its popularity (Hahn et al. 1995). Owing to the massive acquaintance regarding *E. coli* genetics and its metabolic pathways, it plays a significant role in the commercial production of PHAs.

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Recombinant *E. coli* harbouring the *C. necator* PHA biosynthetic genes is able to accumulate PHB with a yield of 80–90% dry cell weight in fed-batch cultivation while a P(3HB) content of 76% dry cell weight can be obtained in a pH-stat fed-batch culture (Kim et al. 1992). Liu and coworkers, obtained a P(3HB) concentration of 80% dry cell weight by growing recombinant *E. coli* containing the *C. necator* PHA biosynthetic genes on molasses (Liu et al. 2008).

Genetically engineered cyanobacteria that accumulated PHB were transformed with the genes encoding PHB synthesis (3-ketothiolase, aceto acetyl-CoA reductase and PHB synthase) (Zhang et al. 1995). Metabolic engineering is being intensely explored to introduce new metabolic pathways to broaden the utilizable substrate range, to enhance PHB synthesis and to produce novel PHB in cyanobacteria. However, this area is totally new as far as cyanobacteria for PHB production and only several reports are published in this field. Various species of cyanobacteria accumulate considerable amounts of PHB, and the non PHB accumulating cyanobacteria have recently been genetically engineered by heterologous transformation with genes involved in the PHB pathway of *R. eutropha*, leading to the accumulation of the polymer. To develop an efficient system for PHB production by cyanobacteria, the genetic characterization of PHB accumulating cyanobacteria was studied in detail (Lee et al. 1994). The production of pigment free PHB granules by genetically engineered cyanobacteria was isolated from the species *R. eutropha*. Bacteria such as *Escherichia coli* are incapable of synthesizing or degrading PHB (Steinbukel et al. 1991). However, *E. coli* grows fast, even at higher temperature and is easy to lyse. Faster growth will enable it to accumulate a large amount of polymer. The easy lysis of the cells saves the cost of the purification of PHB granules (Kars et al. 2008). Hence, *E. coli* has been used to transfer PHB genes. PHB production has been studied mostly in recombinant *E. coli* cells harboring PHB synthesizing genes from *R. eutropha* in the study of Wang et al. (2008) and genetically engineered (recombinant) *E. coli* with the *Aeromonas hydrophila* biosynthetic genes (orf1) from *Aeromonas hydrophila* (orf1) using decanoate and odd-chain fatty acids as carbon sources (Park and Damodaran 1994). In the same context, Lee et al. (1997) examined various recombinants *E. coli* strains or their ability to accumulate a large amount of PHB in a whey-based medium. The highest PHB concentration and PHB content obtained were 5.2 g/L and 81% of dry cell weight respectively.

8.3 BIO-PESTICIDES PRODUCTION

One of the most insurgent contributions of science to the plant disease management is the development of Bt-based biopesticides and thereafter transgenic Bt crops. The growth and development of Bt-based biopesticides in the past and future has covered an extensive research area from dual culture to the spacious arena of omics, i.e., molecule to functional genomics. The genomic constitution of Bt conveys enthralling properties, such as an array of entomotoxin active against

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diverse insects, root dwelling pests, or larvae that after hatching rapidly burrow or bore into plant tissues. More to the point, the crops are frequently affected by different pests that are unable to be controlled by a *Bt* product alone. *Bt* crystal proteins are UV sensitive and degrade rapidly thereby losing their activity. Therefore, several applications are required through the entire growing season that invariably increases the cost of application. Technological advancements have led to the development of advanced *Bt* formulations that are more adaptive to harsh environmental conditions.

The key success of biopesticides lies in its impact on the target pest, market size, and variability of field performance, cost effectiveness, and end-user feedback. Technological challenges such as fermentation, formulation development and efficient delivery systems also affect the success of any biopesticide. In spite of the fact that *Bt* biopesticides have undergone extensive research, several formulations do not deliver effectively under field conditions. An integrated approach, i.e., development of biopesticides that also supports sustainable agriculture can further strengthen its role in plant disease management. Adopting cost-effective fermentations, using conventional and simple adjuvants/additives, and efficient harvesting processes might lead to the development of high potent, efficacious formulations that are also widely accepted. Activity spectrum, persistence, recycling and cost-effective formulation needs to be addressed to establish the biopesticides in an international market particularly for the farming community.

Bt is commercially used to control forests and agriculture insects; however, the utilization of *Bt* has been restricted due to its high cost of production through fermentation. Safe and evocative insects control actually comes with a hefty price tag. The raw materials used for the production of Bt-based biopesticides represent a substantial part of the overall production cost. Stanbury et al. (1995) estimated that 35–59% of the production cost was related to the fermentation medium. Therefore, for commercial purposes, there is an urgent need to find high yielding, low-cost and year-round available raw materials for *Bt* production. Various reports have been published recently on cost reduction of *Bt* production processes through substitution of high-cost medium ingredients of soy flour and fish meal with complex agro-industrial wastes (e.g., cassava starch, maize starch, rice straw, wheat bran, corn steep liquor, sugarcane molasses, cheese whey and coconut waste) (Adams et al. 1999; Abdel-Hameed 2001) and wastewater sludge (Tirado-Montiel et al. 2001). Recently, the concept and theories for using wastewater, wastewater sludge and other agro-wastes as a potential cost-effective technique for *Bt* formulations have become widely accepted, and extensive research has been carried out in the past decade. Different WWTPs were used as raw materials for the production of Bt-based biopesticides. Details are described as follows.

8.3.1 Fermentation

Bt fermentation of wastewater and/or wastewater sludge has been conventionally carried out by using submerged fermentation (Burges 1998), which is more extensively studied and well documented in the literature. Preliminary

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experiments on the utilization of wastewater sludge as a raw material for *Bt* biopesticides production were carried out by Tirado-Montiel et al. (2001). Sludge from various WWTPs, with or without hydrolysis, was tested for *Bt* growth, sporulation, and entomotoxicity production. The entomotoxicity (Tx) level reported was very low to the tune of 3,000−4,000 SBU/μl, (spruce budworm units per micro liters) as the sludge solids concentration was not yet optimized. However, the wastewater and wastewater sludge did show encouraging signs of growth support for the production of Bt biopesticides. Spruce budworm units refer to the toxicity of Bt crystal proteins when measured against spruce budworm larvae. Tirado- Montiel et al. (2001) also noted a low spores concentration of $1.0 \times 10^6 - 1.3 \times 10^7$ CFU/mL (colony forming units/ mL) with non-hydrolyse sludge $1.6 \times 10^6 - 1.8 \times 10^7$ with hydrolysis sludge under acidic conditions and $1.2 \times 10^5 - 2.0 \times 10^6$ CFU/mL with sludge supernatant in wastewater sludge when compared to a soya medium (1.5×10^8 CFU/mL). This research laid the foundation to the fact that the wastewater sludge does contain the necessary nutrients to support the growth, sporulation and crystal formation by *Bt*. Later, Tirado-Montiel et al. (2003) optimized different fermentation process parameters in a shake flask, namely, pH (7), temperature (30°C) and agitation rate (200–250 rpm). The results showed an increasing in the spore concentration to 1.2×10^8 CFU/mL and entomotoxixty (Tx) of 7000 SBU/μl. A linear relation was established between Tx and the maximum specific growth rate, overall Tx increased with the spore count, but specific entomotoxicity (sp Tx) to Tx per 1000 spores decreased with an increase in the spore count.

Yezza et al. (2006) probed Bt production using starch industry wastewater, slaughterhouse wastewater, and secondary sludge as raw materials in a 100-ml fermentor. The Tx of Bt fermented secondary sludge ($12 - 16 \times 10^9$ SBU/mL and starch wastewater (18×10^9 SBU/mL) was higher than the soybean-based synthetic medium (10×10^9 SBU/mL). Secondary sludge and starch industry wastewater proved to be highly effective media for cultivation of Bt at the pilot scale. Furthermore, there was a 30% increase in entomotoxicity in pilot plant fermenters (Yezza et al. 2004). The performance and reproductibility of the *Bt* fermentation process at the bench and pilot scale proved the versatility of Bt production in the wastewater and /or wastewater sludge medium. In fact, employment of the fed-batch strategy in a bench scale fermenter (10 L) increased the spore concentration from 5.62×10^8 to 8.6×10^8 CFU/mL and Tx from 13×10^9 to 18×10^9 SBU/mL (Yezza et al. 2005a). A lower spore concentration in wastewater sludge resulted in higher Tx whereas low Tx was reported at a high spore concentration in a synthetic medium. Yezza et al. (2005b) also tested the possibility of increasing entomotoxicity by using alternative pH control agents, NH_4OH/CH_3COOH as compared to conventionally used $NaOH/H_2SO_4$ for *Bt* fermented secondary sludge wastewater sludge in pilot scale fermenters. Irrespective of the fermentation medium, a sizeable increase in total cell count, spore count, protease activity and entomotoxicity was achieved when pH of the culture was controlled using NH_4OH/CH_3COOH. Entomotoxicity potency was improved by 22% and 14% in secondary sludge and a soybean medium, respectively, as compared to results

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obtained with conventional pH control agents combination of NaOH/H_2SO_4. The improvement of the entomotoxicity was an outcome of the addition of rapidly utilizable carbon (CH_3COOH) and nitrogen (NH_4OH) source through pH control, which stimulated crystal protein production and enhanced sporulation.

The pre-treatment conditions, namely thermal hydrolysis and oxidative hydrolysis optimized by Bernabé et al. (2005) were also tested for their viability in bench scale fermenters by Yezza et al. (2005a). The results proved thermal alkaline treatment to be an effective process in order to enhance the entomotoxicity. On the contrary, oxidatively, pre-treated sludge did not improve the entomotoxicity when compared to raw sludge. This could be due to the complete breakdown of biodegradable organic matter, especially various carbon and nitrogen sources, to innocuous forms. It is well known that H_2O_2 is a strong oxidizing agent and has strong ability to mineralize organic matter completely to carbon dioxide and water (Neyens et al. 2003). The total cell and spores count for *Bt* fermented thermal alkaline wastewater sludge were increased by 40 and 46%, respectively, as compared to Bt fermented raw wastewater sludge, the entomotoxicity increased from 12.0×10^9 SBU/mL (raw sludge) to 17×10^9 SBU mL (thermal alkaline pre-treated sludge).

According to many studies, wastewater sludge seems to be a very good source of carbon, nitrogen, phosphorus, and other nutrient for many microbial processes that could add value to sludge by producing certain valuable products, such as endotoxins, and spores of *Bt* as well as certain others compounds (vegetative insecticidal proteins-Vips, chitinases, proteases, and others) (Kaur et al. 2001), which contribute to the mortality of insects defined with the term of entomotoxicity (or potential biopesticides). A higher level of entomotoxicity is desired to reduce the production cost of biopesticieds further. Higher entomotoxicity depends on the type of raw material, assimilation of nutrients by *Bt* production of different synergistic factors in the fermented broth and post fermentation by adding additives, which synergize the crystal proteins. In this context, many studies were conducted to evaluate the effect of many factors on spore formation and entomotoxicity yield by *Bt,* such as the C:N ratio, oxygen transfer, sludge solid concentration and inoculum, foam formation (Pearson and Ward 1988).

A low C:N ratio in the secondary sludge and a high C:N ratio in the mixed sludge resulted in a higher entomotoxicity. The optimum value of the C:N ratio in combined sludge for *Bt* production was found to be 7.9–9.9. A higher specific sporulation rate and hence higher entomotoxicity were observed in sludge (10,000−12,000 SBU/ml) than the synthetic medium (9,500 SBU/mL). The entomotoxicity value increased linearly with the maximum specific growth rate. The specific sporulation rate (0.55 h^{-1}) exhibited an optimum value for maximum entomotoxicity.

Oxygen mass transfer is essential for any aerobic bioprocess. Maintaining the appropriate concentration of dissolved oxygen has been pointed out as an important factor in the fermentation of *Bt* (Flores et al. 1997). As the oxygen was supplied to meet the oxygen demand of *Bt* culture, the spore and toxin yields increased. However, beyond a certain stage of excess oxygen supply, the cell and

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spore yield decreased and the entomotoxicity remained constant suggesting the possible inhibitory effect of oxygen on metabolic activity of the bacterium, especially on its growth (Avignone-Rossa et al. 1992). Additionally, it is economical to avoid a higher air supply rate.

Increased cell growth, sporulation, and endotoxin production by *Bt* requires higher aeration rates which cause foaming. It is a serious disadvantage to the industry which can cause (1) loss of biopesticide spores and other metabolites that stick to the wall of the vessel after foams are broken, (2) mass transfer problems in the fermenter and (3) fouling of the gas outlet condenser and as a consequence, (4) compromising the aseptic operation of the vessel. Foam formation in biopesticides production is controlled externally by the addition of polypropylene glycol (PPG) and silicone-based antifoam agents (Pearson and Ward 1988). These antifoam agents affect nutrient and oxygen transport across the Bt cell membranes. In this context, Vidyarthia et al. (2000) studied the effect of various anti-foam agents including PPG, silicone, canola, olive on wastewater sludge and soya medium fermentation in bench-scale fermenters. They observed that the chemical anti-foam decreased the entomotoxicity by 25 to 40% whereas the vegetative oils did not cause any inhibitory effect. In fact, the synergistic effect of vegetable oils increased with the monounsaturated fat content supporting *Bt* growth. Foam formation in sludge medium depends on sludge solids differing with the type of sludge (primary, mixed and secondary) and sludge composition, Thus, foam control plays an important role in wastewater sludge- based Bt fermentation, which needs to be carried out prudently to enhance the biopesticide potential.

Bt fermentation is oxygen transfer limited and largely influenced by the rheology of the medium. It was reported that an increase in the oxygen mass transfer rate resulted in a concomitant increase in yield efficiency of the biopesticides (Vidyarthi et al. 2002). The rheological properties (mainly viscosity) of the sludge are determined by many factors, including total solids concentration and particle size distribution.

Viscosities studies performed on raw, pre-treated (sterilized and thermal alkaline hydrolysed or both types of treatment) and *Bt* fermented secondary sludge at different solid concentrations (10—40 g/L) have established correlations between rheological parameter (viscosity), solids (total and dissolved) concentration and entomotoxicity (Brar et al. 2005b). Changes in viscosity with total solids concentrations were represented by the exponential law and sludges, in general, were thixotropic and pseudo-plastic. Moreover, Tx was higher for the hydrolyzed fermented sludge in comparison to the raw ferment sludge, owing to increased availability of nutrients and lower viscosity that improved oxygen transfer in the former case. Interestingly, the shake flask results were reproducible in the fermenter. Similar rheological (viscosity and particle size) studies carried out in all three types of sludge (primer, secondary and mixed) showed exponential correlation with solids concentrations (Brar et al. 2004). The correlation with particle sizes could not be drawn directly, except for the primary sludge where the particle size (50–70 μm) increased proportionally with an increase in viscosity and

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solids concentrations in comparison to the secondary (42–55 μm) and the mixed sludge (27–32 μm). The contribution to non-Newtonian behaviour was a cumulative effect of viscosity and particle size, which were further influenced by the treatment processes, namely, sterilization, hydrolysis, and fermentation. Rheology was mainly influenced by the three factors: solids concentration, type of sludge and type of treatment processes. It is clearly evident from these studies that viscosity and particle size distribution of the fermented broths can have tridentate influence on the selection of growth substrate for fermentation to formulate biopesticides (Chappele et al. 2000).

The biodegradability and bioavailability of wastewater sludge are limiting factors in their efficient utilization in mass scale processes. It is known that, due to the presence of a large amount of bioavailable substrate in wastewater sludge, the microbial fermentation will be enhanced, resulting in a higher concentration of desired end-product biopesticides. However, *Bt* biopesticides production from wastewater sludge is challenging at higher solids which would provide more nutritive elements to produce higher Tx. Thus, Barnabé et al. (2005a) explored pre-treatment strategies to improve the entomotoxicity by *Bt* in wastewater sludge. The developed strategy consisted of hydrolysis (alkaline or thermo-alkaline) alone or in combination with partial oxidation using H_2O_2. After preliminary tests, alkaline hydrolysis, thermal alkaline hydrolysis and the combination of thermo-alkaline hydrolysis with partial oxidation were selected as they increased the entomotoxicity by 50% in mixed and/or secondary sludge. Principal factors contributing to the increase in Tx were: solubilisation of proteins and organic carbon, the presence of high sodium content after the hydrolysis as well as decrease in viscosity. The treatments were then optimized in Erlenmeyer flasks by employing surface response methodology. Finally, when the optimal conditions for alkaline and thermo-alkaline hydrolysis were tested in bench scale fermenters, entomotoxicities between 17 and 19×10^9 SBU/L were obtained in pre-treated sludge containing up to 38 g/L suspended solids. The entomotoxicities were 37 to 49% higher than the untreated /raw sludge (25 g/L SS) and 1.7 to 1.9 times higher than the semi-synthetic conventional medium, soya. Secondary sludge, hydrolyzed or non-hydrolyzed, yielded higher specific entomotoxicity as compared to the soya medium. Further, Barnabé et al. (2005a) showed that the ratio of Tx to purified spores was 0.03–0.048 in the sludge as compared to soymeal (0.013). Thus, the spores of Btk HD-1 produced in the wastewater sludge were more entomotoxic than those produced in the conventional medium containing soya. The improvement of nutrient assimilation by the pre-treatment technologies open doors for utilization of higher solids of sludge as well as the possibility of eliminating the sterilization step in the *Bt* fermentation process so as to compensate for the economics. Meanwhile, Leblanc (2003) also tested the possibilities of increasing entomotoxicity by the addition of nutrients (e.g., glucose, ammonium, sulfate and yeast extract) and mixing of sludge. The result were encouraging as addition of glucose (2 g/L) increased Tx from 11×10^9 SBU/L to 13×10^9 SBU/L in non-hydrolyzed sludge and a minor increase from 14×10^9 SBU/L to 15×10^9 SBU/L in hydrolyzed sludge.

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Bt entomotoxicity is a sum of various factors crystal proteins, spores, enzymes (chitinase, protease), vegetative insecticidal proteins (Vips) and antibiotics. In the case of enzymes, *Bt* strains produce intracellular and extracellular chitinases and protease. Brar et al. (2005a) investigated the production of biopesticides, protease and chitinase activity by *Bacillus thuringiensis* grown in raw wastewater sludge at a high solids concentration (30 g/L). The rheology of wastewater sludge was modified with the addition of Tween-80 (0.2% v/v). This addition resulted in 1.6 and 1.3-fold increase in cell and spore count, respectively. The maximum specific growth rate augmented from 0.17 to 0.22 h^{-1} and entomotoxicity increased by 29.7%. Meanwhile, volumetric mass transfer coefficient ($k_L a$) showed marked variations during fermentation, and oxygen uptake rate (OUR) increased 2-fold. The proteolytic activity increased while chitinase decreased for Tween amended wastewater sludge, but the entomotoxicity increased. The specific entomotoxicity followed power law when plotted against spore concentration and the relation between Tx and protease activity was linear. The vip3 class is the most widely studied Vips. Estruch et al. (1996) reported that the gene coding for Vip3A persists until sporulation. It is secreted in a soluble form by *Bt* with possibility of adsorbing to spores or crystal proteins. It could also be synthesized after the ingestion of spores of *Bt* by an insect (Donovan et al. 2001).

8.3.2 Formulation

Wastewater and wastewater sludge formulations could affect the application strategy as the rheology will be entirely different from conventional formulations. Formulation plays a significant role in determining the final efficacy of a *Bacillus*-based product, as do the processes of discovery, production, and stabilization of the biomass of the bio-control agent. If a *Bacillus* strain reaches the stage of formulation development via poorly conceived discovery, production, or stabilization protocols, the bio-control and, therefore, commercial potential of this agent will be compromised. Useful formulations of biomass of *Bacillus* spp. for biocontrol of plant diseases are currently in the marketplace but this in no way indicates that improvements in formulation technology are not needed. The formulations of commercial products containing *B. thuringiensis* have undergone a wide range of transitions over the years, including aqueous suspensions, wettable powders, oil flowables, insect pellet baits, dry flowable-fluidized bed agglomerates, and dry flowable low pressure extrusion granules. With continued research, similar improvements in formulations can be anticipated for plant disease biocontrol products.

Main factors to be taken into account during formulation development are biopesticides stability, physicochemical proprieties of ingredients, biological activity, mode of action, formulations costs and market preference. Many studies (Brar et al. 2004), focuses on the development of formulation and specifically, development of aqueous flowable (suspension) formulations for *Bt*-based biopesticides from wastewater sludge. Different inserts like sorbitol, sodium monophosphate, sodium metabisulphite, sorbic acid, propionic acid, Tween-80, Triton X-100 and glycerol were tested for formulations. Five different formulations for

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non-hydrolyzed (NH) secondary sludge were tried, and the best combination selected on the basis of various physical parameters like viscosity, particle size, suspendibility, entomotoxicity, and microbiological purity tests. F5 formulations (for secondary sludge) comprising sorbitol, sodium monophosphate and sodium metabisulphite gave better physical and biological characteristics with a small effect on entomotoxicity and spore concentration after 120 days at pH 6, 6.5 and temperatures 40 and 50°C and viscosity change at 40 and 50°C. The formulations were more stable at pH 4.0 to 5.0 and temperatures 4 to 30 degrees C whereas at pH 6.0 and 6.5 and temperatures 40 and 50°C, there was degeneration of the product. Lower proteolytic activity and physical factors like ionic strength and surface group changes at pH 6 and 6.5 were responsible for the instability of the formulation.

Screening of different adjuvants, namely, suspending agents, phagostimulants, stickers, antimicrobial agents, and UV screens to develop aqueous biopesticidal suspensions of *Bt* variety kurstaki HD-1 fermented broths, specifically, nonhydrolyzed sludge, hydrolyzed sludge, starch industry wastewater, and soya (commercial medium), were investigated (Brar et al., 2006). The selected suspending agents [20% (wt:vol)] included sorbitol, sodium monophosphate, and sodium metabisulfite with corresponding suspendibility of 74–92, 69–85, and 71–82%, respectively. Molasses [0.2% (wt:vol)] increased adherence by 84–90% for all fermented broths. The optimal phagostimulants [0.5% (wt:vol)], namely, soya and molasses, caused entomotoxicity increase of 3–13 and 7–13%, respectively. Sorbic and propionic acids showed high antimicrobial action [0.5% (wt:vol)], irrespective of fermentation medium. Sodium lignosulfonate, molasses, and Congo red, when used as UV screens [0.2% (wt:vol)], showed percent corresponding entomotoxicity losses of 3–5, 0.5–5 and 2–16%, respectively. The *Bt* formulations, when exposed to UV radiation, showed higher half-lives (with and without UV screens) than the fermented broths or semisynthetic soya medium and commercial *Bt* formulation. UV screen-amended nonhydrolyzed, hydrolyzed, and starch industry wastewater formulations showed 1.3–1.5-fold higher half-lives than commercial *Bt* formulation. Thus, the recommended formulation comprises sorbitol, sodium monophosphate, sodium metabisulfite (suspending agents); molasses, soya flour (phagostimulants); molasses and skimmed milk powder (rainfasteners); sorbic and propionic acids (antimicrobial agents) and sodium lignosulfate; and molasses and Congo red (UV screens). These waste-based *Bt* formulations offer better UV resistance in comparison with commercial formulation.

8.4 VERMICOMPOSTING BIOTECHNOLOGY

Municipal sewage sludge from domestic wastewater treatment is generated in large quantities, which is hazardous and creates problems for safe disposal due to the presence of certain environmental contaminants, such as organic compounds, heavy metals, and pathogens. Raw sewage sludge generated in vast quantities, with

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its nutrient content, has been used in an indiscriminate and inappropriately-timed manner for fertilizing agricultural fields. The problem of sludge disposal and management exists in developing countries and probably in other parts of the world. The indiscriminate disposal of sewage sludge on agricultural fields induces soil and plant toxicity, which creates depressive effects on the metabolism of soil microorganisms by drastically modifying the soil's physicochemical and biological environments. Therefore, it is absolutely essential for sewage sludge to undergo additional stabilization treatment prior to agricultural use (Hait and Tare 2011).

Heavy metals in domestic and industrial wastewater are concentrated in sewage sludge at high levels with the total content ranging from 0.5 to 2% on a dry weight basis and at 6% in extreme conditions (Gupta and Garg 2008). Therefore, concerns for the safe application of sewage sludge are mainly focused on the heavy metal contamination that can arise. Copper and cadmium often have high concentrations in sewage sludge and may affect the health of people and animals through the food chain if sludge is applied improperly. Methods for decreasing the contents and bioavailability of these elements in sewage sludge are worthy of research. Unlike organic compounds, metals cannot be degraded (Lasat 2000), rather they must be removed. Such an approach can be prohibitively expensive. Also, the metal removing process often employs stringent physicochemical agents, which can dramatically inhibit soil fertility with subsequent adverse impacts on the ecosystem. Another method is to use chemical immobilization amendments to reduce metal bioavailability. The addition of chemical immobilization amendments may only immobilize lethal levels for restricted periods of time and introduce other harmful chemicals. Phytoremediation is recognized as the most commercially and environmentally friendly technology available (Lasat 2000), but up to now, only a limited number of plants have been found to have the phytoaccumulation ability and much less can be used for field phytoremediation because of low biomass production.

There is a need for ecologically as well as economically sustainable technologies enabling recovery of recyclable constituents from sewage sludge as it is rich in nutrients and has high organic matter content. Vermicompost technology is ecologically and economically sustainable and has been widely used for processing of sewage sludge over the years (Sinha et al. 2010). Details of vermicompost are described below.

8.4.1 Wastewater Sludge as Biofertilizer

The recovery of nutrients by modification of wastes, like municipal solid waste, industrial solid waste, agricultural residues, and animal wastes, etc. is necessary for their management and for reducing environmental degradation. Recycling of organic wastes through vermicomposting biotechnology is an emerging trend as an "environmentally sustainable," "economically viable" and "socially acceptable" technology all over the world. In this context, many studies reported on the feasibility of utilization of vermicomposting technology using the earthworm *Eudrilus eugeniae* for managing municipal sewage sludge by conversion into beneficial bio-fertilizer. According to Iwai et al. (2013), sewage sludge was used at

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various concentrations of 1, 5, 10, 15, 20, and 25% to test for avoidance behavior of the earthworm. The mix of sewage sludge with cassava wastes and cow dung was subjected to compost treatment with and without earthworm treatment for 30 days. During the study period, data was collected on the surviving earthworms' biomass, together with chemical analysis of wastes before and after treatment. The results indicate that the 5% concentration of sludge mixed with cassava waste was ideal for *Eudrilus eugeniae* to treat. There was a decrease in pH, organic carbon concentration, C:N ratio, and increase in electrical conductivity (EC), nitrogen, potassium and phosphorus concentrations in all the vermireactors. Total Kjeldahl nitrogen (TKN), available phosphorus and potassium concentrations were increased compared to compost without earthworm treatment at 50 24, and 10%, respectively. The heavy metal concentrations (Cr, Cu, Cd, Pb, and Hg) in final vermicomposts were lower than in the initial feed mixtures. Vermicompost with cassava pulp could increase nutrients and reduce Cr, Cu, Pb and Hg concentrations in sewage sludge by 2.31 14.03 1.80 and 33.75%, respectively and vermicompost with cassava peel could reduce Cu and Hg by 34.3 and 14.5%, respectively. The earthworm biomass was increased by 40–90% and could survive 60% from the beginning.

Zularisum et al. (2010) reported the potential of tiger worms (*Eiseniafetida*) in vermiculturing Municipal Sewage Sludge (MSS) into beneficial vermicompost or biofertiliser. The results showed that vermicomposts produced by tiger worms gradually possessing higher nutrient contents as the composting process progressed. Total nitrogen was found to increase from 19.6 to 35.7 $\text{mg}\,\text{L}^{-1}$, total phosphorus from 9.45 to 10.87 $\text{mg}\,\text{L}^{-1}$ and total potassium from 3.44 to 4.80 $\text{mg}\,\text{L}^{-1}$, respectively. In addition, conversion of MSS to vermicompost was found to be 93% by weight, and worm biomass showed 30% increment from its initial weight within 21 days. Thus, the study shows that vermicomposting of MSS into organic fertiliser is feasible besides providing a safe and practical disposal method for sewage sludge.

8.4.2 Types of Wastes and Earthworm Species Used

The use of different organic substrates and species of earthworms employed and their suitability in vermicomposting is presented in Table 8.2 (Thomas and Trivedy 2002). Substrates, especially agricultural residues, have been tested extensively in combination with a readily biodegradable substrate such as Cow Dung (CD). Kale et al. (1986) reported the suitability of neem cake as an additive in earthworm feed and its significance in the establishment of the micro flora. *E. eugeniae* was tolerant to the neem cake in the culture medium up to a concentration of 1.6–6.4% and had a positive effect on earthworm biomass production. *E. eugeniae* was mass cultured on 6 different feed formulate prepared by mixing CD, sheep and horse dung with other organic wastes such as rice polish, wheat barn and green gram bran vegetable waste and eggshell powder in various combinations (Bano et al. 1987). A laboratory-scale study was conducted to access the suitability of powdered rubber leaf litter as vermiculture substrate for *P. excavatus*, *E. eugeniae*, and *E. fetida*.

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Table 8.2. Earthworm species employed for vermicomposting of solid organic wastes

Solid organic waste	*Species employed*	*References*
Press mud	*Pheretima elongate*	Singh (1997)
	Eudrilus eugeniae, Eisenia fetida	Munnoli (2007)
	Megascolex megascolex	Hand et al. (1988)
Canteen waste	Eisenia fetida	Kale (1994)
Tomato skin *seed*	Pheretima elongate	Singh (1997)
Onion residue	Eisenia fetida/Eudrilus eugeniae	White (1996)
Sericulture waste	Perionyx excavates	Gunthilingaraj and Ravignanam (1996)
Board mill sludge	Lumbricus terrestris	Butt et al. (2005)
Sericulture waste	Phanerochaete chrysosporium	Kallimani (1998)
Sugar cane residues	Pheretima elongate	Bhawalkar (1989)
Gaur *gum*	Eudrilus eugeniae	Suthar (2006)
Agricultural residues	Eudrilus eugeniae	Kale (1994)
Sago *waste*	Lampito mauritii	Rajesh et al. (2008)
Sago waste	Eisenia fetida	Subramanium et al. (2010)
Onion *waste*	Eudrilus eugeniae	Mishra et al. (2009)
Garlic waste	Eisenia fetida	Mishra et al. (2009)
Paper mill *sludge*	Eisenia fetida	Kaur et al. (2010)
Press mud, bagassi, sugar	*Drawida willsi*	Kumar et al. (2010)
Press *mud*	Perionyx ceylanensis	Mani and Karmegam (2010)

8.4.3 Some Important Studies on Vermicomposting Biotechnology

Visvanathan et al. (2005) studied vermicomposting in great details and found that most earthworms consume, at the best, half their body weight of organics in the waste in a day. *Eisenia fetida* can consume organic matter at the rate equal to their body weight every day. Earthworm participation enhances natural biodegradation and decomposition of organic waste from 60 to 80% over the conventional aerobic & anaerobic composting. Given the optimum conditions of temperature (20–30°C) and moisture (60–70%), about 5 kg of worms (numbering ~10,000) can vermiprocess 1 ton of waste into vermicompost in just 30 days. Upon vermicomposting the volume of solid waste is significantly reduced from approximately 1 cum to 0.5 cum of vermi-compost indicating a 50% conversion rate; the rest is converted into worm biomass.

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Kale (1998), Seenappa et al. (1995), Gunathilagraj and Ravignanam (1996), and Lakshmi and Vizaylakshmi (2000) studied the degradation and composting of "wastewater sludge" from paper pulp and cardboard industry, brewery and distillery, sericulture industry, vegetable oil factory, potato and corn chips manufacturing industry, sugarcane industry, aromatic oil extraction industry, and logging and carpentry industry by earthworms. These organic wastes offer excellent feed materials for vermicomposting by earthworms. Kale and Sunitha (1995) also studied the vermicomposting of waste from the mining industry which contains sulfur residues and creates disposal problems. They can also be fed to the worms mixed with organic matter. The optimum mixing ratio of the sulfur waste residues to the organic matter was 4%.

Saxena et al. (1998) studied the vermicomposting of "fly-ash" from the coal power plants, which is considered as a hazardous waste and poses serious disposal problems due to heavy metal contents. As it is also rich in nitrogen and microbial biomass, it can be vermicomposted by earthworms. They found that 25% of fly-ash mixed with sisal green pulp, parthenium and green grass cuttings formed excellent feed for *Eisenia fetida* and the vermicompost was higher in NKP (Nitrogen, Potassium, and Phosphorus) contents than other commercial manures. The earthworms ingest the heavy metals from the fly-ash while converting them into vermicompost.

8.4.4 Effects of Different Parameters in Vermicomposting

pH. Earthworms are very sensitive to pH, and thus, pH of soil or waste is sometimes a factor that limits the distribution, numbers and species of earthworms. In a vermicomposting experiment with different soil proportions (1:3 1:4 1:5 1:6) of CD, the earthworms reduced the pH: *E. fetida*, 6.7 to 6.1; *E. eugeniae*, 6.7 to 6.0 and *M. megascolex*, 6.7 to 6.4 (Munoli and Bhosle 2009). Several researchers have stated that most species of earthworms prefer a pH of about 7.0 (Nayaran et al. 2000). Edwards (2004) reported a wide pH range (5.0–9.0) for maximizing the productivity of earthworms in solid organic waste (SOW) management. Bhawalkar (1989) suggested a neutral substrate pH for vermicomposting using deep burrower species *Pheritima elongata*. Satchell (1955) reported that *Bimastos eiseni*, *Dendrobaena octaedra* and *Dendrobaena rubida* were acid-tolerant species, while *Allolobophora caliginosa*, *Allolobophora nocturna, Allolobophora longa* were acid tolerant. Singh et al. (2005) reported that *P. excavatus* performs well in a wide range of substrate pHs. The decrease in pH values when press mud was treated with *M. megascolex*, *E. eugeniae* and *E. fetida* showed a decreasing trend in pH from 8.6 to 6.7 during vermicomposting over a period of 60 days (Munnoli 2007). A decrease in pH was recorded in CD vermicomposting using *E. fetida* and *L. mauritti* (Suthar 2006) and *Pheritima elongate* using tomato skin seed waste as substrate (Singh 1997) or kitchen waste (Nayaran et al. 2000).

Moisture. In the natural soil-earthworms interaction, when there is a loss of soil moisture, earthworms tend to move to a safer area with more moisture. When

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the whole area is dry, the earthworms adjust themselves and survive through large water loss from the body. *L. terrestris* can lose up to 70% and *A. caliginosa* 75% (Edwards and Lofty 1977). Experiments conducted using *P. elongata* showed an optimum moisture of 70% for the treatments of potato peel waste (Munnoli 1998), whereas press mud required 60–70%. Trials for vermicomposting CD showed the optimum moisture of 60–70% with a higher number of *E. eugeniae*, *E. fetida* and *M. megascolex* earthworms (Munoli 2007). Strains associated with endospore-forming Bacillus survive extreme weather conditions and become active when favorable soil moisture conditions are regained (Munoli 2007). Evans and Guild (1948) reported that *A. chlorotica* produced more cocoons at moisture contents of 28 to 48%. Juveniles, who show high tolerance to low moisture, when transferred to a new environment with favorable moisture, adjust faster than adult worms (Singh 1997). Such experiments were also carried out with the cocoons of *E. fetida* and *E. eugeniae*, which were transferred to culture boxes containing CD while adult earthworms were separately transferred. More juveniles were found in culture boxes with cocoons than in culture boxes with adults (Munoli 1998). Therefore, moisture level is a significant factor in the set-up of a vermicomposting unit (Scheu 1987) in village environments units and needs to be carefully designed to hold water without causing water logging.

Temperature. Evans and Guild (1948) reported that the activity, metabolism, growth, respiration, reproduction, fecundity and growth period from hatching to sexual maturity of earthworms are greatly influenced by temperature. Cocoons hatch sooner at higher temperatures. A temperature range of 20–30°C for vermibeds was suggested using *E. fetida, E. eugeniae* and *P. excavatus* (Bhiday 1994).

Organic Matter. Earthworms use a wide variety of organic materials for food, and even in adverse conditions, they extract sufficient nourishment from the waste or soil to survive. The kind and amount of food available influences not only the size of an earthworm population but also the species present as well as their rate of growth and fecundity. Zezonc and Sedor (1990) reported that greatest weight increase in *E. fetida* was obtained when 50 g of soil was mixed with 150 g cellulose waste. Nayak and Rath (1996) claimed that organic residues comprising city, industrial, agricultural farms, household and kitchen wastes with dead or decaying materials can be used as bedding materials for vermicomposting. Joshi (1997) suggested that animal manure, dairy and poultry waste, food industry waste, slaughterhouse waste or biogas sludge could be used for recycling through vermicomposting. The best results of vermicomposting were obtained from paper and food manufacturing industries when treated with *E. fetida, E. andrei* and *P. excavatus* (Piccone et al. 1986).

Micro- and Macro-nutrients and Microbial Population in Vermicasts (VCs). There are varying reports on the nutrient contents of VCs (Narayan et al. 2000) whereas Ranganath et al. (2001) ascertained nutrient values for a good VC, based on their study on urban wastes, also suggested the rate of application of VC. Ghilarov (1963) claimed that the number of microorganisms in VCs was 1.64 1.35 and 1.97 fold higher than in regular soil in three different fields, namely oak forest,

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rye and grass, respectively. A 5 and 40 fold higher level of bacterial counts was reported in VC more than the surrounding soil in the case of potato peel waste (Munnoli et al. 1998) and paper industry sludge (Kavian and Ghatnekar 1996), respectively. An increase in hydrolytic microflora in vermicomposting of SOWs was reported by Singh (1997) and Munnoli (2007). Monson et al. (2007) reported an increase in nutrients in kitchen waste vermicomposted by *E. eugeniae*: in N, from 1.31 to 2.12%; in P, from 0.121 to 0.7%; in K, from 0.45 to 0.48% and the C:N ratio decreased from 32.45 to 13.66%. A higher microbial load was also observed in paddy fields to which VC was applied (Kale 1994). An increase in the microbial population was recorded with potato waste using *Pheretima elongata* (Munoli 1998) and with press mud waste using *E. fetida, E. eugeniae* and *Megascolex megascolex* when compared with the surrounding soil (Munnoli 2007). Kavian and Ghatnekar (1996) reported an increase in nutrients when press mud was blended with saw dust and treated using three different earthworm species *E. fetida, E. eugeniae* and *P. excavatus* individually (Monocultures) and in combination (Polycultures). Kale et al. (1986) reported that earthworm's burrows lined with VCs are an excellent medium for harbouring N-fixing bacteria. Loquet et al. (1977) and Bhattacharya et al. (2000) also recorded an increase in the microbial count of VCs compared to traditional compost. Kumar et al. (2010) reported the contents of VCs. *E. fetida* VCs from sheep manure alone or mixed with cotton wastes were analyzed for their properties and chemical composition every 2 weeks for 3 months and compared with the same manure without earthworms. Earthworms accelerated the mineralization rate and resulted in castings with a higher nutritional value and degree of humification, suggesting that this kind of industrial wastes can be used in vermicomposting (Alabanell et al. 1988). Madhukeshwar et al. (1996) claimed that any kind of organic waste generated in an agro-based industry or biotechnology unit when treated with earthworms would be resourceful VC. When *E. fetida* was used for vermicomposting, it resulted in an increase in P, Ca, Mg and a decreased of K (Orozco et al. 1996).

Giraddi and Tippanavar (2000) studied the biodegradation of waste from the fruit-pulp, biscuit and sugar industries were bio-degradable in field designs using *E. eugeniae, E. fetida* and *Perionyx excavatus*, for waste management. The wastes were bio-converted to compost in 40–90 days. The quality of compost obtained had increased micro and macro nutrients. Butt (1993) explored the possibility of treating paper mill sludge with spent yeast from the brewery industry using *L. terrestris* whereas the same industrial waste was treated with *E. andrei* by Elvira et al. (1998). They also investigated the vermicomposting of sludge from paper mill and dairy industries mixed with cattle manure using *E. Andrei* in 6-months pilot-scale experiments where the number of earthworms and biomass increased significantly. The VCs were rich in N, P, and K and had a good structure, a low level of heavy metals, lower conductivity, high humic acid contents and good stability and maturity. They also reported the growth of *E. andrei* by using the paper mill and dairy mill sludge in pure wastes by mixing with different proportions of cattle manure (Elvira 1998). Studies on the possible use of paper and dairy mill sludge during vermicomposting confirmed that such material might

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be a valuable component of breeding media for *E. fetida* earthworms. But the content of mineral N and total K were low (Zablocki et al. 1999).

8.4.5 Applications of Vermicomposting Biotechnology

Carbon Mineralization during Vermicomposting. Like the other members of the organic matter decomposing community, earthworms can assimilate carbon from the most recently deposited organic matter fractions, consisting mainly of readily degradable substances. In all cases, the degradation process resulted in carbon losses by mineralization, which decreases the amounts of total organic carbon, and thus, reduces the carbon contributions to the organic matter (Dominguez et al. 2000). Although earthworms consume and process large amounts of organic matter, their contributions to the total heterotrophic respiration is very low due to their poor assimilation efficiency and only when there are large active earthworm populations, as in vermicomposting systems, can they contribute to an appreciable extent to the heterotrophic respiration.

Role in Nitrogen Cycle. Earthworms had a significant impact on nitrogen transformations in the pig manure by enhancing nitrogen mineralization, so that most mineral nitrogen was retained as nitrate. The net total nitrogen, in all treatments and times, decreased with N losses being more marked during the final stages when earthworm activity was higher. The different nitrogen fractions followed trends similar to the total nitrogen. In all treatments, during the final stages of the process, when the earthworm population was bigger and more active, important reductions in organic nitrogen content and a high nitrification rate were noted (Dominguez et al. 2000). This implies that earthworm (*Eisenia andrei* in this case) modified conditions in the manure that favoured nitrification, resulting in the rapid conversion of ammonium into nitrates. Similar results have been reported by Hand et al. (1988) who found that *Eisenia fetida* in cow slurry increased the nitrate concentration of the substrate.

Vermicomposting and Heavy Metal Availability. It is important to know the changes in total and available contents of heavy metals in the organic matter during the vermicomposting process, because they may cause problems in some animal manures, sewage sludge, and industrial organic wastes. Dominguez et al. (2000) reported that, as a consequence of carbon losses by mineralization during vermicomposting, the total amounts of heavy metals increased (between 25 and 30%) and the amounts of bioavailable heavy metals tended to decrease with a decrease of between 35 and 55% in the bioavailable metals in two months. Similar results were reported in other studies for both composting and vermicomposting, implying a lower availability of these elements for plants from vermicomposts. During vermicomposting, heavy metals tend to form complex aggregates with the humic acids and the most polymerized organic fractions.

Vermicomposting biotechnology used for waste and land management and for improving soil fertility to promote crop productivity and production of valuable bioactive compounds of great medicinal values has grown considerably in recent years all over the world and has been scientifically improved (UNSW 2002). It is like getting “gold from garbage” (e.g., from SOWs to highly nutritive biofertilizer). The three versatile species *E. fetida*, *E. euginae* and *P. excavatus* performing extensive social, economic & environmental functions occur almost everywhere.

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8.5 ENZYMES PRODUCTION

Macromolecular organic substrates must be enzymatically hydrolyzed to smaller subunits before they can be taken up and metabolized by the microbial cell (Gessese et al. 2003). The initial hydrolytic reaction is believed to be the rate-limiting step in the overall process of organic matter degradation (Dueholm et al. 2000). Several studies have indicated that enzymatic hydrolysis of organic compounds by activated sludge microorganisms under aerobic conditions are distinguishably more efficient than under anaerobic and/or anoxic conditions (Henze et al. 1995). In recent years, there has been growing interest in the study of enzymatic activities in wastewater treatment (Goel et al. 1998; Watson et al. 2004). Particularly, there has been a growing interest in the study of exoenzymes in natural water bodies and wastewater treatment plants (Gessesse et al. 2003). Knowledge of the spatial and temporal variation of enzymes in such ecosystems, the organisms producing the different enzymes, and factors affecting enzyme activity, are essential to understand and optimise organic matter removal in wastewater treatment plants. It is strongly believed that the enzymatic approach will significantly contribute to knowledge of the biochemical factors controlling the treatability of wastewater and sludge, and may greatly help the optimization of the process of hydrolyzing and mineralizing organic pollutants. In addition, it may yield technological information on the production of a variety of exogenous enzymes, which can be applied to improve wastewater purification systems (Kibret et al. 2000).

8.5.1 Enzymatic Sludge Hydrolysis

In the activated sludge process, bacteria tend to aggregate and form sludge flocs, which consist of microbial, prokaryotic (bacteria, archaea), and eukaryotic (algae, fungi) microorganisms kept together by extracellular polymeric substances (EPS). Various studies reported that sludge flocs constitute 60–70% of the organic fraction (Xu 2003). In fact, microbial cells undergo lysis or death, during which the cell contents (substrates and nutrients) are released into the medium and provide an autochthonous substrate that is subsequently used in microbial metabolism. Microbial metabolism and a portion of the carbon are released as products of respiration, resulting in a reduced overall biomass production. This process is known as lysis-cryptic growth, which was first introduced by Ryan (Guo et al. 2007). Lysis-cryptic growth involves two stages: lysis and biodegradation. As the first step in cell fractionation, cell lysis refers to the cell destruction of microbial cells as catalyzed by a hydrolytic enzyme (mainly protease). During this process, the cell contents (substrates and nutrients) are released into the medium and provide an autochthonous substrate that is used in microbial metabolism. The biomass then grows on an organic lysate; however, this growth is different from that on the original substrate and is therefore termed as cryptic. The rate-limiting step of lysis-cryptic growth is the lysis stage (Guo et al. 2007) An increase in the lysis efficiency can, therefore, lead to an overall reduction in sludge production and play an important role in reducing investment and operational costs as well as in optimizing the existing sewage treatment system.

Hydrolase can enhance the sludge hydrolysis. Previous studies have shown that some microbial strains exhibit extracellular hydrolytic enzyme secretion, and other commercial hydrolytic enzymes are often directly used in reactors to promote sludge lysis. Table 8.3 lists some enzymes that the hydrolysis of complex organic structures in the degradation of biodegradable particulate organic matters heavily depends on hydrolytic enzymes. Hydrolases, including protease, amylase, and lipase enzymes, are produced by a large number of mixed flora. Hydrolysis is the primary agent of deflocculation, hydrolysis, and oxidation of sludge flocs. It is also the first step in breaking down big molecules. The large, insoluble organic molecules in activated sludge flocs can be broken down into simpler carbohydrate molecules by the action of hydrolytic enzymes. The first step in protein degradation involves breaking the protein down into peptides, or into two peptides and amino acids. Amino acids can be further converted into some low-molecular-weight organic acids, ammonia, and carbon dioxide.

Sludge floc hydrolysis heavily depends on hydrolytic enzymes. Furthermore, this process can be enhanced by the combination of enzymes, as demonstrated by Roman et al. (2006). The combination of protease, lipase, and endoglycanases can accelerate the solubilization of municipal sludge. According to Molla et al. (2001) and Fleury (2007), mixed fungal cultures can enhance substrate utilization

Table 8.3. Enzymes with enhancement in the hydrolysis of sludge microbial hydrolases

Material	*Enzyme*	*Source*	*References*
Cellulose materials	Cellulose	RutC	Roman et al. (2008)
Chitin	Chitinase	*Actinobacteria*	Metcalfe et al. (2002)
Keratin	Keratinase	*Chysosporium keratinophilum*	Sngh et al. (2002)
Sewage sludge	muramidase	*Ba2cillusstearotherm ophilus*	Xu et al. (2003)
Starch materials	Amylase	*Bacillus licheniformis*	Zhang et al. (1995)
Protein	Protease	*Raoultella*	Azize et al. (2005)

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through the combination of enzymes, and that the symbiotic association of a mixed fungal culture can improve the fungal colonization of the substrate. The mixed fungal culture of *Aspergillus niger* and *Penicillium corylophilum* reportedly degraded sludge more efficiently (COD, 92%) compared with the control (uninoculated) after six days of sludge fungal treatment (TSS, 4% w/w) (Alam et al. 2003). Wawrzynczyk et al. (2003) confirmed the enhancement of sludge floc hydrolysis through a combination of enzymes in batch experiments, and a direct correlation between the hydrolase dose and the sludge dissolution efficiency was found. Although hydrolytic enzymes play an important role in sludge dissolution, the organisms in the traditional activated sludge secrete smaller amounts of enzymes that can enhance the sludge dissolution efficiency. Therefore, sludge minimization technologies are typically accomplished by adding bacteria with hydrolytic enzyme secretory function, commercial enzymes, or antibiotics, among others. However, such an approach is relatively expensive. Therefore, an effective and inexpensive solution for sludge minimization in water treatment facilities is needed.

An appropriate and effective way of addressing this problem is to culture microorganisms with hydrolytic enzyme secretory function. Filamentous fungi, which are naturally present in sewage sludge either as spores or vegetative cells, were the selected species. Filamentous fungi have an exceptionally high capacity to express and secrete proteins, enzymes, organic acids, and other metabolites and can produce secondary metabolites in large quantities. Furthermore, the degradation of the refractory organic substrate in sludge can be enhanced by some enzyme excretion of these fungi (Wawrzynczyk et al. 2003). Alam et al. (2003) offered a similar conclusion using liquid state bioconversion, which can be used to treat domestic wastewater sludge using fungal biomass to reduce the amount of organic materials. Many academics supported this finding, and a number of studies were conducted. According to Fleury et al. (2007), the amount of dry matter in the sludge treated with the microfungi is reduced by approximately 10% to 50%, typically by approximately 20% to 30%, compared with that of the untreated sludge. Depending on the control parameters, this degradation can be greater. According to Alam et al. (2003), a mixed culture leads to higher enzyme production with comparatively little increase in their cell biomass. Cameron et al. (2003) reported that the white rot fungus *Phanerochaete chrysosporium* degrades a variety of persistent environmental pollutants. Mannan et al. (2005) reported that the filamentous *fungi P. corylophilum* and *A. niger* comprised almost 95–98% of the existing microorganisms in the sludge treatment process, with 10 15, and 20% of the inoculum treatment dose in two days. However, at the 5% fungal inoculum treatment dose, no significant fungus dominance over other existing microorganisms was observed. The 5% fungal inoculum dose was insufficient to adapt in the sludge under natural conditions. The filamentous fungi *Mucor hiemalis* broth reportedly removed 87% of the COD in treated sludge, with a 98% removal of suspended solids after six days (Fakhru et al. 2002). Mannan et al. (2005) reported that *P. corylophilum* is suitable for the biodegradation of domestic activated sludge. In general, the extracellular enzyme of filamentous fungi has a potent capacity to degrade domestic activated sludge. Thus, a filamentous fungus culture can enhance the biodegradation of sludge floc as well as cryptic growth.

8.5.2 Using Sludge to Produce Useful Enzymes

Enzymes in activated sludge have been used as indicators of specific microbial populations and measures of active biomass and specific process indicators such as phosphorus and COD removal. Similarly, the presence of redox enzyme activity in activated sludge is a direct indicator of efficient treatment plant operation and sludge composition. The presence of enzymatic (esterase, dehydrogenate, α-glycosidase and alanine-aminopeptidase) activity in activated sludge confirmed the microbial abundance and their heterotrophic activity in sludge. The wastewater sludge can be used as a cost effective raw material to produce useful enzymes for industrial applications. Details are described as follows.

Lysozyme. The key to lysis-cryptic growth is lysis as well as the disruption of the microorganism cell structure because the major components of activated sludge are the microbial cells bound in the sludge flocs. Lysozyme, which is an enzyme that can dissolve polysaccharides as substrates in the bacterial cell wall, is also known as muramidase or N-acetylmuramide glycanhydrolase. Its mechanism of action involves the lysis of β-1,4 glycosidic that bonds between N-acetyl glucosamine and N-acetylmuramic acid in the bacterial cell wall. The insoluble mucopolysaccharide in the bacterial cell wall can then be dissolved into a soluble glycopeptide. The bacterial cell wall is then ruptured and dissolved, and the cytoplasm is released. Lysozyme not only affects lysis, but it can also degrade organic molecules. Yasunori et al. (1994) compared the difference between the removal of volatile suspended solids (VSS) in a concentrated excess sludge with or without inoculation of slime bacteria that secrete lysozyme. They found that the removal of VSS in the inoculated sludge reached 62%, whereas that in concentrated excess sludge without inoculation was only 9.8% after five days of shake cultivation. Masahiko et al. (1997) isolated a new thermophilic bacterium, *Bacillus stearotherm ophilus* SPT2-1 [FERM P-15395], which can secrete lysozyme. They applied it to the liquefaction of the sludge floc and obtained highly desirable results. Ogawa et al. (2003) activated the bacterial strain *B. stearotherm ophilus* SPT2-1 [FERM P-15395] and inoculated four batches of excess sludge after sterilization. The average VSS removal in the concentrated excess sludge reached 30–50% with the bacterial strain, whereas that without the bacterial strain was 11.9% after five days of shake cultivation at 30°C, 40°C, 50°C, and 60°C. At present, bacterial strains that secrete lysozymes belong to major fungal classifications or are parts of viruses. Ogawa et al. (2003) found that aside from the Bacillus species, the *B. Brevis*, *B. Cereus*, *B. Circulans*, *B. Coagulans*, *B. Firmus*, *B. Licheniformis*, *B. Macerans*, *B. Megaterium*, *B. Mycoides, B. Pumilu, B. sphaericus, B. Subtilis, and B. Thuringiensis* species all had the ability to secrete lysozymes.

Lipase. Lipids are essential components of sludge with larger molecular weights and are also important materials in microorganisms. There is an extremely high lipid content present in the wastewater sludge of some specific

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industries, particularly those of oil refineries and restaurants. Thus, lipid hydrolysis in the sludge using lipase plays an important role in sludge degradation (Parmar et al. 2001). Concurrently, lipase has a relevant function in sludge digestion. It is one of the earliest known enzymes and has some catalytic activities. It can catalyze triacylglycerols and other water-insoluble esters of hydrolysis, esterification, and alcoholysis, as well as transesterification and the contrary synthetic of the ester. Lipase is widely distributed in microorganisms, and the primary producing strains are mildew and bacteria. Fungoids, which are known to secrete lipase, comprise 33 kinds, 18 of which are filamentous fungi, and 7 are bacteria. Dharmsthiti and Kuhasuntisuk (1998) used *Pseudomonas aeruginos,* which has the lipase secretion capacity, to treat restaurant wastewater and obtained good results. Felice et al. (1997) used tame *Yarrowia lipolytica* ATCC 20255 to treat wastewater from an olive oil factory, and the COD was significantly reduced. Palma et al. (2000) studied *P. Restrictum* and found that it not only has the ability to secrete lipase, but it also secretes proteinase and amylase. Therefore, *Restrictum* has high potential in sludge reduction. Leal Marcia et al. (2006) also studied the optimization parameters for *P. restrictum*. Other researchers (Sunil et al. 2009) investigated *Mucor, Aspergillus, Rhizopus, and Penicillium,* all of which have the ability to secrete lipase.

Cellulase. The chemical structure of cellulose was first confirmed in 1930 (Palma et al. 2000). It is composed of high-molecular-weight linear polymers mainly polymerized by p-β-glucose monomers through β-1- and β-4-glycosidic bonds. Its polymers vary significantly. The molecular weight of cotton polymers and other plants can reach 10,000 or more, whereas those of some industrial material handlings are only about 500 (Leal Marcia et al. 2006). Cellulose does not dissolve in water and in common organic solvents. It is widely distributed in plants and some microorganisms and is the most abundant type of polysaccharide in nature. In urban sewage treatment plants, particularly in the paper and textile industries, the activated sludge contains large amounts of cellulose and other organic substances. Meanwhile, cellulase can efficiently enhance sludge hydrolysis (Parmar et al. 2001). The use of cellulase to hydrolyze cellulose in sludge floc treatment is a significant development. Cellulase is a highly efficient recombination enzyme, and filamentous fungi are considered as its primary source. At present, cellulase is believed to be mainly composed of endoglucanase (EG, Ee3.2.1.4.), exoglucanase (CBH), and β-glucosidase (glucosidase, Ee3.2.1.21) (Warren et al. 1996). Domingues et al. (2000) studied the RutC-30 cellulase production and mycelial morphology of Trichoderma reesei as influenced by the composition of the culture medium and the inoculum size using shake flask experiments. Svetlana et al. (1997) investigated the cellulase produced by T. reesei RutC-30 under environmental conditions and established the enzyme kinetic model for batch fermentation. In addition, studies have been made on Aspergillus, Penicillium, Rhizopus, Myrothecium, and others, all of which have the ability to produce cellulose (Hageskal et al. 2009).

Protease. Proteases are large molecules in a living organism, and their basic structural unit is the aminophenol. Proteases, which primarily exist in the

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intracellular space and the external EPS of living microorganisms, are abundant in activated sludge. Hong et al. (2002) reported that proteins and carbohydrates are the main components of activated sludge and that their proportions vary with the sludge sample. Meanwhile, proteins and carbohydrates are still the main components of EPS in activated sludge (Houghton et al. 2001). However, which component has the higher proportion remains to be determined (Hong et al. 2002). Some studies reported that the highest proportion was that of carbohydrates, whereas others suggested that the protein content was the highest (Flemming and Wingender 2001). Pei et al. (2010) reported that the protein content was the highest at 70.78%, whereas that of polysaccharides was only 8.04%. Protease activities are the primary factors affecting protein hydration and translation. Protease has the peculiarity of catalyzing the hydrolysis of peptide bonds in proteins to produce peptide chains and amino acids, which is prepared for microorganism use. Azize et al. (2005) reported that the recombination action of protease, lipase, and endoglucanase can significantly enhance the efficiency of sludge lysis. At the same time, Ayol (2005) reported that protease, amylase, and cellulase can enhance the efficiency of sludge lysis. Roman et al. (2006) reported that the reaction of a procatalyzing peptide bond is the main enzymatic action in surplus sludge assimilation and lysis, and that protease activity is an important factor affecting the efficiency of activated sludge process minimization. Therefore, protease can catalyze and hydrolyze proteins to enhance the lysis efficiency of total sludge, thereby significantly enhance sludge reduction. At present, the main bacterial types with protease lactation activities are partial bacteria and filamentous fungi. Watson et al. (2004) reported that *Raoultella* and *Pandorae*a of the *Acinetobacter* family also exhibit protease lactation activities.

Protease Production. The production of enzymes by bioprocesses is an excellent value added to agro-industry residues. A comparative study was carried out on the production of protease using different varieties of rice broken (PONNI, IR-20, CR-1009, ADT-36 and ADT-66) from Rice mill wastes, substrates in solid-state fermentation (SSF) by *Aspergillus niger*. Among all of the tested varieties of rice broken PONNI produced the highest activity as 67.7 U/g while ADT-66 produced the lowest protease as 44.7 U/g/ under solid state fermentation conditions. The optimized conditions for producing a maximum yield of protease were incubation at 35°C, 96 h and pH 7.0. The protease production from waste treatment could be commercially used in detergents and leather industry (Paranthaman et al. 2009).

Bacterial cellulose and enzymes were produced through sequential fermentations with the bacterium *Gluconacetobacter xylinus* and the filamentous fungus *Trichoderma reesei*. Fiber sludge from sulfate (SAFS) and sulfite (SIFS) processes were hydrolyzed enzymatically without prior thermochemical pretreatment, and the resulting hydrolysates were used for BC production. The highest volumetric yields of BC from SAFS and SIFS were 11 and 10 g/L dry weight, respectively. The BC yield on initial sugar in a hydrolysate-based medium reached 0.3 g/g after seven days of cultivation. The tensile strength of wet BC from a hydrolysate medium was about 0.04 MPa compared to about 0.03 MPa for BC from a glucose-based reference

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medium, while the crystallinity was slightly lower for BC from hydrolysate cultures. The spent hydrolysates were used for the production of cellulase with *T. reesei*. The cellulase activity (CMCase activity) in spent SAFS and SIFS hydrolysates reached 5.2 U/mL (87 nkat/mL), which was similar to the activity level obtained in a reference medium containing equal amounts of reducing sugar. It was shown that waste fiber sludge is a suitable raw material for the production of bacterial cellulose and enzymes through sequential fermentation. The concept studied offers efficient utilization of the various components in fiber sludge hydrolysates and affords a possibility to combine production of two high value-added products using residual streams from pulp mills and biorefineries. Cellulase produced in this manner could tentatively be used to hydrolyze fresh fiber sludge to obtain medium suitable for production of BC in the same biorefinery (Xiang et al. 2013).

Investigation of the recovery of alkaline protease from *B. licheniformis* ATCC 21424 fermented wastewater sludge was carried out by centrifugation and ultrafiltration. Optimization of ultrafiltration parameters (transmembrane pressure (TMP) and feed flux) was carried out with 10 kDa membrane. TMP of 90 kPa and feed flux of 714 LHM (L/h-m^2) gave the highest recovery (83%) of the enzyme from the centrifuged supernatant. The recovered enzyme had a maximum activity at a temperature of 60°C and at pH 10. It was stable between pH 8 to 10 and retained 97% activity at 60°C after 180 min of incubation. Enzyme activity was significantly augmented by metal ions like Ca^{2+} and Mn^{2+}. Protease inhibitors like phenylmethyl sulphonyl fluoride (PMSF) and diisopropyl fluorophosphates (DFPs) completely inhibited the enzyme activity. The partially purified protease showed excellent stability and compatibility with various commercial detergents. The detergent (Sunlight) removed the blood stains effectively along with the enzyme as an additive. In this study, the enzyme was concentrated and characterized to apply as an additive in detergents as detergent industry needs concentrated enzyme in order to have higher efficiency. The recovery of alkaline protease using ultrafiltration process with an optimum transmembrane pressure of 90 kPa and feed flux of 714 LHM showed a recovery of 83% of the protease activity. The protease from *B. licheniformis* ATCC 21424 is thermostable and alkali-tolerant serine alkaline protease, as it is stable at alkaline pH and high temperature. Recovered alkaline thermostable protease by ultrafiltration can be exploited in the detergent industry as an additive because it showed excellent stability at a wide range of temperature and compatibility with commercial detergents. More importantly, the supplementation of the enzyme preparation to detergent could remarkably remove the blood stains of white cotton cloth (Jyothi et al. 2011). A study was carried out on thermophilic bacterial strains that produce thermostable proteases. The bacterial strains were first isolated from municipal wastewater sludge. In contrast to the conventional strains used in industries, like Bacillus sp., the new strains were the Gram-negative type. In semi-synthetic medium, a maximal protease activity of 5.25 IU/ml (International Unit per mL) was obtained at a pH of 8.2 and at a temperature of 60°C, which is higher than the stability temperature of 37°C for a similar protease obtained from the conventional producer *Bacillus licheniformis*. Moreover, growth and protease activity of the strains were tested in wastewater sludge. It is expected that the complexity of sludge could stimulate/enhance the protease production and their characteristics. In conclusion, reuse of the wastewater sludge will help to reduce their quantity. In addition, the value-added products will replace chemical products used in industries (Chenel et al. 2008).

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8.6 CONCLUSIONS

In this chapter, a special attention has been given to the production of value-added bioproducts from wastewater sludge for the purposes of not only producing sustainable and environmentally friendly products but also solving waste disposal problems. As we confirmed, sludge is a potential economical source which possesses high nutritional values and has zero or minimal cost as well, which is known as a source for a well-adapted natural microbial community for conversion of different value-added products. It has been a great challenge to appropriately deal with a large amount of sludge as we detailed in various sections of the chapter. To conclude, the wastewater sludge could be used as a potential source for isolation of microorganisms, and can be a very good carbon source of many microbial possesses that could add value to sludge by producing valuable metabolic products. The emerging value-added products include, but are not limited to, construction aggregates, adsorbents, fuels, biotechnological products (e.g., biopesticides, bioherbicides, enzymes, bioplastics, bioflocculants) and miscellaneous products like animal feed, secondary metabolites and electricity. The emerging value-added products are at different levels of production, facing challenges in terms of process conditions, yield, scale-up or formulation.

8.7 ABBREVIATIONS

(Bt)	Bacillus thuringiensis
(CBH)	exoglucanase
(CD)	Cow Dung
(COD)	chemical oxygen demand
(CFU/mL)	colony forming units/ mL)
(DAHP)	di-ammonium hydrogen phosphate
(DFPs)	di-isopropyl fluorophosphates
(EC)	electrical conductivity
(EG)	endoglucanase
(EPS)	extracellular polymeric substances
(Tx)	entomotoxicity
(IU/ml)	International Unit per mL
(L/h-m2)	LHM
(MSS)	Municipal Sewage Sludge

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(NH)	non-hydrolyzed
NKP	(Nitrogen, Potassium, Phosphorus)
(PBS)	poly(butylene succinate)
(PCL)	poly(ε-caprolactone)
(PHA)	polyhydroxyalkanoates
(PHB)	Poly-3-hydroxybutyrate
(PHBHHx)	3hydroxybutyrate-co-3-hydroxyhexanoate)
P(3HB-co-3HV)	poly(hydroxybutyrate-hydroxyvalerate)
(PHV)	pol-3-hydroxyvalerate
(PLA)	polylactide
(PMSF)	phenylmethyl sulphonyl fluoride
(POME)	palm oil mill effluent
(PPG)	polypropylene slycol
(PPDO)	poly(p-dioxanone)
(SAFS)	Fiber sludge from sulfate
(SBU/μl)	spruce budworm units per micro liters
(SIFS)	Fiber sludge from sulfite
(SOW)	solid organic waste
(SS)	suspended solids
(TKN)	Total Kjeldhal nitrogen
(TMP)	transmembrane pressure
(TOA)	technical oleic acid
(VCs)	Vermicasts
(VSS)	volatile suspended solids
(UASB)	Upflow anaerobic sludge blanket
(WFFA)	waste free fatty acids from soybean oil
(WFO)	waste frying oil
(WWTPs)	wastewater treatment plants

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CHAPTER 9

Anaerobic Treatment of Wastewater

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9.1 INTRODUCTION

Anaerobic wastewater treatment is a process in which a mixed culture of microorganism degrades the biosolids present in the wastewater in the absence of oxygen. The absence of oxygen leads to the controlled conversion of complex organic pollutants into carbon dioxide and methane through different types of biochemical reactions. The conversion process is effective as compared to the most of the conventional aerobic processes (Hulshoff Pol et al. 1998) and produces only 5–10% of the sludge (Metcalf and Eddy Inc 2003), which saves the significant cost associated with the sludge disposal. More than 200 years ago, in November 1776, an Italian physicist Alessandro Volta performed his experiments disturbing the sediments of a shallow lake, collecting the gas and demonstrating that this gas was flammable. Till then the anaerobic plants began to set up in various countries like Britain, United States of America, China and other Asian countries including India. A comprehensive survey by Hulshoff Pol et al. (1998) revealed that anaerobic wastewater treatment were practiced worldwide mainly in Japan, Germany, Netherland, United States of America, India, etc. with over 1200 full scale plants being operated successfully. The numerous leading international companies such as Paques, Biothane, Enviroasia and ADI have installed more than 700 anaerobic wastewater treatment plants in various countries (Fang and Liu 2001). In the view of the popularity of the anaerobic processes for the treatment of various domestic and industrial wastewaters, Lettinga (1995) criticized the attitude of USA wastewater pollution control authority not to encourage more field-scale applications of innovative anaerobic processes.

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Literature suggests that upon realization of the potential of anaerobic treatment processes, large quantity of innovative research has been developed. Already, a lot of advancements in this area have been made and a number of studies are in progress with different types of organic wastes in various industrial and domestic wastewaters. Numerous studies in this area depicted that researchers were working on the anaerobic treatment of different types of synthetic wastewaters at lab-scale and striving very hard for the applicability of the results at the pilot and industrial scales. The present chapter focuses on the description of numerous topics related to the anaerobic wastewater treatment such as fundamentals of anaerobic treatment, effects of different parameters on the process, various types of anaerobic processes as well as kinetic modeling of the treatment process.

9.2 FUNDAMENTALS OF ANAEROBIC TREATMENT

Anaerobic digestion consists of several mutually dependent sequential and parallel biochemical reactions. These groups of reactions are termed as "process catabolism" in which a product from one group of microorganisms serve as a substrate for the next step, leading to the transformation of organic materials into a mixture of methane, carbon dioxide and some other anaerobic gases in trace amounts (Figure 9.1). During this transformation, different types of acids (volatile fatty acids) are also generated as the precursors. Many microorganisms, including bacteria and archaea, affect the anaerobic digestion process by promoting a number of chemical reactions for the conversion of organic matter into the biogas. Unlike aerobic digestion, the anaerobic conversion of waste into the biogas yields relatively a small amount of energy to the microorganisms and therefore, their growth-rate is slow. That means only a small fraction of the waste is converted into new cells. A major fraction of the waste is then converted to biogas after several biochemical reactions. This converted waste, known as "stabilized waste", generates insoluble methane gas. The conversion stages consist of different groups of growing microorganism consortia, which are capable of degrading particular types of acid precursors. The presence of three groups of microorganisms such as hydrolyzing and fermenting microorganisms, obligate hydrogen producing acetogenic bacteria and two groups of methanogenic archaea

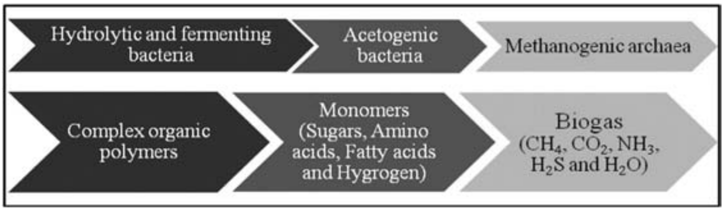

Figure 9.1. Different groups of microorganisms associated with anaerobic digestion

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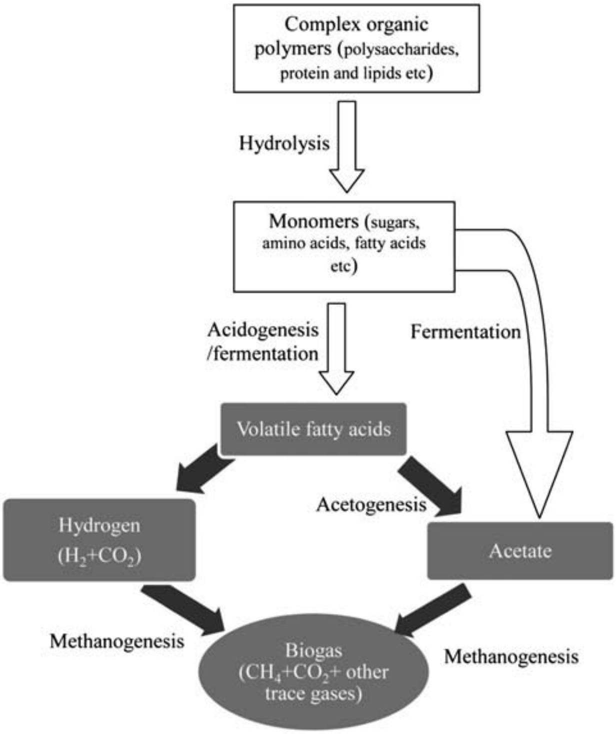

Figure 9.2. The process stages of anaerobic digestion

(acetoclastic and hydrogen utilizing) prevails in the overall digestion process. The process is operational only when the sufficient amounts of methane formers of all the groups are established.

There are four key biochemical stages for an anaerobic digestion (Figure 9.2):

1. Hydrolysis;
2. Acidogenesis;
3. Acetogenesis; and
4. Methanogenesis.

Generally, wastewater contains biomass in the form of complex organic polymers of a very high molecular weight with long chains. To utilize the energy potential of these materials for anaerobic digestion, these chains must first be converted into their monomers, such as sugars or amino acids and fatty acids that are readily available and easily accessible to the other bacteria. The process of breaking down the complex organic matter into their simpler units through microorganism mediated conversion is termed as "hydrolysis." Therefore, the hydrolysis of high molecular weight complex polymers is the first step of the anaerobic digestion. The hydrolyzing microbial consortia are responsible for the initial attack on complex polymers and produce the monomers. Further, the

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fermenting microorganisms attack on the monomers to produce acetates and hydrogen along with different types of volatile fatty acids (VFAs) such propionates and butyrates as well as some alcohols. This process is called "acidogenesis." Ammonia, carbon dioxide and hydrogen sulfide along with the other byproducts are also produced during the acidogenesis. In the acetogenesis process, the precursors of previous stage are readily accessible to the obligate hydrogen producing acetogenic bacteria which converts the propionates and butyrates into acetates, carbon dioxide and hydrogen. Methanogenesis is the last stage of anaerobic digestion where methanogens convert the intermediate precursors of the preceding steps to methane, carbon dioxide, hydrogen sulfide, water along with the other anaerobic gases (biogas). Methanogenesis is a pH dependent process, sensitive to both the high and low pH, optimally take place between pH 6.5 to 8.

In a study on anaerobic wastewater treatment, Lettinga (1995) had described the following conditions to accommodate the high loading rates for an anaerobic treatment of wastewater:

- High retention of the viable sludge in a reactor under operational conditions;
- Sufficient contact between viable bacterial biomass;
- High reaction rates and absence of serious transport limitations;
- The viable biomass should be sufficiently adapted and/or acclimatized; and
- Prevalence of favorable environmental conditions for all required organisms inside the reactor under all imposed operational conditions.

For a stable and efficient operation of anaerobic treatment systems, fulfilling the above described conditions is obligatory. To obtain the higher loading potential, the presence of the viable microorganisms is necessary. Contact time or the retention time determines the potential of microorganism to convert a portion of waste into secondary products. Further, the degradation kinetics is also one of the most important factors. It is essential that the intermediate precursors of the anaerobic digestion process are being degraded easily and end products of the process are escaped out. Regular monitoring and maintenance of the environmental and operating conditions are crucial to assure good working performance of the overall process.

9.2.1 Advantages

Unlike aerobic treatments where waste is mixed with the large amount of microorganisms and air, an anaerobic treatment is described with the mixing of microorganisms and waste in the absence of air. In the aerobic process, aerobic microorganisms utilize and oxidize food, using oxygen from the air and in turn receive large amounts of energy for their growth and reproduction. The aerobic treatment is therefore called "the energy utilizing process" which generates huge amounts of activated sludge (live biomass). In the anaerobic process, only those microorganisms that are capable of degrading the organic waste into the carbon dioxide and methane gas can grow. During this process, a relatively small amount of energy is released to the microorganisms. Thus their growth-rate is limited. Only a

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small portion of the waste is converted into new cells whereas a large fraction of the waste is transformed into the biogas, which can be utilized further as a viable energy source. The anaerobic treatment is therefore called "the energy yielding process". The numerous advantages of the anaerobic process are given below:

- Less biological sludge production;
- Less nutrient requirements;
- High degree of biomass stabilization;
- Less energy requirements;
- Production of biogas as a useful by product;
- Lower running cost;
- Supports reductive dechlorination;
- Shows excellent denitrification capability; and
- Also efficient at relatively higher temperature and organic contents.

9.2.2 Disadvantages

Although the processes are environmentally sustainable, the anaerobic treatment processes possess several disadvantages. Their main disadvantage is their ineffectiveness in removing non-organic pollutants such as nutrients and pathogens. In addition, the process is biochemically sensitive and therefore, requires a regular monitoring and control with respect to different physicochemical parameters as pH, temperature etc. Moreover, most of the anaerobic processes provide only a partial treatment, which requires further treatment before treated wastewater can be discharged into the environment. The processes demand higher startup time (2 to 3 months) for the mixed microbial population being acclimatized. The startup time also varies with the nature and the strength of wastewater. The processes also require high alkalinity for an effective treatment. They are highly dependent on different groups of microorganisms which are truly different in their preferences of environmental conditions and nutrition needs as well as their growth kinetics. Thus, it is very difficult to maintain the optimal conditions for all microorganisms. The imbalance between various groups of microorganism leads to the instability of the process (Chernicharo and Augusto 2007). Odor is also one of the major limitations associated with the process.

9.3 EFFECTS OF DIFFERENT PARAMETERS

9.3.1 Characteristics of Wastewater

Characteristics of wastewater play an important role in the process's performance. One of the crucial characteristics of wastewater is its strength in terms of its biodegradable content. The best measurement method of the biodegradable material is ultimate BOD (BOD_u). The COD of wastewater may also give the

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rough estimation of ultimate BOD by multiplying some factors. 5-day BOD (BOD_5) may also be correlated to ultimate BOD (~68% of the BOD_u). Generally, COD value is higher than BOD_u because it takes into account non-biodegradable organic matters. For example, lingo-cellulosic substances have low BOD value, so they may give an erroneous correlation with COD in their wastewater. These non-biodegradable materials are not stabilized under an aerobic environment in the BOD test and are susceptible to the degradation under the anaerobic environment. Apart from the organic strength of wastewater, the nature of organic matters, i.e. soluble form or suspended form, is also a control parameter. Depending on these forms, the degradation rates could be different.

9.3.2 Effect of Temperature

Temperature is also a critical parameter to control the anaerobic treatment processes. It can be divided into two ranges, mesophilic (28 to 38 °C) and thermophilic (50 to 60 °C). The metabolic rate of microorganisms increases with the rise of temperature within their tolerance ranges. Thermophilic digestion is more sensitive to thermal changes and therefore, is unstable compared to mesophilic digestion (Espinoza-Escalante et al. 2008). For an efficient anaerobic treatment process, maintenance of mesophilic range is desirable. Despite biochemical reactions proceeding at a much faster rate in the thermophilic range than in the mesophilic range, the maintenance of thermophilic range is not economically viable. Recent studies (Alvarez et al. 2008; Aydinol et al. 2010) of the anaerobic wastewater treatment at low temperature (below 20 °C) suggested that a slow hydrolysis rate of the waste and accumulation of a high amount of suspended solids on the biomass bed, which reduced the volume of active biomass and its specific methanogenic activity, would affect the treatment efficiency.

9.3.3 Effect of Hydraulic Retention Time

The hydraulic retention time (HRT) is the average time that wastewater spends inside the reactor. Since anaerobic treatment is a slow process, it requires long HRT which means larger reactor volumes. Short retention times may cause wash-out of the microbial consortia from the reactor if a completely-mixed tank reactor without recycle is used. Methanogens are also sensitive to short HRT since they have longer doubled time. Acetogens and sulfate reducing bacteria are affected by short HRT while the impact is less on hydrolytic bacteria (Zhang and Noike 1993). Espinoza-Escalante et al. (2008) reported that a long HRT favours acetate accumulation. Additionally, the maximal activity of microorganisms was reached close to wash-out. Increased HRT has also been reported to contribute to pathogen destruction (Salminen and Rintala 2002). Long HRT however requires large reactor volumes to cope up with the same amount of substrate.

9.3.4 pH and Alkalinity

Alkalinity or buffering capacity of wastewater is also one of the major influencing factors on the treatment efficiency, as it affects the pH. The pH of anaerobic

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digestion should be near neutrality. In the active anaerobic digestion process, generation of VFA and its breakdown into simpler precursors is a continuous phenomenon. The activity of methanogens largely depends upon the buffering conditions of the treatment process. As a result, to ensure buffering conditions is a must for the degradation of VFA to methane. At least 1500 mg/L bicarbonate alkalinity as $CaCO_3$ is desired in the presence of an environment containing about 30% of CO_2 (McCarty 1964). A higher alkalinity (2000–4000 mg/L as $CaCO_3$) is more desirable as it provides the shielding mechanism against the drop of pH and maintenance of the neutral conditions even at higher percentage of CO_2 generation. The pH of the treatment system can also be controlled by feeding at an optimal loading rate, since the degradation products (CO_2 and the VFA) are the main drivers affecting the pH (Yadvika et al. 2004) and alkalinity (Lahav and Morgan 2004). The problem with pH drop can be overcome by the reduction of the OLR or by the provision of the carbonate salts (sodium bicarbonates). Apart from affecting the growth-rate of microorganisms, pH also affects the composition of ammonia in the reactors. Ammonia can appear as ammonium ions (NH_4^+) at pH equal to or lower than 7.2, and free-ammonia (NH_3) at higher pH which is toxic to the microorganisms (Chen et al. 2008).

9.3.5 Macro- and Micro-Nutrients

During anaerobic treatment, an insignificant fraction of organic waste is converted to new bacterial cells while the remaining is converted to methane and carbon dioxide. The generation rate of new bacterial cells is slow in the anaerobic process, thereby requires less amount of macronutrients such as nitrogen and phosphorus for the biomass growth. Despite that, many industrial wastewaters still lack the sufficient nutrients. In these cases, to maintain a sound biological activity, it is essential to supply nutrients from external sources. The nutrient requirements also depend upon types of substrate and sludge retention time (SRT). Wastewater must be nutritionally balanced to maintain an adequate anaerobic treatment. Lacking of phosphorus leads to a decrease in methanogenic activities. Methanogens use ammonia and sulfide as nitrogen and sulfur sources, respectively. Speece et al. (1983) reported the toxicity of un-ionized sulfide to methanogens at the levels exceeding 150–200 mg/L. The recommended C:N:P ratio for anaerobic microbial consortia is 700 : 5 : 1 (Lettinga 1995). The trace elements such as iron, magnesium, copper, cobalt, molybdenum, and nickel are also necessary. Nickel, at a concentration below 10 mM, considerably increases the methane production in laboratory digesters. Nickel addition can also increase the acetate utilization rate of methanogens (Speece et al. 1983). An excess of a particular element may saturate the carrier molecules and thereby restricts the uptake of other essential metal ions. An excessive metal ion may also replace an essential metal in an enzyme. This would result in a decrease in methanogenesis (Fatherpure 1987).

9.3.6 Effect of Organic Loading Rate

The performance of anaerobic digestion depends upon the organic loading rates (OLRs) but not on the influent substrate concentration. The OLR affects the

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sludge morphology inside the reactor. Granular sludge was formed when a high ORL of above 0.6 kg COD/kg VSS.d was applied (Hulshoff et al. 1983). Low OLR may be detrimental to the sludge settleability. At low loading (less than 0.3 kg COD/kg VSS.d), extremely voluminous bulking sludge was generated, which can be washed out easily (Hulshoff et al. 1983). The loading above 1–2 kg COD/m^3 d is essential for proper functioning of the reactor (Lettinga et al. 1993). A very high loading is also detrimental to the granule formation. At very high loadings, a large quantity of biogas is produced, creating a vigorous mixing condition at the top of the reactor. As a result, a large quantity of sludge gets disintegrated or washed out of the reactor. It is suggested not to start the reactor with OLR $>$ 4.0 kg COD/m^3 d because higher loading results in the production of high VFA concentration which is unfavorable for the growth of microorganisms in the sludge.

9.3.7 Effect of Solids Retention Time

Solids retention time (SRT) is the average time that a biological solid particle (sludge) retains in the reactor. Conventional anaerobic sludge digestion reactors with artificial mixing are suspended growth reactors which exhibit the same SRT for all the solid particles, irrespective of their biological origin. An increase in SRT results in an increase of sludge in the reactor. Washout of the active microorganisms can be avoided by maintaining a minimum SRT. It is impossible to obtain any treatment below the minimum SRT. An increase in SRT beyond the minimum value produces an increase in the substrate removal. The amount and concentration of sludge in the system is directly related to the SRT value. Higher SRT causes excessive sludge, which helps to maintain the process's stability by reserving the excess biomass that needs to adapt to the changes in the influent substrate. A safety factor of 3 to 20 times of the minimum SRT was generally reported for a successful operation of biological reactors (Lawrence and McCarty 1969).

9.3.8 Presence of Toxic Compounds

Toxicity is mainly caused by the presence of excessive amounts of heavy metals, alkalis, sulphate, sulphide, chloroform, cyanide, phenols, chlorides, nitrate and oxygen, etc. These toxic compounds should not be present at concentrations inhibitory to the growth and granulation of microorganisms. A large amount of NH_4^+ ($>$1000 mg/L) is toxic to anaerobic bacteria, especially at a high pH values (Brunetti et al. 1983). Another substance is sulphate which is eventually reduced to H_2S. Since sulphide, mainly undissociated H_2S, highly toxic to bacteria, it is necessary to keep the COD/SO_4 ratio be higher than 10 (Lin and Yang 1991). Besides, H_2S may cause odor and corrosion problems. The effect of Cr(III) and Cd on the anaerobic acidogenesis of simulated dairy wastewater were reported. An improvement in acidogenesis was reported for this wastewater at a Cd dosage of less than 20 mg/L. In contrast, it inhibited the acidogenesis at the dosage over 20 mg/L. Similarly, at the values exceeding 5 mg/L, Cr(III) caused severe inhibition to the acidogenesis (Yu and Fang 2000).

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9.4 ANAEROBIC SUSPENDED GROWTH PROCESSES

Suspended growth processes are those biological treatment processes in which microbes responsible for the conversion are maintained in suspension within the liquid medium by proper mixing methods. Many suspended growth processes are used for treatment of sludge, animal manure slurry and high-strength organic wastewaters of municipal and industrial origins. In anaerobic suspended growth processes, the organic matters are converted to a variety of end products, including methane (CH_4) and carbon dioxide (CO_2) under anaerobic condition. The principal anaerobic suspended growth processes used for removal of carbonaceous organic matters are (1) completely mixed process, (2) contact process, and (3) anaerobic sequencing batch reactor. Each of these processes will be characterized in the following section.

9.4.1 Completely Mixed Process

The most widespread anaerobic suspended growth process used for wastewater treatment is the completely mixed anaerobic digestion. The process is carried out in an airtight reactor equipped with a stirrer (Figure 9.3). This reactor's configuration is simple to operate and has the ability to treat a large amount of effluent (Azbar et al. 2001). The constant stirring, the typical characteristics of the continuously stirred tank reactor (CSTR), keeps the reactor content completely mixed (Johanssen 2008) and homogenized. It aims to maintain the concentration uniform in all parts of the reactor as well as in the withdrawn substrate. The uninterrupted mixing results in the equalization of the hydraulic retention time (HRT) and the solid retention time (SRT) (Azbar and Speece 2001). Thus, the outstanding property of the first generation type reactors is that HRT is always equal to the SRT.

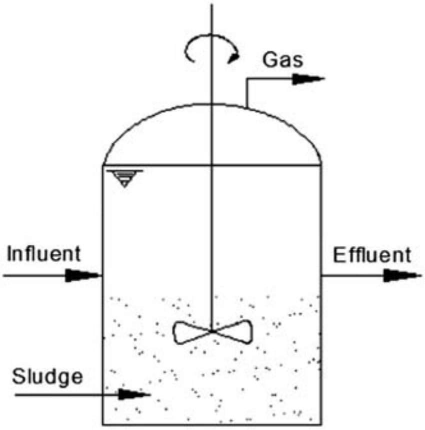

Figure 9.3. Completely mixed anaerobic reactor

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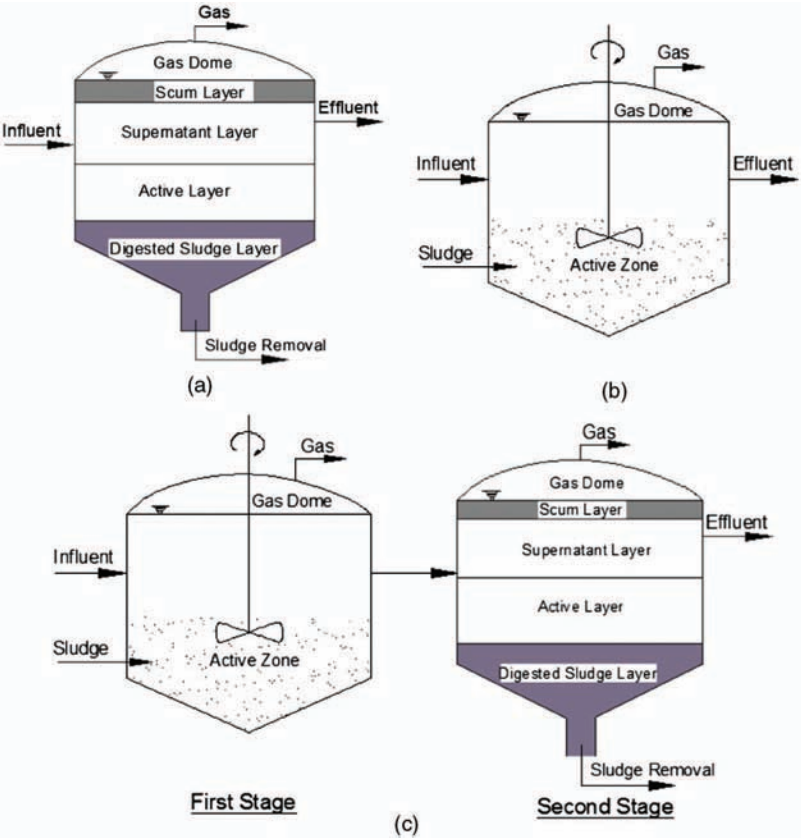

Figure 9.4. (a) Standard-rate single-stage anaerobic reactor; (b) High-rate single-stage anaerobic reactor; (c) Two-stage anaerobic reactor

The fundamental complete mix process configurations are shown in Figure 9.4. The conventional standard-rate reactors (Figure 9.4(a)) are characterized by un-mixing or intermittent mixing, intermittent sludge feeding and intermittent sludge withdrawal. Detention time varies between 30 and 60 days (Reynolds 1982). The digester has several zones, namely, (1) a gas dome, for collection of produced bio gas, (2) a scum layer, for floatation of undigested portions forming the scum, (3) a supernatant zone to store the clarified water from the reaction, (4) an active layer where anaerobic reaction takes place and (5) a stabilized zone where digested sludge is stored temporarily (Kiely 2007). In contrast, in case of high-rate digestion process (Figure 9.4(b)), the contents of the reactor are heated and mixed continuously, except at the time of sludge withdrawal. An incorporation of mixing leads to the non-establishment of different zones that are found in conventional digesters. However the gas dome is still present. The required detention time is typically of 15 days or less to provide sufficient safety factors for operation and stability (Parkin and Owen 1986). The

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anaerobic reactors may be designed to operate as two-stage processes as depicted in Figure 9.4(c) by combining these two basic processes. The first stage would be the high-rate stage whereas the second stage would be similar to that of the standard rate conventional reactor. The first stage is where the reaction takes place while the key function of the second stage is to separate the digested sludge from the supernatant.

The completely mixed process is suitable for wastes containing high dissolved organic concentrations, where settling the effluent solids is difficult. Therefore it is more practical to operate in the condition that HRT equals to SRT, rather than sludge recycling. In the complete mix process, the mixing can minimize dead volume accumulation and flow channeling whilst maintain a uniform temperature, substrate and pH conditions in the reactor. Nevertheless, outsized reactor volume may be required to provide effective longer SRTs as the process stability may be compromised due to loss of biomass associated with short SRT (Lilly 2010).

9.4.2 Contact Process

In the complete mix process there is no option for sludge recycling, so the suspended biomass is continuously being lost with the effluent since the HRT and SRT are the same (Lilly 2010). To overcome the disadvantages of the complete mix process, contact process (Figure 9.5) has been introduced. Contact process includes an external settling tank for separation and recycling of the effluent biomass to the complete mix reactor, so that process SRT will be longer than HRT. This separation of the SRT from the HRT results in a decreased volume of the anaerobic reactor, an increased organic loading rate and a shortened HRT. In the process, the contents of the reactor mixed completely and after digestion, the mixture is separated in a clarifier. The supernatant is discharged as effluent and the settled sludge is then recycled to supplement the process. Gravity separation is a common method for settling the sludge prior to recycling. However, settling by gravity can be a problem for sludge with poor settling properties. In that case,

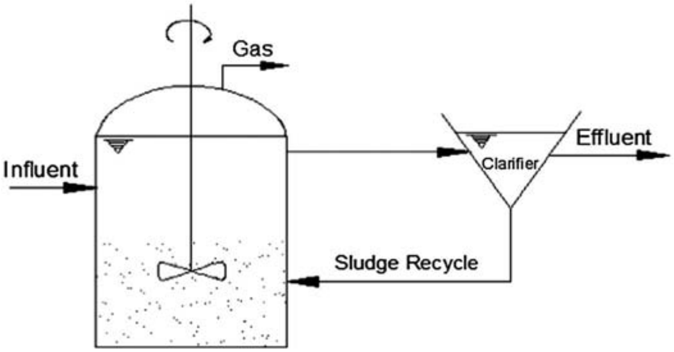

Figure 9.5. Anaerobic contact process

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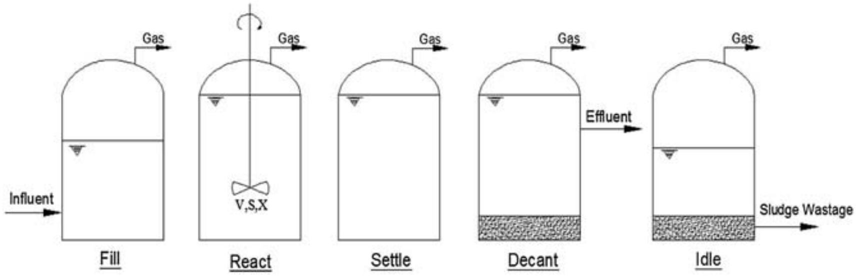

Figure 9.6. Anaerobic sequencing batch reactor

separation of solids is done by the gas floatation method. Solid-liquid separation may further be interrupted by the biogas produced during the reaction and separation processes. Various methods such as gas stripping, inclined plate separators, addition of coagulants etc. have been used to minimize the effects of trapped gas bubbles and to improve the sludge settling (Metcalf and Eddy Inc 2003).

9.4.3 Anaerobic Sequencing Batch Reactor

Anaerobic sequencing batch reactor (ASBR) is a fill-and-draw type suspended growth process where the reaction and the solid-liquid separation/clarification take place in the same reactor vessel sequentially as demonstrated in Figure 9.6. ASBR is a modification of conventional continuous flow activated sludge process. The major differences between SBR and a conventional continuous flow activated sludge system is that the ASBR tank carries out the functions of equalization and sedimentation in a time sequence rather than in the conventional space sequence. Thus, it is more flexible than in a space sequence. Treatment in ASBR was more economical than a conventional activated sludge process by a magnitude of 20% (Grady et al. 1999).

All operations of an ASBR such as filling, reacting, settling, drawing and idling are carried out in sequence in a single anaerobic batch reactor. During the "fill" operation, wastewater is added to the reactor. Then, in the "react" phase, intermittent mixing for a few minutes in each hour is done to provide uniform mixing of the content of the reactor. The purpose of the "settle" phase is to allow solids separation to occur, so that a clarified supernatant can be discharged as effluent. Consequently, in the "decant" phase, the supernatant is removed as effluent from the reactor. The "idle" phase is not always necessary and can be omitted sometimes. This is the time gap between the "draw" phase of one cycle and the "fill" phase of the next cycle. Sludge wasting is not included as one of the basic steps, rather it is done during the "settling" or "idling" phase. In the ASBR, there is no concept of recycling of the sludge, since both reaction and settling take place in the same reactor. The process could be applied for the treatment of high COD-containing industrial wastewater such as food processing industry effluents, landfill leachates, tannery wastewater etc.

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9.4.4 Basics of Anaerobic Suspended Growth Process Design

To design a process means customizing the process and its parameters according to the requirements. It deals with multiple aspects such as reaction kinetics, mass and energy balance, mass transfer, heat transfer, mixing and so on. The process design will have a significant impact on the overall performance. The design of the anaerobic suspended growth process includes the following parameters:

a) Microbial metabolism;
b) Biomass concentration in the reactor, kg VSS/m^3;
c) Volatile Suspended Solids loading rate, kg VSS/m^3-d;
d) Suspended Solids production rate, kg SS/m^3-d;
e) Hydraulic Retention Time, days;
f) Solid Retention Time, days;
g) Gas production rate, m^3/d;
h) Agitation system;
i) Heating system;
j) Product removal;
k) Product inhibition;
l) Digester/reactor configuration;
m) Nutrient requirements;
n) Sludge wastage; and
o) Flow rate, m^3/d.

Choosing optimal parameters and balancing the economic value of the chosen parameters results in a successful process design. The basic process design depends upon the mode of operation of the reactor, e.g., batch mode or continuous mode. In case of batch reactor, the process design may involve the determination of the time (t) required to achieve a fractional conversion of reactants into products. However, in continuous mode, the process design basically stresses upon the estimation of the volume (V) of the system required to achieve a specific rate of product formation. Based on essential features of the process design, design equations can be developed. A design equation of a process is nothing but a set of data and equations that is used to evaluate the process performance under various operational and environmental conditions. Design equations can be developed considering the mass balance or energy balance of the system.

A mass balance for the biomass in the completely mixed process as shown in Figure 9.7, can be written as follows:

$$\underset{\text{(Into the system)}}{\text{Biomass input}} + \underset{\text{(With in the system)}}{\text{Biomass generation}} = \underset{\text{(Out of the system)}}{\text{Biomass output}} + \underset{\text{(With in the system)}}{\text{Biomass accumulation}} \qquad \text{(Eq. 9.1)}$$

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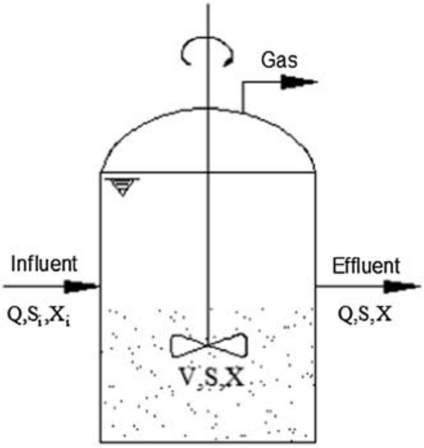

Figure 9.7. Mass balance of a completely mixed anaerobic reactor

$$QX_i + r_x V = QX + \frac{dx}{dt} V \tag{Eq. 9.2}$$

where Q = flow rate, m^3/day; X_i = biomass concentration in the influent, kg VSS/m^3; X = biomass concentration in the effluent, kg VSS/m^3; r_x = rate of biomass growth, kg VSS/m^3d; V = volume of reactor, m^3; $\frac{dx}{dt}$ = rate of change of biomass in the reactor, kg VSS/m^3 d.

In both batch and continuous culture systems, the rate of biomass growth can be represented as below:

$$r_x = \mu X \tag{Eq. 9.3}$$

where μ = specific growth rate, time^{-1}; X = biomass concentration, mass/unit volume

In steady state condition, $\frac{dx}{dt} = 0$ and considering the initial concentration of microbes to be negligible ($X_i \cong 0$), Eq. 9.2 can be written as:

$$r_x V = QX \tag{Eq. 9.4}$$

Putting r_x value from Eq. 9.3 in Eq. 9.4

$$\mu = \frac{Q}{V} = \frac{1}{\theta} \tag{Eq. 9.5}$$

where θ = hydraulic retention time $= \frac{V}{Q}$

If the decrease in cell mass due to death, predation and endogenous metabolism (the energy required for cell maintenance) is considered and all together termed as endogenous decay (r_d), then the net biomass growth rate (r'_x) can be expressed as:

$$r'_x = r_x - r_d \tag{Eq. 9.6}$$

$$r_d = -k_d X \tag{Eq. 9.7}$$

where k_d = endogenous decay coefficient, time^{-1}

$$\text{So } r_x = \mu X - k_d X \tag{Eq. 9.8}$$

Replacing r_x in Eq. 9.4 by r'_x, the new equation can be written as:

$$(\mu X - k_d X)V = QX \tag{Eq. 9.9}$$

$$\mu - k_d = \frac{Q}{V} = \frac{1}{\theta} \tag{Eq. 9.10}$$

$$\mu = \frac{1 + k_d\theta}{\theta} \tag{Eq. 9.11}$$

Now applying mass balance for the biomass in the conventional anaerobic reactor (around the active layer) as shown in Figure 9.8, the resultant equation can be written as follows:

$$Q_i X_i + r_x V = Q_e X_e + Q_w X_w + \frac{dx}{dt} V \tag{Eq. 9.12}$$

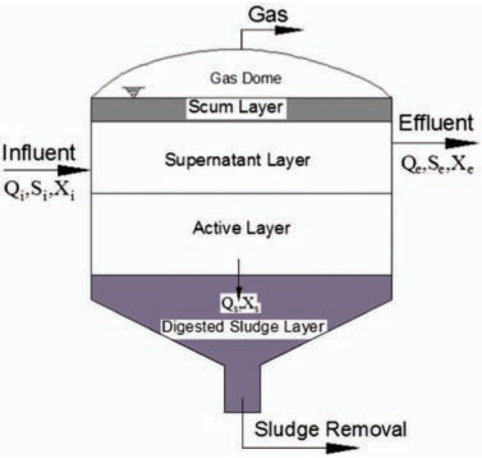

Figure 9.8. Mass balance of a conventional anaerobic reactor

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where Q_i = influent flow rate, m^3/d; Q_e = effluent flow rate, m^3/d; Q_s = sludge flow rate from active layer to digested sludge layer, m^3/d; X_i = biomass concentration in the influent, kg VSS/m^3; X_e = biomass concentration in the effluent, kg VSS/m^3; X_s = biomass concentration in the sludge flowing from active layer to digested sludge layer, kg VSS/m^3.

Since there is no accumulation in the active zone, assuming the steady state condition and neglecting endogenous decay, Eq. 9.12 can be reduced to

$$\mu = \frac{Q_eX_e + Q_sX_s - Q_iX_i}{XV} = \frac{1}{\theta_c} \qquad \text{(Eq. 9.13)}$$

where θ_c = cell residence time = solid retention time = SRT. θ_c can also be expressed as:

$$\theta_c = \frac{\text{Biomass present inside the reactor}}{\text{Biomass wastage from the reactor}} = \frac{XV}{Q_eX_e + Q_wX_w - Q_iX_i} \qquad \text{(Eq. 9.14)}$$

Taking endogenous decay into account, e.g., $\mu - k_d = \frac{1}{\theta_c}$, Eq. 9.13 can be rewritten as:

$$\frac{1}{\theta_c} = \frac{Q_eX_e + Q_sX_s - Q_iX_i}{XV} - k_d \qquad \text{(Eq. 9.15)}$$

However, according to Sincero and Sincero (2011), in the case of anaerobic digestion of sludge since no food is being served, specific growth (μ) is equal to zero. So the Eq. 9.13 can be simplified as:

$$-k_d = \frac{Q_eX_e + Q_sX_s - Q_iX_i}{XV} = \frac{1}{\theta_c} \qquad \text{(Eq. 9.16)}$$

which can be further written as:

$$\theta_c = \frac{XV}{Q_iX_i - Q_sX_s - Q_eX_e} \qquad \text{(Eq. 9.17)}$$

Similarly for the anaerobic contact process as shown in Figure 9.9, if sludge wasting is done from the recycle line, then the mass balance equation for the biomass can be written as below:

$$Q_iX_i + r_xV = Q_eX_e + Q_wX_r + \frac{dx}{dt}V \qquad \text{(Eq. 9.18)}$$

where, X_r = biomass concentration in the recycle line, kg VSS/m^3

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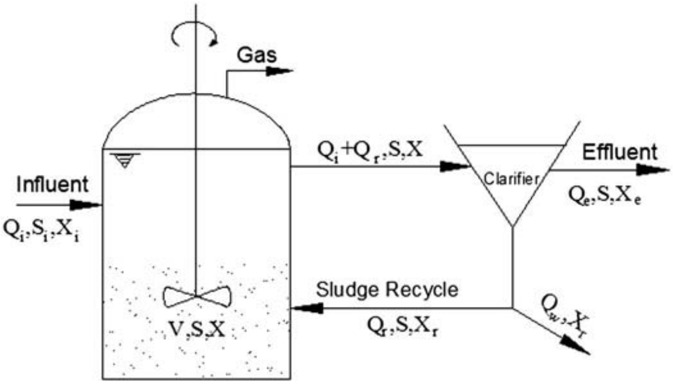

Figure 9.9. Mass balance of a contact process

Considering endogenous decay and steady state condition, Eq. 9.18 can be simplified as:

$$\theta_c = \frac{XV}{Q_eX_e + Q_wX_r - Q_iX_i} - \frac{1}{k_d} \qquad \text{(Eq. 9.19)}$$

Because of the stumpy synthesis rate of anaerobic microbes, the excess sludge that has to be disposed of is in negligible amount. Therefore, equating the factor $Q_wX_r \cong 0$ and the equation in that case can be written as

$$\theta_c = \frac{XV}{Q_eX_e - Q_iX_i} - \frac{1}{k_d} \qquad \text{(Eq. 9.20)}$$

Example 9.1 Wastewater generated from a cattle farm with 2500 cattle is to be treated anaerobically. What will be the volume of the complete mix anaerobic reactor, assuming sludge load = 1.5 kg/d per cattle, density = 1.05 kg/L and hydraulic retention time = 20 days?

Solution:

Given $\theta = 20$ d

Density = 1.05 kg/L

Sludge loading rate per cattle = 1 kg/d

Sludge loading rate from the farm = $2500 \times 1.5 = 3750$ kg/d

Flow rate $Q = \frac{\text{mass loading rate}}{\text{density}} = \frac{3750}{1.05} = 3571.43$ L/d = 3.57 m^3/d

Required reactor volume, $V = Q \cdot \theta = 3.57 \times 20 = 71.4$ m^3

In order to provide head space, it is safer to design the volume of the reactor >75 m^3.

Example 9.2 An industrial waste is to be treated in an anaerobic contact process to reduce its Mixed Liquor Suspended Solids (MLSS) value to 40 mg/L. The reactor volume is 20 m^3, $\theta_c = 5$ days, endogenous decay coefficient,

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$k_d = 0.05\ d^{-1}$. Influent Mixed Liquor Volatile Suspended Solids (MLVSS) value is negligible, return sludge concentration = 5000 mg/LMLVSS, effluent MLVSS = 0.8 × effluent MLSS. If the industry generates 60 $m^3\ d^{-1}$ of effluent and $Q = Q_e$, then calculate the biomass wasting rate from the anaerobic contact process in order to maintain 2500 mg/L of MLVSS.

Solution:

Given: Effluent MLSS = $S_e = 40$ mg/L = 40 $g\,m^{-3}$

Reactor volume = V = 20 m^3

Cell residence time = $\theta_c = 5$ days

Endogenous decay coefficient = $k_d = 0.05\ d^{-1}$

Influent MLVSS = $X_i \cong 0$

MLVSS in return sludge = $X_r = 5000$ mg/L = 5000 g/m^3

MLVSS in effluent = $X_e = 0.8 \times S_e = 0.8 \times 40 = 32$ mg/L = 32 g/m^3

Flow rate = Q = 60 $m^3/d = Q_e$

MLVSS = X = 2500 mg/L = 2500 g/m^3

For anaerobic contact process cell residence time (θ_c) can be calculated as:

$$\theta_c = \frac{XV}{Q_eX_e + Q_wX_r - Q_iX_i} - \frac{1}{k_d}$$

Putting all the values in the above equation

$$5d = \frac{(2500\ g/m^3)(20\ m^3)}{(60\ m^3/d)(32\ g/m^3) + Q_w(5000\ g/m^3) - (60\ m^3/d)(0)} - \frac{1}{0.05\ d}$$

Solving the equation we will get $Q_w = 0.016\ m^3/d$. Therefore 16 L/d sludge needs to be wasted from the contact process in order to maintain 2500 mg/L of MLVSS.

Example 9.3 Solve the example 9.2 using a conventional anaerobic reactor. Calculate biomass concentration in the wastage sludge considering $Q_w = 0.016\ m^3/d$ as obtained in the previous example. Assume reactor volume = 45 m^3 and cell residence time = 35 days.

Solution:

Given: Sludge wastage rate = $Q_w = 0.016\ m^3/d$

Reactor volume = $V = 45\ m^3$

Cell residence time = $\theta_c = 35$ d

Rest of the values as per example 9.2

For a conventional anaerobic reactor

$$\theta_c = \frac{XV}{Q_eX_e + Q_wX_w - Q_iX_i} - \frac{1}{k_d}$$

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Putting all the values from example 9.2

$$35\text{d} = \frac{(2500\ \text{g/m}^3)(45\ \text{m}^3)}{(60\ \text{m}^3/\text{d})(32\ \text{g/m}^3) + (0.0166\ \text{m}^3/\text{d})(\text{X}_\text{w}) - (60\ \text{m}^3/\text{d})(0)} - \frac{1}{0.05/\text{d}}$$

Solving the equation we will get $\text{X}_\text{w} = 7411.38\ \text{g/m}^3$. Therefore $7411.38\ \text{g/m}^3$ of MLVSS need to be wasted through sludge wasting from the conventional anaerobic digester in order to maintain, 2500 mg/L of MLVSS.

9.5 ANAEROBIC SLUDGE BLANKET PROCESSES

The technological advancement in anaerobic processes in the last three decades has significantly reduced their past weaknesses. Historically, the anaerobic treatment process was not favored for wastewater treatment, particularly for the medium- and low-strength wastewater because of its high HRTs. Since the work of Young and McCarty in 1969 on the application of anaerobic processes for the treatment of industrial and domestic wastewater, a significant advancement in the last three decades has been achieved. Today, anaerobic treatment technology has emerged as one of the best treatment processes for different types of wastewater. In the past, retention of sufficient active sludge under short HRTs was one of the most severe problems in an anaerobic treatment. The limitation now has been overcome by the successful development of high-rate anaerobic processes such as upflow anaerobic sludge blanket (UASB), expanded granular sludge bed (EGSB), anaerobic baffled (AB) and anaerobic migrating blanket (AMB) reactors. One common feature of these processes is the ability to achieve high solid retention time, even at short hydraulic retention time.

9.5.1 Upflow Anaerobic Sludge Blanket (UASB) Reactor

This is the modified version of contact process in which an upward movement of wastewater through a dense blanket of anaerobic sludge takes place. The sludge blanket consists of biological granules or thick flocculent sludge. The UASB reactor is one of the reactor types with high loading facility and is distinctive from other processes by its simple design. UASB process is a combination of physical and biological processes. The main aspect of physical process is separation of solids and gases from the liquid and that of biological process is stabilization of biodegradable organic matter under the anaerobic environment. The gases produced cause the internal mixing in the reactor. Some of the gas produced within the sludge blanket becomes attached to the biological granules. The free gas and the sludge particle with the attached gas rise up to the top of the reactor. The particle that rise to the liquid surface strike the bottom of the degassing baffles,

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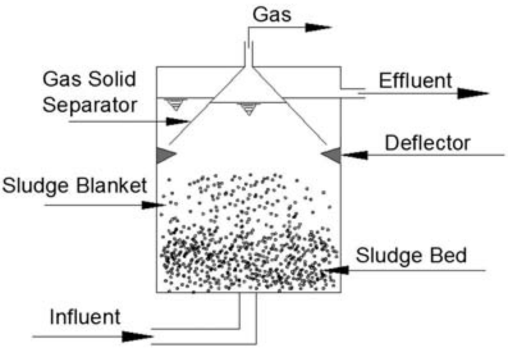

Figure 9.10. Schematic diagram of upflow anaerobic sludge blanket reactor

which causes the attached gas bubbles to be released. Then the degassed granules drop back to the surface of sludge blanket. The free gas and the gas released from the granules are captured in the gas collection assembly located in the top of the reactor. Liquid containing some residual solids including biological granules then passes through the settling chamber where residual solids are separated from the liquid. The separated solids fall back through the baffle system to the top of the sludge blanket. The granular biomass from the existing UASB reactor can be used as inoculum material to start-up the new UASB reactor. Non-granular material such as cow manure, waste activated sludge, anaerobically digested sludge etc. may also be utilized as inoculum in the absence of granular sludge. Over a period of time, these non-granular materials generally grow to form the granular sludge if proper feeding was done.

The schematic diagram of a typical UASB reactor is shown in Figure 9.10. The reactor has three main sections: (1) sludge bed, (2) sludge blanket, and (3) gas solid separator (GSS). The sludge bed is the layer of biomass settled at the bottom of reactor. In this section, the organic matters present in the wastewater gets converted into their end product (biogas) and the new cells as the flow passes upward through the active sludge granules. Relatively highest concentration (60 to 100 g SS/L) of sludge is maintained in this section. The sludge blanket exists on the top of the sludge bed, which is a suspension of sludge particles with a concentration of 2 to 5 g SS/L mixed with the biogas produced in the process. Mixing occurs in this section due to the evolution of the biogas. The degradation of residual organic matters also takes place within this section. Gas is separated from the liquid by the GSS provided at the top of the reactor. The inverted-cone-like structure acts as GSS, where gas is released to the gas collection assembly after its separation from the sludge. The deflector provided on the lower top section of the reactor helps to prevent the sludge granules from washout in case they rise along with the trapped gases. The GSS device generally occupies 16–25% of the total reactor volume (Hashemian and James 1990).

UASB process is successful for the wastewater treatment in intermittent mode of operation, which overcome the problem of buoying in the initial days of the

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reactor start-up due to poor quality of inoculums used (Ghangrekar 1997). Recent studies also demonstrated the successful implementation of UASB for a wide variety of wastewaters (Isik and Sponza 2008; Coskun et al. 2012).

Calculation of hydraulic design of UASB. Example 9.4 Design an UASB with an internal diameter of 10 cm and height of 100 cm operating for a COD concentration of 3000 mg/L with an HRT of 24 hours. Check for the flow rate, hydraulic loading, organic loading rate and upflow velocity.

Solution:

Considering a circular cross-section UASB reactor.

Volume of the Reactor

$V = \pi r^2 h$

Internal Diameter of the Reactor = 10 cm

Volume of the reactor $= 7.85 \times 10^{-3}\ \text{m}^3 = 7.85\ \text{L}$

Flow rate, $Q = \frac{\text{Volume}}{\text{Time}} = \frac{7.85}{1} = 7.85\ \text{L/d}$

Hydraulic Loading $= \frac{Q}{V} = \frac{7.85}{7.85} = 1.0/\text{d}$

Organic Loading Rate $= \text{OLR} = Q \times \frac{S_0}{V} = 7.85 \times \frac{3}{7.85} = 3.0\ \text{g COD/L d}$

Up-Flow Velocity $= (v) = \frac{Q}{A}$ (or) $Q \times \frac{H}{V} = 1.0\ \text{m/d}$

$V = 1.15 \times 10^{-5}\ \text{m/s}.$

9.5.2 Expanded Granular Sludge Bed Reactor

An expanded granular sludge bed (EGSB) reactor is a variation of the upflow anaerobic sludge blanket (UASB) reactor (Figure 9.11). The most important feature of EGSB design is that a faster upflow velocity wastewater passing through the sludge bed is incorporated. The increased flux allows expansion of the sludge bed, improving wastewater-sludge contact and improves separation of suspended solids from the sludge bed. EGSB reactor also accommodates higher loading

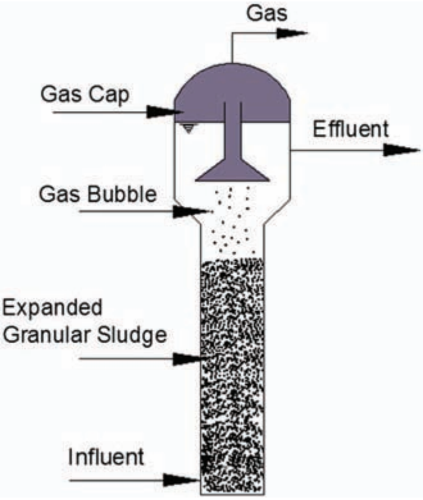

Figure 9.11. Schematic diagram of expanded granular sludge bed (EGSB) reactor

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rates as compared to the UASB reactor. The EGSB design is appropriate for low-strength wastewaters (less than 1 to 2 g soluble COD/L) or for wastewaters that contain inert or less biodegradable suspended solids which should not be allowed to accumulate in the sludge bed. The organic substances in the wastewater are degraded to their end products as they flow through the granular sludge bed. The upwards movement of evolved biogas and wastewater mixes the whole reactor. The produced biogas is collected in a biogas collection assembly and used for energy production. It was reported that the EGSB reactor was efficient in the removal of soluble organic matter even at low temperatures (Haandel and Lettinga 1994). This may be explained by the rigorous contact between the incoming organic matter and sludge granule as a result of high upflow velocity. Under the conditions of decreased biogas production rate and mixing intensity (observed at low temperatures and for low-strength wastewater), the higher kinetic energy of the influent and the extended height of the expanded granular bed result in a better treatment efficiency, compared with the conventional UASB reactor. EGSB reactors are inadequate for the removal of particulate organic matters due to the high upflow velocity.

9.5.3 Anaerobic Baffled Reactor

An anaerobic baffled reactor (ABR) is an improved septic tank, with regard to the series of baffles under which the wastewater is forced to flow (Figure 9.12). The increased contact time with the active biomass leads to a better treatment. The majority of settleable solids are removed in the sedimentation chamber at the beginning of the process, which typically represents 50% of the total volume. The design parameters of an ABR include a HRT between 48 to 72 hours, upflow velocity of the wastewater less than 0.6 m/h and a number of upflow chambers. The upflow chambers provide additional removal and digestion of organic matter. BOD may be reduced by up to 90%, which is far greater to that of a conventional septic tank. As sludge is accumulating, de-sludging is required in every 2 to 3 years.

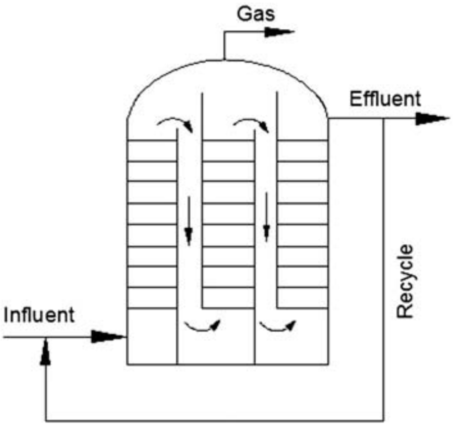

Figure 9.12. Schematic representation of ABR

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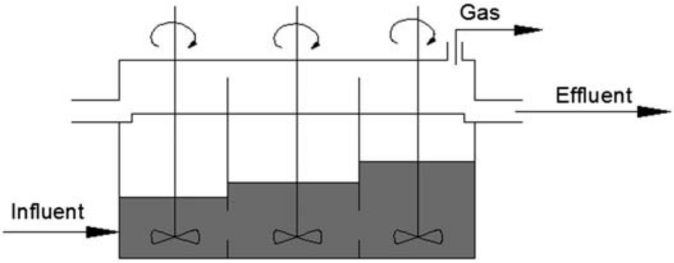

Figure 9.13. Schematic representation of anaerobic migrating blanket reactor

Anaerobic baffled technology is easily adaptable and can be useful at the household level. An ABR can be designed for a single house or a group of houses that are using a considerable amount of water for clothes washing, showering, and toilet flushing. It is mostly appropriate if wastewater flow-rate is relatively constant. This technology is also suitable for areas of limited space since the tank is installed underground. It should not be installed where there is a high groundwater table as infiltration will affect the treatment efficiency and contaminate the groundwater. Effluent and sludge must be handled with care because they contain high levels of pathogens. To prevent the release of potentially harmful gases, the tank should be vented.

9.5.4 Anaerobic Migrating Blanket Reactor

The AMBR is a continuously fed, compartmentalized reactor without the requirement of elaborate gas-solids-separation and feed-distribution systems (Figure 9.13). Effluent recycling is not necessary, but gentle intermittent mixing is needed to maintain sufficient contact between biomass and substrate due to the absence of an upflow hydraulic pattern. The influent flows horizontally into one end of the reactor and the effluent leaves from the other end. Consequently, the final compartment receives the lowest substrate concentration, and therefore the substrate utilization rate of the microbes in this compartment is small. This results in low biogas production, which enables the final compartment to serve as an internal clarifier preventing biomass loss in the effluent. Due to the flow pattern and the observed biomass migration, biomass accumulate in the final compartment. To prevent excessive accumulation of biomass in this compartment, the flow needs to be reversed periodically. As a consequence, the final compartment becomes the initial compartment and the earlier initial compartment serves as the internal clarifier (final compartment). To prevent a breakthrough of substrate when the flow is reversed, at least three compartments are required in a continuously fed AMBR. The influent is supplied for a short period of time into the middle compartment before the flow is reversed.

The AMBR inherits advantages of the anaerobic sequencing batch reactor (ASBR) such as mechanical mixing, biomass retention, simple design (no gas-solids separation and feed-distribution systems required because of the absence of

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a hydraulic upflow pattern), and granulation. In addition, the hydraulic retention time (HRT) in a continuously fed AMBR is shorter than the batch-fed ASBR (Prakash and Gupta 2000).

Example 9.5 A wastewater with a flow of 4000 m^3/d and a soluble COD of 2000 mg/L was processed at a temperature of 27 °C in an anaerobic reactor. Biomass yield of 0.045 g VSS/g COD was observed at 90% COD removal efficiency. Calculate the amount of methane produced in m^3/d. (COD of cell tissue = 1.42 g COD/g VSS).

Solution:

(a) COD mass balance.

At steady state condition

Influent COD - effluent COD – COD of new cells – COD of methane = 0

$COD_i = COD_e + COD_{vss} + COD_{methane}$

$COD_i = (4{,}000\ m^3/d)(2{,}000\ mg/L) = 8{,}000{,}000\ g/d$

$COD_e = (1 - 0.9)(8{,}000{,}000) = 800{,}000\ g/d$

$COD_{vss} = (1.42\ gCOD/gVSS)(0.045\ gVSS/gCOD)(0.90)(8{,}000{,}000\ g/d) = 460{,}080\ g/d$

$COD_{methane} = 8{,}000{,}000 - 800{,}000 - 460{,}080 = 6{,}739{,}920\ g/d$

(b) Amount of methane produced at 27°C.

Volume of gas occupied by 1 mole of gas at 27°C.

$V = \frac{nRT}{P} = ((1\ mole)(0.082\ atm/l\,moleK)(273 + 27)K)/1.0\ atm = 24.60\ L$

COD of methane.

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

COD of methane = 2(32 g O_2 per mole) = 64 g/mole of CH_4.

The volume of methane at 27°C = (24.60 L/mole)/(64 g/mole) = 0.38 LCH_4/g COD

Methane production = (6,739,920 g/d)(0.38 LCH_4/gCOD) = 2,591 m^3/d.

9.6 ANAEROBIC ATTACHED GROWTH PROCESSES

Attached growth processes are those biological treatment processes in which the microbes are attached and concentrated onto an inert medium such as sand, slag, rocks, granular activated carbon, gravels, ceramic and plastic materials. In this process, a biofilm that consists of microbes, their extracellular polymeric substances (EPS), and particulate materials covers the inert support medium. So this is otherwise called as biofilm or a fixed film process. Substrate consumption takes place within the biofilm. Retention of a large amount of biomass in the biofilm results in extended SRTs even with the application of low HRTs. This property (SRT > HRT) enables the attached growth process to fit the criteria of high-rate treatment processes. These processes are best suited for treatment of dilute and soluble organic wastewaters but not for particulate-containing wastewater as particulate matters lead to clogging (Buitron et al. 2006). Depending upon direction of the influent flow inside the reactor, attached growth anaerobic

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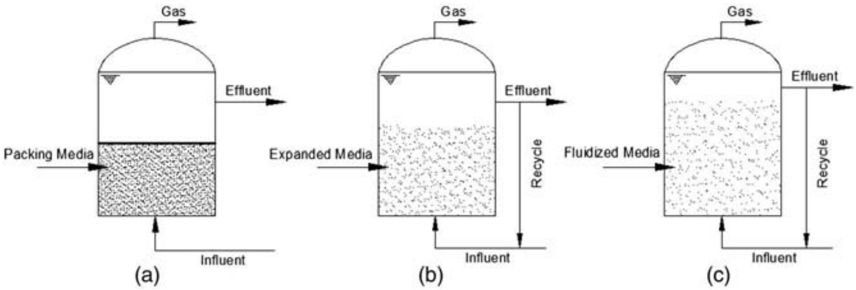

Figure 9.14. (a) Up flow anaerobic packed bed reactor; (b) Up flow anaerobic expanded bed reactor; (c) Up flow anaerobic fluidized bed reactor

treatment processes can be divided into two types, namely (1) up-flow anaerobic attached growth process and (2) down-flow anaerobic attached growth process. The configuration of up-flow attached growth process relies on types of packing used and degrees of bed expansion. Accordingly, there are three types of reactor configurations: (i) up-flow anaerobic packed bed reactor, (ii) up-flow anaerobic expanded bed reactor and (iii) up-flow anaerobic fluidized bed reactor are discussed (Figure 9.14). The brief description of each type is carried out in the following sections.

9.6.1 Up-Flow Anaerobic Packed Bed Reactor

In this type of reactor, packing materials are fixed inside the reactor and influent flows in an upward direction through the void spaces between the packing materials as shown in Figure 9.14(a). The packing materials provide a uniform flow through the reactor, allow accumulation of the large amount of biomass (long SRT) and also establish proper contact between the waste constituents and the biomass. The commonly used packing materials include rocks and synthetic plastics (i.e. corrugated plastic cross flow, tubular modules and plastics pall rings). The packing materials can be arranged in continuous or multiple stage manners. A significant proportion of the biomass inside the reactor is not attached to the packing materials. Instead, it is loosely held in the void spaces between packing materials. Large void spaces not only result in the maximum available reaction volume but also offer space for the accumulation of unattached biomass. Cylindrical or rectangular tanks with width and diameters ranging from 2 to 8 m and heights from 3 to 13 m are used in constructing large-scale up-flow anaerobic packed bed reactor. It is necessary to maintain low up-flow velocities in the range of 0.6 to 0.9 m/h to prevent washing out the biomass (Metcalf and Eddy Inc 2003). With the due course of time, the biomass will accumulate in the packing and will pose clogging and short circuiting problems. Therefore flushing and draining of the reactor need to be done at regular intervals to maintain performance efficiency. These reactors have relatively small reactor volume and simple operations while the cost of packing material is a drawback.

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9.6.2 Up-Flow Anaerobic Expanded Bed Reactor

The up-flow anaerobic expanded bed reactor is characterized by the presence of packing materials that can be expanded or mobilized by the up flow velocity of the influent. Packing materials with the diameter in the range of 0.3 to 3 mm like silica, sand, resins, grave, coal etc. are used to support biomass growth and attachment. Smaller packing materials make available a greater surface area per unit volume, thus supporting a greater amount of biomass. The cylindrically configured reactors as shown in Figure 9.14(b) are generally packed about 10% of its volume and the expansion is maintained between 10–20% of the bed volume (de Lemos Chernicharo 2007). The bed expansion is maintained at a level required for each particle of the packing material to preserve its relative position with other particles. Effluent recycling is necessary in this process in order to guarantee a flow rate sufficient to elevate the biomass-attached packing materials. The expansion of the sludge bed ensures good contact between the wastewater and the biomass and eliminates clogging problem. The biomass attachment to small-sized particles results in formation of thinner bio film compared to packed bed. The retention of biomass leads to long SRT and short HRT, whereas the thin film formation overcomes the substrate or mass transfer difficulties associated with thick film. In this reactor, the factors like retention of high concentration biomass, formation of thin films, longer SRT, shorter HRT and filtration by fine packing materials are accountable for the high quality effluent in terms of COD and suspended solids.

9.6.3 Up-Flow Anaerobic Fluidized Bed Reactor

This reactor is a variant of the up-flow anaerobic expanded bed reactor. This system relies on an internal microbial growth medium, which is fluidized by the up-flow velocity of the influent within it. The physical design and working principles of the fluidized bed reactor (Figure 9.14 (c)) are identical to that of the expanded bed reactor. Both of the reactors differ with respect to rates of expansion, particle sizes of the packing materials and sludge positioning. The rate of expansion usually varies between 30 to 100%. The particle size of the packing materials is in the range of 0.2–0.5 mm (de Lemos Chernicharo 2007). In this case, sludge is distributed over the entire reactor volume whereas in case of expanded bed, sludge is present in the lower part of the reactor. For fluidized bed, higher up-flow influent velocity e.g., tenfold more than that of the expanded bed reactor, is required to obtain the desired expansion. Higher recirculation rate does not allow the independent particles to maintain a fixed position to each other inside the reactor, it is still vital to get the preferred up-flow velocity. The advantages of the fluidized bed reactor include no clogging, small working volume, high biomass concentrations, high mass transfer characteristics, relatively high organic loadings, and the ability to handle shock loads due to its mixing and dilution with the recycled flow. On the other hand, the requirements of a long start up time, difficulties in maintaining the good flow-rate, difficulties in controlling the thickness of the biofilm, requirements for pumping and costs of reactor packing are their limitations (Morawicki 2011).

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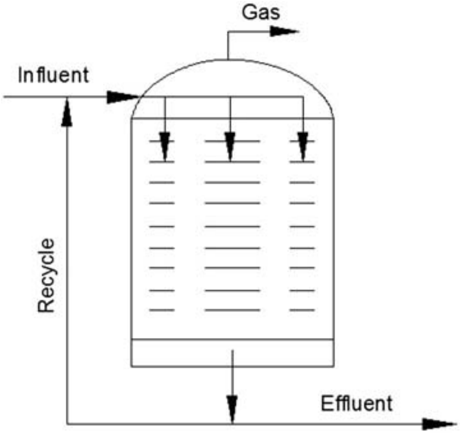

Figure 9.15. Down flow anaerobic attached growth reactor

9.6.4 Down-Flow Anaerobic Attached Growth Reactor

Down-flow anaerobic attached growth reactor as shown in Figure 9.15 is an advanced high-rate reactor based on the principle of biomass retention. It differs from other types of advanced reactors on the basis of down flow mode of operation and the packing material used. Varieties of packing materials generally with high void volume like random plastics, tubular plastics and cinder blocks are used to prevent clogging. The reactor is designed to recycle the effluent when desired. The biomass attach themselves to the channel walls of the packing materials and form biofilm. The down-flow mode helps remove the settleable materials from the effluent, thus reducing the risk of clogging. The mixing operation is achieved via the effect of rising gas bubbles. Due to the self-mixing feature, these reactors are used to treat high-strength wastewater (Metcalf and Eddy Inc 2003). These reactors withstand harsh hydraulic overloading and organic shock loads without any major harm to the system. The advantages include simplicity in construction and operation, no clogging problem, better stability at a higher loading rate, relatively small reactor volume etc. In contrast, cost of the packing materials, lower performance efficiency (in case of high influent suspended solid concentration) etc. are the major limitations.

9.7 ANAEROBIC LAGOONS

The term lagoon stands for a confinement or an impoundment that receives raw sewage. So anaerobic lagoons are the deep confinements of earthen basins, essentially free of dissolved oxygen, thereby promoting anaerobic conditions for the treatment of the received raw sewage. These are used for high strength organic wastewater such as industrial wastewaters or a mixture of industrial and domestic

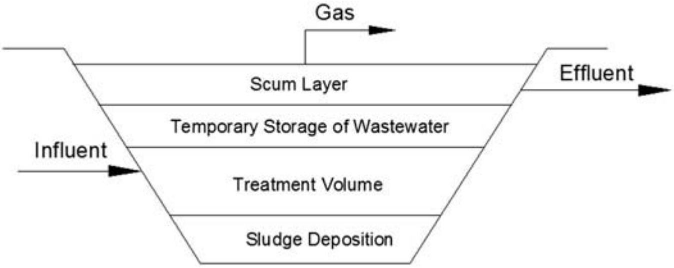

Figure 9.16. Schematic diagram of an anaerobic lagoon

wastewaters. The industries include slaughterhouses, dairies, meat processing plants, and vegetable processing facilities (U.S. EPA 2002). The detention time varies from 20–50 days with a lagoon depth of 5–10 m (Metcalf and Eddy Inc 2003). Such depths diminish the effects of oxygen diffusion from the surface, allowing anaerobic conditions to prevail, except for the shallow surface layer in which excess undigested grease and scum are concentrated. With the formation of an impervious surface layer by grease and scum, a complete anaerobic condition develops, allowing the anaerobic bacteria to break down the organic wastes.

The anaerobic lagoons as shown in Figure 9.16 have high volume sufficient enough to (1) permit sedimentation of settleable solids, (2) retain sludge for a longer time, (3) digest retained sludge, and (4) anaerobically reduce some soluble organic substrates of the sludge. The inlet is located near the bottom of the lagoon through which the raw sewage enters the lagoon and mixed the active microbial mass in the sludge blanket. The effluent is taken from the outlet located in the side of the lagoon and opposite to the inlet side. A treatment process includes anaerobic digestion of organic wastes inside the lagoon. During the detention period, several events take place. Those includes (i) removal of suspended solids by sedimentation, (ii) reduction in the number of some of the pathogenic elements like fecal coliform due to the long detention times, (iii) floatation of excess undigested grease, oil and floating matters such as plastics, cigarette butts to the top forming the scum layer on the surface of the flow, (iv) release of gases such as CO_2, CH_4, and H_2S and (v) synthesis of new biomass, adding to the sludge blanket as an active biomass. The effluent from anaerobic lagoons is sometimes not able to meet the discharge standards. So there is a requirement of additional treatments. Therefore anaerobic lagoons must be followed by other anaerobic, aerobic or facultative lagoons to provide a proper treatment.

There are two general types of anaerobic lagoons, (i) single-stage and (ii) multiple-stage. In multiple-stage lagoons, individual lagoons can be arranged in series or parallel as in Figure 9.17. In case of series arrangement, the effluent produced in the first stage will be the influent for the secondary stage and so on. However, in case of parallel arrangement, step feed flow pattern is observed, where a portion of the raw sewage flow to the primary stage and the remaining sewage flow to the secondary stage. The primary effluent will also flow to the secondary stage. This helps in removing some of the organic loading from the first stage and

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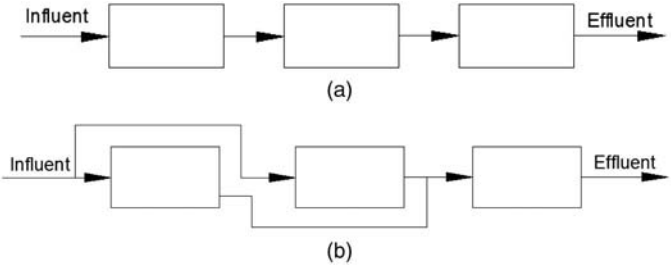

Figure 9.17. Arrangement of multi stage lagoon (a) Lagoons in Series; (b) Lagoons in parallel

distributes it to avoid organic overloading. Benefits of using multiple stages are reduced solids and odor potential of the lagoon water.

Anaerobic lagoon design includes two key parameters: (1) detention time and (2) loading volumes. While designing an anaerobic lagoon, it should be kept in mind that the effective volume of the lagoon gradually reduces due to the deposition of sludge and therefore the design should be based on the real lagoon volume. Some of the design parameters of the anaerobic lagoon as per Natural Resources Conservation Service guideline code- 359 (NRCS#359) (NRCS 2003) are given below:

$$V_{\text{lagoon}}(\text{m}^3) = (\text{L} \times \text{W} \times \text{D}) - (\text{S} \times \text{D}^2) \times (\text{W} + \text{L}) + (4 \times \text{S}^2 \times \text{D}^3 \div 3) \tag{Eq. 9.21}$$

where L=Length (m), W=Width (m), D=Depth (m) and S=Slope (m).

$$\text{Minimum treatment volume}(\text{m}^3) = \frac{\text{Daily total volatile solid loading (kg/d)}}{\text{Volatile solid loading rate (kg/m}^3\cdot\text{d)}} \tag{Eq. 9.22}$$

$$\text{Sludge accumulation}(\text{m}^3) = \text{Volume of the lagoon} - \text{Minimum treatment volume} \tag{Eq. 9.23}$$

$$\text{HRT} = \frac{\text{Minimum treatment volume (m}^3)}{\text{Hydrulic flow rate (m}^3/\text{d)}} \tag{Eq. 9.24}$$

where HRT=Hydraulic retention time of day.

The advantages of using anaerobic lagoons include inexpensive construction, flexible operation and maintenance (either in series or in parallel mode), less biomass production (fewer sludge handling and disposal issues) and large volume (equalization of wastes and higher organic loading rate). The disadvantages are large area requirement, undesirable odor problem, long detention time, infiltration of wastewater into groundwater, and unstable effluent quality.

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9.8 ANAEROBIC HYBRID REACTORS

The anaerobic hybrid reactor as depicted in Figure 9.18 is an amalgamation of the positive attributes of the UASB reactor and upflow anaerobic packed bed reactor. The bottom part of the hybrid reactor is functionally identical to the UASB reactor whereas a region of attached biomass representing the anaerobic packed bed reactor is located in the upper part of the hybrid reactor. This reactor was incited to overcome the shortcomings of both the UASB and anaerobic packed bed reactor. In the UASB, failure to produce dense granules and granule floatation or disintegration occasionally leads to process break-down. Similarly, in the packed bed reactor, it is difficult to retain the poorly attached/settled biomass as there is a high chance of sludge wash-out. As mentioned earlier, the hybrid reactor incorporates the advantages of both the reactors. Firstly, the bottom portion is responsible for granular sludge formation and ensures good contact between biomass and substrate. Secondly, the packed media in the upper portion of the reactor provides a surface for attachment of biomass and also plays a key role in gas-liquid-solids separation for further enhancement of biomass retention within the reactor (Lettinga 1995). The attached growth along with the formed granular sludge bed adds up significant biomass inventories, which result in the process stability and higher removal efficiency. The hybrid reactor finds its application in the treatment of the wastewaters where granular sludge formation is difficult to obtain, such as dairy, distillery, pharmaceutical, petrochemical, textile, tannery, and chemical industries. The advantages of hybrid reactor include long SRT (independent from HRT), biomass accumulation in the unpacked zone, a

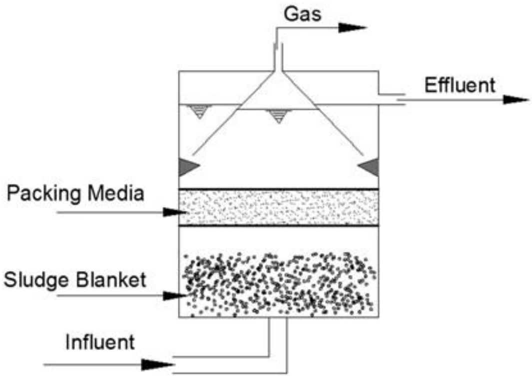

Figure 9.18. Schematic representation of anaerobic hybrid reactor

gas-liquid-solid separator in the packed zone, retention of the non-attached sludge, prevention of sludge washout, process stability and reduced cost of packing media. This hybrid reactor is used very frequently to treat medium- to high-strength wastewater, but has very limited application in treatment of low-strength wastewater.

9.9 ANAEROBIC MEMBRANE BIOREACTORS

An anaerobic bioreactor unit in combination with a membrane filtration unit results in an anaerobic membrane bioreactor. This reactor integrates biological degradation of waste products in an anaerobic condition with membrane filtration. This reactor design permits substantial biomass retention in the bioreactor by the application of micro- or ultra-filtration process. The retention of biomass by the filtration membrane ensures the effective uncoupling of SRT from HRT, enabling the treatment of large volumes of wastewater in short HRT (Nicolella et al. 2000). Anaerobic membrane bioreactor finds its application in the situations (1) where granule formation cannot be assured, (2) where settling and clarification problems are regularly encountered, (3) when a complete retention of the biomass must be ensured or (4) when to deal with wastewater which can be difficult to treat without long SRTs. Along with biomass retention, the membrane also prevents the flee of exocellular enzymes and soluble oxidants, creating a more active biological blend capable of degrading a wider range of carbon sources (Cicek et al. 1999). So this reactor can be effectively used to remove biological entities, organic and inorganic components of the wastewater. Recent applications of anaerobic membrane filters include municipal wastewater treatment for small communities, landfill leachate treatment and industrial wastewater treatment (Manem and Sanderson 1996).

Depending upon the positioning of the membrane filtration component, anaerobic membrane bioreactor exists in two configurations: (1) external loop or side stream and (2) internal submerged (Liao et al. 2006) as depicted in Figure 9.19. In an external loop configuration, the membrane unit is placed outside the bioreactor and the membranes operate under pressure to produce permeate. The mixed liquor in the bioreactor is pumped into the membrane module creating a positive pressure which leads to permeate production. The retentate is returned to the bioreactor. In an internal submerged configuration, the filtration membrane is submerged directly in the mixed liquor in the bioreactor and permeate is produced by exerting a vacuum on the membrane. External loop configurations are more energy-intensive than those of the internal submerged configuration. On the other hand, the membrane cleaning operations can be performed more easily in external configuration than that of internal configuration since membrane removal from the reactor is required in the latter case. Advantageous energy consumption leads to more commercial applications of the internal submerged configuration in the current scenario.

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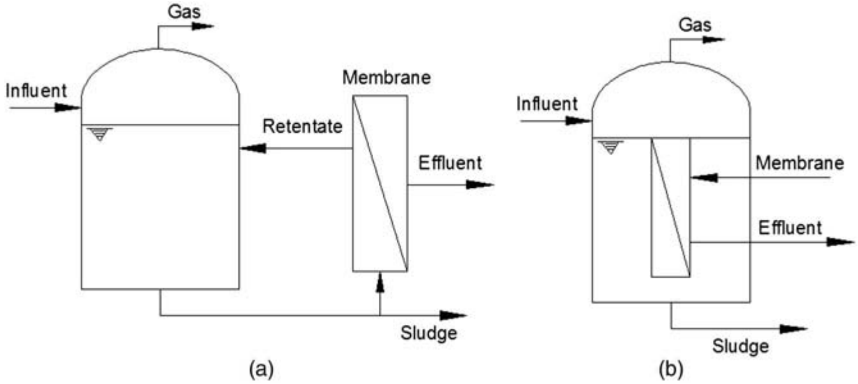

Figure 9.19. Anaerobic membrane bioreactor (a) External loop; (b) Internal submerged

The advantages of using anaerobic membrane reactor are (1) small footprint of the reactor, (2) removal of suspended and soluble component leads to high effluent quality, (3) retention of microbes in the membrane results in disinfected effluent, (4) high biomass concentration in the reactor, (5) handling capacity of large volume of wastewater, (6) tolerance of high strength wastewater, (7) low sludge production with no sludge bulking. The major disadvantages include high capital cost of the membrane, energy consumption, membrane fouling, frequent cleaning or changing of the membrane etc.

9.10 KINETIC MODELING OF ANAEROBIC TREATMENT PROCESSES

Kinetic model analysis is an accepted pathway for describing the performance of biological treatment systems and for predicting their performance. Models are generally used to optimize the plant design, predict the operational performance, and evaluate the experimental results. Different models described here may be used to predict the performance of anaerobic reactor treating different types of wastewater.

9.10.1 Modified Stover-Kincannon Model

This model considers the substrate removal rate as a function of OLR at steady-state. The original Stover-Kincannon model is expressed with the Eq. 9.25 (Stover and Kincannon 1982).

$$\frac{dS}{dt} = U_{max} \cdot \frac{(Q \cdot (S_0/V))}{K_B + (Q \cdot (S_0/V))} \qquad \text{(Eq. 9.25)}$$

where dS/dt is defined as Eq. 9.26.

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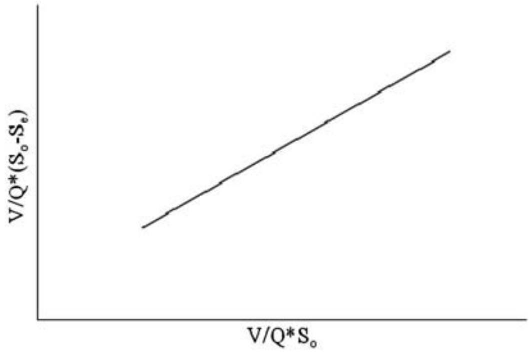

Figure 9.20. Plot of linearized Eq. (9.27)

$$\frac{dS}{dt} = \cdot \frac{Q}{V} \cdot (S_o - S_e) \qquad \text{(Eq. 9.26)}$$

Linearisation of Eq. (9.25) and (9.26) yields Eq. 9.27

$$\frac{V}{Q \cdot (S_o - S_e)} = \frac{K_B}{U_{max}} \frac{V}{Q \cdot S_o} + \frac{1}{U_{max}} \qquad \text{(Eq. 9.27)}$$

The plot of $\frac{V}{Q \cdot (S_o - S_e)}$ versus $\frac{V}{Q \cdot S_o}$ will be a straight line (Figure 9.20). The intercept and the slope of this line will give $\frac{1}{U_{max}}$ and $\frac{K_B}{U_{max}}$, respectively.

9.10.2 Grau Second-Order Multi-Component Substrate Removal Model

The general equation of the second-order kinetic model is exemplified in Eq. (9.28) (Grau et al. 1975):

$$-\frac{dS}{dt} = k_s \cdot X \cdot \left(\frac{S_e}{S_o}\right)^2 \qquad \text{(Eq. 9.28)}$$

Integrated and linearized form of Eq. (9.28) is represented as Eq. (9.29):

$$\frac{S_o \cdot \theta_H}{S_o - S_e} = \theta_H - \frac{S_o}{k_s \cdot X} \qquad \text{(Eq. 9.29)}$$

If the second term of the right part of Eq. (9.29) is considered as a constant, then the Eq. (9.30) will be obtained (Grau et al. 1975):

$$\frac{S_o \cdot \theta_H}{S_o - S_e} = b \cdot \theta_H + a \qquad \text{(Eq. 9.30)}$$

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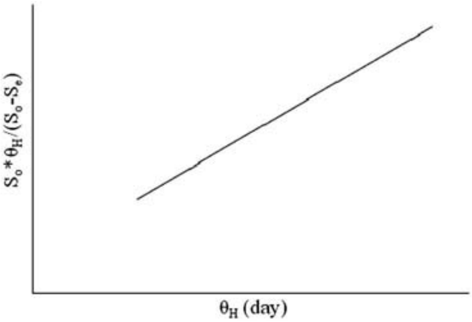

Figure 9.21. Plot of linearized Eq. (9.30)

(So-Se)/So represents the substrate removal efficiency and is symbolized as 'E'. Therefore, Eq. (11-30) can be written as

$$\frac{\theta_H}{E} = a + b \cdot \theta_H \qquad \text{(Eq. 9.31)}$$

From the linearized plot of Eq. (9.30), the constants 'a', 'b', and k_s can be obtained (Figure 9.21). The coefficient 'b' in Eq. (9.31) is close to one and generally reflects the impracticality of attaining a zero value of COD.

9.10.3 Monod Kinetic Model

The rate of change of biomass and substrate in UASB reactor without biomass recycle can be expressed as Eqs. (9.32) and (9.33):

$$\frac{dX}{dt} = \frac{Q}{V_b} \cdot X_o - \frac{Q}{V_b} \cdot X_e + \mu \cdot X - K_d \cdot X \qquad \text{(Eq. 9.32)}$$

$$-\frac{dS}{dt} = \frac{Q}{V_b} \cdot S_o - \frac{Q}{V_b} \cdot S_e - \frac{\mu \cdot X}{Y} \qquad \text{(Eq. 9.33)}$$

The ratio of the total biomass in the reactor to the biomass wasted per given time is called as mean cell residence time (θ_c) or sludge retention time (SRT) and calculated from the following equation:

$$\theta_c = \frac{V_b \cdot X}{Q \cdot X_e} \qquad \text{(Eq. 9.34)}$$

Specific growth rate and the concentration of rate limiting substrate can be related by Monod equation as follows:

$$\mu = \frac{\mu_m \cdot S_e}{K_s + S_e} \qquad \text{(Eq. 9.35)}$$

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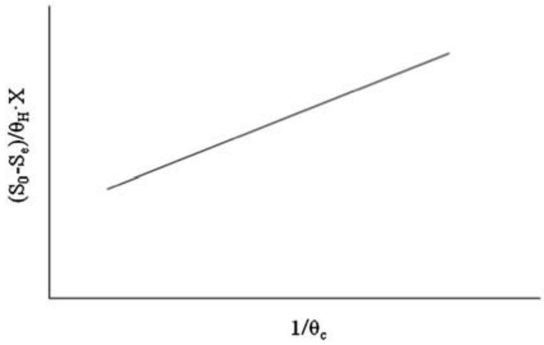

Figure 9.22. Plot of linearized Eq. (9.36)

The concentration of the biomass in the influent can be considered as negligible (i.e., X_o) and at the steady-state conditions, dX/dt and −dS/dt = 0. Therefore, at steady-state, the following equation can be obtained after substitution of Eq. (9.35) in Eq. (9.33)

$$\frac{Q \cdot (S_o - S_e)}{V_b \cdot X} = \frac{1}{Y}\left(\frac{1}{\theta_c}\right) + \frac{1}{Y} \cdot K_d \qquad \text{(Eq. 9.36)}$$

The plot of $\frac{Q \cdot (S_o - S_e)}{V_b \cdot X}$ versus $\frac{1}{\theta_c}$ will be linear one (Figure 9.22), and from this one can determine the kinetic constants Y and K_d.

At steady-state, Eq. (9.33) can be linearized in three different ways such as Lineweaver-Burk plot (Eq. (9.37)), Eadie-Hofstee plot (Eq. (9.38)) and Hanes-Woolf plot (Eq. (9.39)) after substituting the value of μ as per Eq. (9.35).

Lineweaver-Burk equation:

$$\frac{X \cdot V_b}{Q \cdot (S_o - S_e)} \cdot \frac{1}{Y} = \frac{K_s}{\mu_m} \cdot \left(\frac{1}{S_e}\right) + \frac{1}{\mu_m} \qquad \text{(Eq. 9.37)}$$

Eadie-Hosftee equation:

$$\frac{Q \cdot Y \cdot (S_o - S_e)}{X \cdot V_b} = \mu_m - K_s \cdot \frac{Q \cdot Y \cdot (S_o - S_e)}{X \cdot V_b \cdot S_e} \qquad \text{(Eq. 9.38)}$$

Hanes-Woolf equation:

$$\frac{V_b \cdot S_e \cdot X}{Q \cdot Y \cdot (S_o - S_e)} = \frac{S_e}{\mu_m} + \frac{K_s}{\mu_m} \qquad \text{(Eq. 9.39)}$$

These linearized forms of the Monod type model can also be used to predict the goodness of fit of the data based on the correlation coefficient (R^2).

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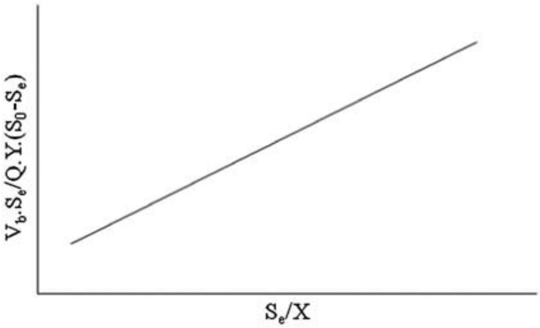

Figure 9.23. Plot of linearized Eq. (9.41)

Furthermore, these equations are used to determine the value of Monod kinetic parameters μ_m and K_s (Ong 1990; Bhunia and Ghangrekar 2008). Eqs. (11-37) to (11-39) can be used to calculate the value of K_s and μ_m.

9.10.4 Contois Kinetic Model

Contois type model is a modification over the Monod type model. The modification of the Contois growth model over Monod model is that in case of Contois model, cell-mass growth rate depends upon the concentrations of both substrate and cell-mass with growth rate being inhibited at high concentrations of the cell-mass. According to the Contois kinetic model

$$\mu = \frac{\mu_m \cdot S_e}{\beta \cdot X + S_e} \qquad \text{(Eq. 9.40)}$$

The substitution of Eq. (9.40) to the Eq. (9.32) and linearization gives:

$$\frac{V_b \cdot S_e}{Q \cdot Y \cdot (S_o - S_e)} = \frac{1}{\mu_m}\left(\frac{S_e}{\mu_m}\right) + \frac{\beta}{\mu_m} \qquad \text{(Eq. 9.41)}$$

The values of kinetic constants, μ_m and β can be obtained from the intercept and slope of the plot (Figure 9.23) versus as per Eq. (9.41).

9.11 SUMMARY

This chapter offers an overview of the fundamentals and applications of anaerobic wastewater treatment processes. The features like resistance to toxicity, production of biogas, less accumulation of biomass and no requirement of aeration make the use of anaerobic microbes to remove contaminants from wastewater with an effective and industrially feasible manner. Therefore a deep understanding of the metabolism of anaerobic microbes is essential, which ultimately helps in the conception, design, and optimization of anaerobic treatment unit processes. The main focuss of discussion of this chapter includes (1) the fundamentals of anaerobic wastewater treatment processes, (2) the effects of various environmental/physico-chemical parameters on anaerobic wastewater treatment processes, (3) classifications of different types of anaerobic treatment processes based on mode of microbial growth, (4) demonstration of different types of reactors associated with anaerobic treatment processes, and (5) description of the anaerobic wastewater treatment process kinetics using different kinetic models.

9.12 LIST OF NOMENCLATURE

HRT	Hydraulic retention time (d);
SRT	Sludge retention time (d);
MLSS	Mixed liquor suspended solids (mg/L);
MLVSS	Mixed liquor volatile suspended solids (mg/L);
VFA	Volatile fatty acids (mg/L);
COD	Chemical oxygen demand (mg/L);
BOD	Biochemical oxygen demand (mg/L);
OLR	Organic loading rate (kg COD/m^3 d);
CSTR	Continuous stirred tank reactor;
ASBR	Anaerobic sequencing batch reactor;
UASB	Upflow anaerobic sludge blanket;
EGSB	Expended granular sludge bed;
ABR	Anaerobic baffled reactor;
AMBR	Anaerobic membrane bioreactor;
GSS	Gas solid separator;
S_o	Influent substrate concentration (mg/L);
S_e	Effluent substrate concentration (mg/L);
Q	Inflow rate (L/d);
V	Reactor volume (L);
V_b	Sludge bed volume (L);
K_B	Saturation value constant (g/Ld);
U_{max}	Maximum substrate utilization rate (g/Ld);
k_s	Grau second-order substrate removal rate constant (d^{-1});
X_o	Biomass concentration in influent wastewater (g/L);
X	Biomass concentration in reactor (g/L);
X_e	Biomass concentration in effluent wastewater (g/L);
θ_H	Hydraulic retention time (d);
a, b	Kinetic constant for Grau second-order model;
μ	Specific growth rate (d^{-1});
μ_m	Maximum specific growth rate (d^{-1});
K_s	Half saturation constant (g/L);
K_i	Inhibition constant (g/L or mg/L);

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k	Maximum specific substrate utilization rate (d^{-1});
K_d	Endogenous decay constant (d^{-1});
Y	Yield coefficient (g VSS/g COD);
θ_c	Mean cell residence time (d);
β	Kinetic parameter for Contois model (g COD/g VSS).

9.13 ACKNOWLEDGMENTS

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CHAPTER 10

Constructed Wetlands for Wastewater Treatment: Sustainability Revolution in Water Management

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10.1 INTRODUCTION

At present, there are severe environmental problems related to water crisis including water shortages, water pollution and deterioration of water quality worldwide, especially in developing countries. Furthermore, the situation is becoming more serious because of low water use efficiency and worsening man-made pollution or natural contamination. Therefore, growing public awareness of environmental issues is pushing the government to implement more stringent water and wastewater treatment standards for environmental protection (Werker et al. 2002). However, in an increasingly harsh economic climate, conventional energy-intensive wastewater treatment systems (such as membrane bioreactors and sequencing batch reactors) are becoming disadvantageous. In addition, these treatments could not reduce nutrient (nitrogen and phosphorus) pollution effectively although they are known to be efficient in removing organics. Therefore, natural technologies that are primarily based on naturally occurring

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energies and significantly lower the impacts of nutrient pollution can be an alternative (Gumbricht 1992; Kadlec and Knight 1996; Vymazal 2005).

Constructed wetland (CW) treatments are a reasonable option for treating wastewater by simulating natural wetlands, owing to their lower cost, less operation and maintenance requirements, and little reliance on external energy inputs (Vymazal 2005). As a green treatment technology, it could remove various pollutants from wastewater and has been successfully used to treat various kinds of wastewater such as domestic and municipal sewage, stormwater, polluted river water, agricultural and urban runoffs (Tanner et al. 1995; Vymazal et al. 1998; Ansola et al. 2003; Solano et al. 2004; Vymazal 2007; Maine et al. 2009; Wu et al. 2011).

While much advancement has been made in design methodology and pollutant processing for CWs over the years (Gearheart et al. 1999), its sustainable application in water quality improvement remains a challenge. Plants are considered the main biological component of CWs (Weisner 1993), which also are an essential component of the design. They not only assimilate pollutants directly (Lombardi et al. 1997), but also increase the environmental diversity in the rhizosphere and enhance a variety of chemical and microbial processes for pollutant removal (Jenssen et al. 1993). Selecting the plants (e.g., be tolerant to high pollutant loadings, rich biomass) used in CWs designed for wastewater treatment should therefore be the focus of the current research on sustainable design of CWs (Vymazal 2011).

Besides, there are still knowledge gaps between the varied and limited removal performance of CWs and the current target of CW performance optimization (Stefanakis et al. 2011). The performance of CWs is critically dependent on the selection of optimal environmental and operating conditions. In view of above facts, it is necessary to develop and evaluate enhancing techniques (such as artificial aeration and feed mode), which can be potentially applied in sustainable design and operation of CWs for water quality improvement (Saeed and Sun 2012).

When evaluating the success of a CW treatment, all the components from design to operation and maintenance that are closely related to CWs should be considered. It is clear that an in-depth knowledge on developing reclamation and recycling of resources (mainly wetland plants) in CWs can appreciates the value of CW treatments. For example, dead wetland plants are often abandoned or burned as firewood. However, their porous caudex system and abundant quantity may offer a good opportunity for the production of activated carbon (Wang et al. 2010). Evaluating the potential of developing this type of activated carbon and investigating its ability to treat wastewater are important for the sustainable maintenance of CWs.

This chapter introduces CWs for wastewater treatment, with a focus on the definition, classification, structures and common removal mechanisms of pollutants. The chapter overviews the application of CWs for wastewater treatment in recent years, and summarizes the existing methodologies used in practice and other potential technologies. These technologies are useful for improving the

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sustainability of CW wastewater treatments, including improvement and optimization in system design, operation and external enhancing technologies for better treatment performance and recycling methods of wetland resources. A comprehensive understanding of CW treatment technologies would better prepare us for future applications of CW treatments.

10.2 CONSTRUCTED WETLANDS FOR WASTEWATER TREATMENT

Wetlands occur in a wide range of landscapes and may support permanent shallow or temporary standing water. CWs are artificially engineered ecosystems designed and constructed to manipulate biological processes within a semi-controlled natural environment. The growing knowledge about wetland functions and values have caused a radical change of attitude toward CWs. They are found for wastewater treatment on every continent except Antarctica (Vymazal 2011).

10.2.1 Fundamentals of Constructed Wetlands

Definition. CWs involve the use of engineered systems that are designed to utilize natural processes. These systems mimic natural wetland systems, utilizing emergent/floating/ submerged plants, saturated or unsaturated substrates, and a large variety of microbial communities to remove contaminants from wastewater effluents.

Classification. In general, two prevalent types of CW systems are most commonly applied, i.e., the Free Water Surface (FWS) systems and the Subsurface Flow (SSF) systems (Kadlec and Knight 1996). FWS systems are similar to natural wetlands, with shallow flow of wastewater over a saturated substrate. In SSF systems, wastewater flows horizontally or vertically through the substrate, which is composed of soil, sand, rock or artificial media.

Pollutant removal in CW systems. CWs are highly complex systems that separate and transform contaminants by physical, chemical, and biological mechanisms. The mechanisms may occur simultaneously or sequentially as the wastewater flows through the system. The two major mechanisms in most CW treatment systems are liquid/solid separations and constituent transformations. Separations typically include gravity separation, filtration, absorption, adsorption, ion exchange, stripping, and leaching. Transformations may be chemical, including oxidation/reduction reactions, flocculation, acid/base reactions, precipitation, or a host of biochemical reactions occurring under aerobic, anoxic, or anaerobic conditions. CW systems can remove many contaminants, including organic compounds, suspended solids, nitrogen, phosphorus, trace metals, and pathogens. Suspended solids that are not removed in pre-treatment system are effectively removed by filtration and settlement. Organic matter is decomposed by both aerobic and anaerobic microbial processes, as well as by sedimentation and filtration of particulate organic matter. The intensities of aerobic and anaerobic degradation are highly dependent on the oxygen content in the wastewater flowing

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through the CW. The major removal mechanism for nitrogen in CWs is nitrification and denitrification, whereas volatilisation, adsorption and plant uptake play a much less important role.

Historical development of CW systems. Wastewater purification with the use of plants can be classified as one of the fairly old technologies. Kadlec and Knight (1996) give a good review of the historical use of natural and CWs for wastewater treatment. As they pointed out, natural wetlands have probably been used for wastewater treatment for as long as wastewater has been collected, documented dating back to 1912. Some early CWs researchers probably began their efforts based on observations of the apparent treatment capacity of natural wetlands. At the end of the 20th century, in Europe, CW systems were most frequently designed on the basis of recommendations of CWs researchers. Research efforts in the US also increased with the significant involvement of Federal government. On other continents (such as Australia and New Zealand) also numerous recommendations have been developed for the design of CW systems.

10.2.2 Free Water Surface Constructed Wetlands

FWS CWs closely simulate natural wetlands in appearance and function, with a combination of open-water areas, vegetation, varying water depths, and other typical wetland features. Figure 10.1 shows the main components of a FWS CW. A typical FWS CW consists of several components that may be modified among various applications but retain the same features. These components include the berms that enclose the treatment area, the inlet structures that distribute influent wastewater, the various combinations of open-water areas and fully vegetated surface areas, and the outlet structures that complement the even distribution

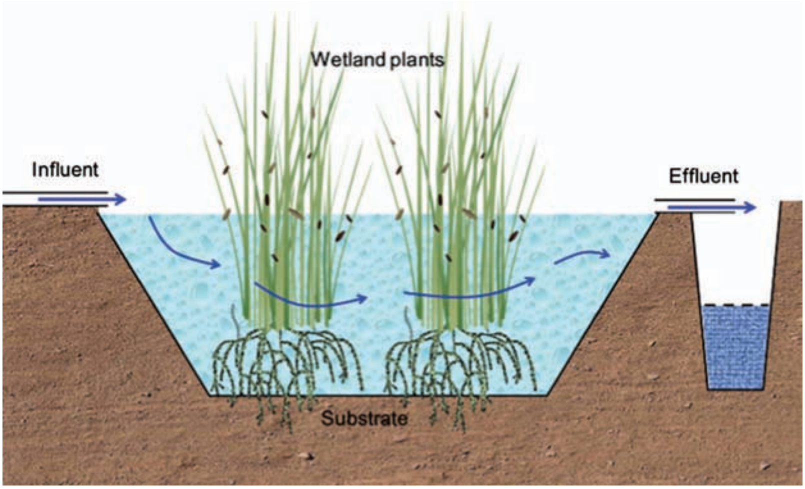

Figure 10.1. Typical elements of a FWS CW

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Table 10.1. Advantages and disadvantages of FWS CWs

Advantages	*Disadvantages*
• Low operation and maintenance cost • Easily built and repaired with locally available materials • Can be combined with aquaculture and agriculture • Aesthetically pleasing with less odour and flies • Construction can provide short-term employment to local laborers	• May facilitate mosquito breeding • Long start up time to work at full capacity • Requires large land area • Not very tolerant to cold climates

provided by the inlet structures and, meanwhile, allow adjustment of water levels (Vymazal 2011).

The FWS CWs are very effective in the removal of organics (through microbial degradation) and suspended solids (through filtration and sedimentation). Nitrogen removal is variable and depends on many factors such as inflow concentration, chemical components of nitrogen, temperature, season, carbon availability, and dissolved oxygen concentration. Ammonia can be effectively removed through nitrification in aerobic zones followed by denitrification of nitrate in anaerobic zones in the litter layer at the bottom (Vymazal 2011). However, phosphorus removal rate in the FWS systems is low due to little contact between water column and the soil. Table 10.1 shows advantages and disadvantages of FWS CWs.

FWS CWs are commonly used to treat of runoffs from urban areas, road and highway, airport, agriculture as well as drainages from coal mines, metal ore mines or pastures. In addition, they are applied for treatment of concentrated agricultural wastewaters from swine, dairy or farmyard operations. In many countries, FWS CWs are employed to treat municipal sewage and other types of wastewater such as landfill leachate, refinery process waters, pulp and paper effluents, fish hatcheries, abattoirs and sugar factory (Vymazal 2013). They provide greater storm capacity and thus, less chance for hydraulic failure. FWS CWs are suitable in all climates, including the cold weather in the far north areas. However, icing can reduce the rates of some removal processes, especially nitrogen removal (Kadlec and Wallace 2008).

In America, according to the North American Treatment Wetland Database (NADB), about 28 percent of wetland systems utilize natural wetlands, 69 percent of the wetlands are constructed. About 65 percent of the natural wetland systems are receiving conventional secondary treated wastewater. More than 45 percent of the CW systems are treating pond effluent and 22 percent are treating conventional secondary effluent. With regard to pretreatment levels, one-third of the

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wetland systems receive pond effluent, one-third receive conventional secondary effluent, and the remaining third are distributed among primary, advanced secondary, tertiary, and other.

The survey by Shi et al. (2004) demonstrated that the quantity of CWs was growing swiftly in South and a part of northern China since 2000. In addition, from 2000 to 2010, the annual growth rate of the completed CWs was significantly higher than that of the number in planning (Zhang et al. 2012). The treatment capacity of CWs in China ranged from 1000 m^3/d to 20,000 m^3/d. They have been used for treating as many as 20 kinds of wastewaters. In accordance with the source of wastewater, it may be classified into domestic sewage, aquaculture water, polluted lake and river water, landscape water, composite wastewater, industrial wastewater and so on. Among all these types of wastewaters, the domestic sewage and polluted river water were the top two influents to the CWs.

Zhang et al. (2009) summarized the application of the FWS CWs in China and reported relative treatment efficiencies. Compared with the discharge standards set by the Chinese government, the main effluent qualities in terms of total suspended solids (TSS), biological oxygen demand (BOD), and chemical oxygen demand (COD) were generally lower than the corresponding discharge standards. In all seasons except winter, the levels of BOD and TSS in the effluent of every system could reach the standards achieved by biological secondary treatment. However, perhaps due to lack of information and design/operation expertise, few FWS CWs were applied in practice in the last years. At present, in order to improve the water quality to meet the Grade-III standards in Nansi Lake Basin of Shandong Province, lots of FWS CWs have been built for purifying polluted water. The typical surface CW located in Weishan County, Shandong province, north China was built on the southern side of the mouth of Xinxue River for treating the polluted river water. This system (approximately 1.33 km^2) was has been operated since 2008. It was reported that the treated river water met Grade-III water quality in China. In addition, the wetland systems partially rehabilitated the degenerated lakeshore wetland (Wu et al. 2012).

10.2.3 Sub-Surface Flow Constructed Wetlands

SSF wetlands mostly employ gravel as the main media to support the growth of plants; wastewater flows vertically or horizontally through the substrate where it comes into contact with microorganisms, living on the surfaces of plant roots and substrate (Kadlec and Knight 1996), allowing pollutant removal from the bulk liquid. SFW wetlands are further divided into two groups: (1) vertical flow (VF), and (2) horizontal flow (HF) systems. Figure 10.2 illustrates the main components of a SSF CW. Table 10.2 shows advantages and disadvantages of SSF CWs.

In a HF CW where a large gravel and sand-filled channel is planted with aquatic vegetation, the wastewater is fed in at the inlet and flows through the medium under the surface of the planted system to the outlet where it is collected before leaving via a water level control structure (Vymazal 2011). The most important properties of these CWs are filtration bed insulation during the winter, substrate for growth of attached bacteria, oxygen release to the rhizosphere,

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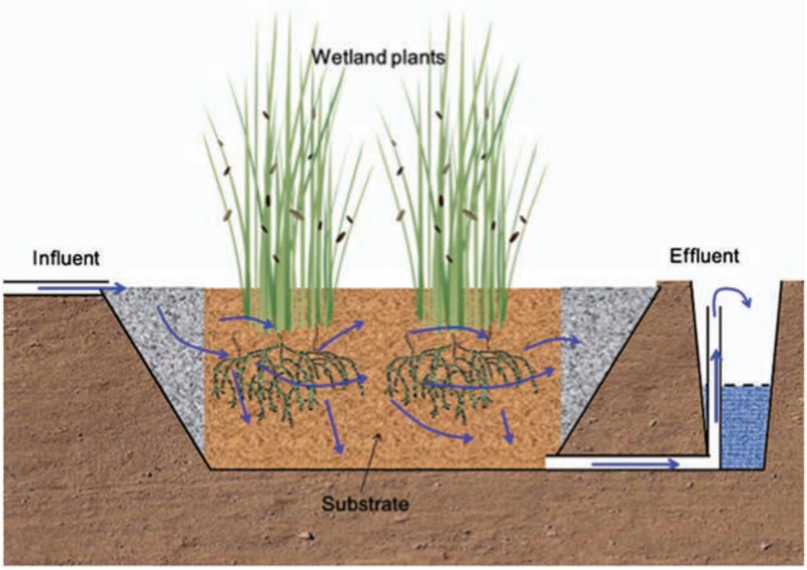

Figure 10.2. Typical elements of a SSF CW

Table 10.2. Advantages and disadvantages of SSF CWs

Advantages	*Disadvantages*
• Low operation and maintenance – process stability • Can be built and repaired with locally available materials • Requires less space than a free-water surface CW • High reduction in BOD, suspended solids and pathogens • Does not have the mosquito problems compared to (FWS) CWs	• Permanent space required • Requires expert design and supervision • Pre-treatment is required to prevent clogging • Moderate capital cost depending on land, liner, fill, etc. • High quality filter material is not always available and expensive

nutrient uptake and storage, and root exudates with antimicrobial properties (Brix 1987, 1997). To avoid clogging of the wetland, pre-treatment is necessary. VF CWs comprise a flat bed of graded gravel topped with sand vegetated with plants. Contrary to HF CWS, wastewater in VF CWs is intermittently applied onto the surface and then drains vertically down through the filter layers towards a drainage system at the bottom. In some cases, the distribution pipes are covered with gravel to avoid open water puddles. HF CWs are commonly used for

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secondary treatment of municipal wastewater as they are very effective in the removal of organics, suspended solids, microbial pollution, and heavy metals. As compared to HF CWs, owing to less land requirement, VF CWs are commonly used to treat on-site domestic wastewaters or sewage from small communities, though other uses such as industrial wastewaters or stormwater runoff have been reported (Vymazal 2011).

In Europe, wetlands have been studied intensively in the past 30 years. In the Czech Republic, it is estimated that about 100 full scale CWs are in operation by the end of 1999. At present, it is difficult to estimate the exact number of CWs there. Most of the systems are horizontal subsurface flow (HF) CWs and are designed for the secondary treatment of domestic or municipal wastewater. Several systems were designed for tertiary treatment. Other CWs treat wastewater from dairy, abattoir, and bakery facilities, landfill leachate, and stormwater runoff (Vymazal 2002). The size of CWs ranges between 18 and 4500 m^2. The treatment efficiency is high in terms of BOD (88%) and suspended solids (84%). Average removal efficiencies for total phosphorus and total nitrogen are 51 and 41%, respectively.

In China, the statistical data indicated that, in the recent 20 years, the VF CWs was the major types used to treat a variety of wastewater, predominantly domestic sewage (Zhang et al. 2012). Since the beginning of the 21th century, China's domestic sewage amount has accounted for above 50% of the total amount of national wastewater discharge. The number of the VF CWs used for treating the domestic sewage was greatly higher than the other types of CWs. Compared to the discharge standards set by the Chinese Government, the majority of the effluent values of TSS, BOD and COD in HF CWs are generally lower. Compared with HF CWs, VF CWs usually require smaller foot print, and it is therefore an attractive alternative for southern China where land is scarce and population density is high. In a pilot VF system near Longdao River in Beijing, an improved CW occupied less than half of the area of a conventional CW. The researchers compared the Longdao VF system with other HF systems in other countries, and found that the removal efficiencies of BOD (87%), COD (81%) and TSS (85%) of the VF CWs are similar, while the removal efficiencies of TP (98%) and NH_4-N (77%) are much higher than that in other countries. Additionally, the effluent concentrations of all substances were stable even during the winter (Chen et al. 2008).

10.2.4 Major Problems of Sustainability

The increasing application of CWs coupled with increasingly strict water quality standards has been an incentive for the development of better design tools. The construction number and treatment capacity of CWs worldwide increased year by year, but there are still many problems of sustainability in CWs. The major problems include: 1) Selecting the proper wetland plants (i.e. be tolerant of high pollutant loadings, rich biomass) applied in CWs for wastewater treatment; 2) Selecting the optimum enhancing techniques applied in sustainable operation of CWs for water quality improvement; 3) developing reclamation and recycling of resources in CWs. Therefore, it is necessary to further advance CWs.

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10.3 SUSTAINABLE DESIGN–PLANT SELECTION IN CONSTRUCTED WETLANDS

Wetland plants play an important role in CWs. However, only a few plant species have been widely used in CWs. Wetlands plants should be adapted to climate conditions and tolerant of the water quality, such as high-ammonia and organic pollutants levels, and be able to propagate, like through rhizome spread.

10.3.1 Plant Adaptability to Climate Conditions

In CWs, selected plants must be able to survive in the local climate. Climate is a potent selective force in plant population. As many species are unlikely to migrate fast enough to track the rapidly changing climate of the future, adaption must play an increasingly important role in their response (Jump 2005). Wetlands are affected by solar radiation and ambient temperatures, which cycle on an annual and daily basis. These biotic factors mediate the temperature of the wetland environment causing cyclical patterns in evapotranspiration, photosynthesis and microbial activity (Picard 2005). The true influence of temperature, season and plants species selection on CWs performance has not been evaluated adequately.

The growth of wetland plants are greatly influenced by soil matrix, climate, temperature and so on. The ability of wastewater treatment changes in accordance to the plant growth and physiological conditions. The selection of CW plants should adapt to the local soil and climate conditions, otherwise, it is difficult to achieve the ideal treatment efficiency. Therefore, the selection should be on the basis of extensive investigation, giving priority to local aquatic species. As for the introduced species, the choice should be made after experimental research. *Phragmites communis Trin* and *cattail* stem are the most common plants in underflow CWs. These two kinds of plants are common species both the north and the south of China, and they are among the best wetland plants in the world (Gopal 1999).

10.3.2 Plant Tolerance to Pollutants in Wastewater

Water pollution can cause direct damage to aquatic plants; for example, eutrophication causes reduction or even disappearance of aquatic plants (Cao et al. 2007). These damages are particularly common and obvious when CWs are used in wastewater treatment. As a result, the sustainable operation of CWs can be negatively affected.

When CWs are used to remove various pollutants in water, wetland plants also suffer from stress. Extreme conditions of wastewater may exceed the tolerance of aquatic plants, which would limit both plant survival and treatment potential (Arnon 1949). For example, excessive amounts of ammonia will damage the physiology of plants. External ammonia can cause chlorosis in leaves, suppression of growth, lowering of root, and yield depressions in visual symptoms as well as trigger oxidative stress expressed through the enhancement of catalase (CAT) and peroxidase (POD) (Nimptsch and Pflugmacher 2007; Xu et al. 2010).

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Net photosynthetic rate. Photosynthesis is a process used by plants and other phototrophic organisms to convert light energy, normally from the sun, into chemical energy that can be used to fuel the organisms' activities. Carbohydrates, such as sugars, are synthesized from carbon dioxide and water. Oxygen is also released, mostly as a waste product. Photosynthesis maintains atmospheric oxygen levels and supplies all of the organic compounds and most of the energy necessary for all life on Earth. However, ammonia may influence the coupling of photophosphorylation to electron transport (Platt et al. 1977). Excessive ammonia can suppress the net photosynthetic rates of wetland plant, such as *P. australis*. COD can cause oxygen deprivation in water bodies, which reduces aerobic respiration and enhanced anaerobic respiration in plants. Anaerobic respiration results in the production of acetaldehyde and ethanol, both are harmful to cells. This increase in ethylene production may have caused chlorosis and the premature senescence of leaf tissues, thus leading to a decrease in photosynthetic rates.

Enzymatic activities. To mitigate oxidative stress, plants develop a complex defense antioxidant system, such as antioxidant enzymes, including SOD, CAT, and POD (Wolfe and Hoehamer 2003). Oxidative stress may be the consequence of accumulation of reactive oxygen species (ROS), which may provoke enzyme inactivation, protein degradation, DNA damage, lipid peroxidation, and ultimately cell death (Barata et al. 2005). SOD, as an antioxidant enzyme, is an important component in the antioxidative defense system of plants and the first line of defense. It can dismutate superoxide to H_2O_2. SOD appears to act as the first defense in combating oxidative stress in plants. POD is another component of the antioxidative defense system existent in the growth, development, and senescence processes of plants. It affects the synthesis of lignin and ethylene, decomposition of IAA, resistance against pathogens, and wound healing. CAT is one of the most important enzymes that scavenge for ROS in plant cells.

Many studies have shown that ammonia can excite the activity of antioxidative enzymes in plants, such as SOD, POD, and CAT (Nimptsch and Pflugmacher 2007), suggesting that excessive ammonia leads to oxidative stress in plants. Oxidative stress triggered by excessive ammonia was also verified. We found that several antioxidative stress responses occurred in the *P. australis* leaves exposed to high ammonia concentrations. Nimptsch and Pflugmacher (2007) also showed that both CAT and POD activities in *Myriophyllum mattogrossense* increased upon exposure to higher ammonia concentrations. Excessive ammonia may cause severe damage, and intense responses may be induced. The plants would be beyond retrieval after long-time exposure to excessive ammonia. Reactive oxygen species (ROS) can be induced by various stresses. It was observed that COD induced oxidative stress in *P. australis*, further causing the variety of antioxidative enzymes found in the leaves. This may be due to the inhibition of enzyme synthesis or the fact that the assembly of enzyme subunits may have changed under a high COD (Xu et al. 2001).

Lipid peroxidation. MDA is one of the major products of membrane lipid peroxidation, which expresses cell membrane plasmalemma peroxide degree and plant reaction to the adverse conditions. The plasma membrane is the most

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sensitive part of the cell and is the site that first starts to show damage when plants are exposed to environmental stress. Under stress, reactive oxygen species accumulate in the plant body, and lipid peroxidation begins, resulting in membrane lipid and protein damage. The stability of the membrane structure and its functions are undermined. Membrane damage due to the lipid peroxidation was often expressed as a change in MDA content, which is triggered by the accumulation of ROS in cells. Lipid peroxidation products are always present because ROS balancing is a dynamic process. Therefore, MDA content increases correspondingly when the balance is destroyed by excessive ROS resulting from stress. Increasing both of ammonia and COD cause increased the content of MDA in *P. australis.*

Accumulation of proline. Proline is a compatible solute that can maintain cellular osmotic balance. It has an important role against various abiotic and biotic stresses (Umezawa et al. 2006) by accumulation of proline in the *P. australis* leaves. It is one of the mechanisms of plant tolerance to pollutants. Proline is a kind of amino acid that easily accumulates in plants under stress. It plays an important role in resisting stress. Proline has a strong capability to hydrate, making plant proteins bind to water. Thus, the protein could prevent the dehydration of cells placed under infiltration stress. In stress conditions, proline assists to maintain balance between penetrations, and protects the cell structure. It is an important organic osmotic adjustment material, capable to stabilize the cell protein structure, prevent the degeneration of enzyme inactivation, and maintain the nitrogen content in plants.

10.3.3 Capacity of Plants in Pollutants Removal from Wastewater

Wetland plant has been reported to be one of the main factors influencing water quality in wetlands. Their role, particularly macrophytes, in the treatment processes is well documented (Brix 1997). Macrophytes are considered to be the main biological component of CWs. They do not only directly take up nitrogen and phosphorous (key nutrients in the life cycles of wetland plants for the growth and reproduction), but also act as intermedium for purification reactions by increasing the environmental diversity in the rhizosphere and enhancing a variety of advantageous chemical and microbial processes (Jenssen et al. 1993). Table 10.3 summarizes the nutrient uptake capacities of commonly used macrophytes in wetlands.

Capacity in organic matter removal. Wu et al. (2012) evaluated the performance of four native macrophyte species (*T. orientalis, P. australis, S. validus and I. pseudacorus*) in CWs for removing COD from polluted river water. Results showed that the effluent COD concentrations in the pilot scale wetland systems meets the Grade-III (COD 20 mg/L) of the national surface water standards in China, while no significant difference were observed among the different wetland plants. CWs were always efficient in organic matter removal under low loading rates.

Capacity in nitrogen removal. In CWs, nitrogen retention is generally thought to occur mainly via a pathway of ammonification (dissolved organic

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Table 10.3. Nutrient uptake capacities of several macrophytes

	Uptake capabilities (kg ha^{-1} yr^{-1})	
Macrophyte	*Nitrogen*	*Phosphorous*
Cyperus papyrus	1100	50
Phragmites australis	2500	120
Typha latifolia	1000	180
Eichhornia crassipes	2400	350
Pistia stratiodes	900	40
Potamogeton pectinatus	500	40
Ceratophylum demersum	100	10

$N \rightarrow NH_4^+$) and then coupled with nitrification ($NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^-$), and canonical denitrification ($NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$) followed. Nitrification and denitrification are the most important processes in the nitrogen cycle. Plant has a vital capacity in nitrogen removal. According to Wu et al (2011), plant uptake removed 8.4–34.3% of the total nitrogen input of CW, which indicates that plant uptake is the key factors limiting nitrogen removal. Although considerable research has been done on the nitrogen purifying capacity of CWs, N removal processes in different CWs treatments could be different in magnitude. Several studies have studied the respond of different macrophytes to N transformations and balance in CWs. According to Maltais-Landry et al. (2009), N removal capacity are different among the macrophytes (*T. angustifolia* > *P. australis* ≈ *P. arundinacea*). While in Brisson and Chazarenc's (2008) research, there is typically no obvious difference in N removal capacity between *T. angustifolia* and *P. australis*.

Capacity in Phosphorus Removal. The removal capacity of phosphorus (P) in different CWs varied significantly. Research by Wu et al. (2011) showed that plant uptake removed 4.81–22.33% of P input, while media storage contributed to 36.16–49.66%. The average total P removal rates ranged between 2.69 and 20.84 $\text{mg m}^{-2}\ \text{d}^{-1}$ in different seasons and is influenced significantly by vegetation types, HRT, and water temperature.

10.4 SUSTAINABLE OPERATION–ENHANCING TECHNIQUES USED IN CWs

The removal of pollutants in wetland systems is critically dependent on a variety of factors such as oxygen availability, operational strategies, and plant selection and allocation. In order to achieve sustainable CWs, some major enhancing techniques were adopted, including artificial aeration, intermittent operation, hybrid CWs and allocation of plants.

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10.4.1 Improving Oxygen Availability in Constructed Wetlands

Oxygen availability in CWs is a crucial environmental parameter in degradation of organic matters and transformation of ammonium-nitrogen, both of which are oxygen limiting process. Previous studies by Dong et al. (2011) showed that the oxygen released by wetland plant roots to the substrate was limited as more than half was used for roots respiration.

10.4.1.1 Intermittent Aeration Strategy

Great attentions have been dedicated to the feasibility of SSF CWs (SSFCWs) for treatment of various types of wastewater (Tanner et al. 2002; Fan et al. 2012) in the past several decades. However, most conventional SSFCWs failed to fulfill this first step due to insufficient oxygen supply (Hu et al. 2012). Therefore, nitrification is usually the limiting step for nitrogen removal in subsurface CWs (Maltais-Landry et al. 2009).

Another benefit of artificial aeration could be attributed to their potential application in CWs under colder climates. This was supported by Nivala et al. (2007), where the authors documented 93–98% NH_4^+-N removal efficiencies from landfill leachate in aerated HF wetlands, in summer and winter periods. Such observations indicate that, additional oxygen input may counterbalance the temperature dependence of bio-reaction kinetics, at an extra operating costs. Continuous aeration always lead to contradiction between the removal of NH_4^+-N and TN because of the lacking in favorable (i.e. alternate aerobic/anaerobic) conditions for nitrification and denitrification (Saeed and Sun 2011). The high operation cost also remains questionable. Compared with to commonly-used continuously aerated CWs, intermittent artificial aeration can well create alternate aerobic and anaerobic conditions in SFCWs. Furthermore, intermittent aeration provides a greater energy-saving than continuous mode.

Figure 10.3 shows cyclic DO distribution in aerated and non-aerated VFCWs. Sharp decrease of DO concentration was observed immediately after inflow in both aerated wetland VFCWs and non-aerated wetland VFCWs. For non-aerated wetland VFCWs, fast exhaustion of DO mainly occurred during the first 4 hours and then DO concentration almost remained constant before drainage. Intermittent aeration was adopted to markedly enhance oxygen supply to the substrate.

There is always a contradiction among the removal of organic matters NH_4^+-N and TN in conventional CWs mainly because of the competence for limited oxygen supply (Saeed and Sun 2011). The oxygen availability was therefore considered as one of the main rate-limiting factors for organics degradation and nitrification. The alternate anaerobic and aerobic conditions developed by the intermittent aeration simultaneously promoted the activity of microbes in biodegradation of organic matter, nitrification and denitrification. Sufficient supply of oxygen to this group will greatly elevate the aerobic degradation rate of organic matters. According to Fan et al. (2013), the mass removal of COD can be as high as 57.02 $g\,m^{-2}\,d^{-1}$, which was much higher than the results in other studies (Jia et al. 2010). (See Table 10.4)

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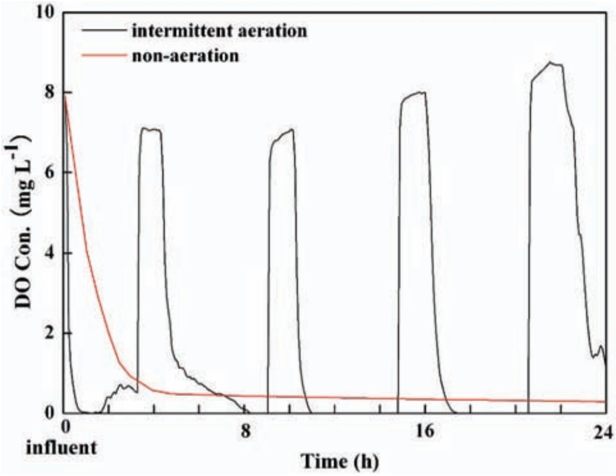

Figure 10.3. Typical profile of DO in the VFCWs with and without aeration

The removals of NH_4^+-N and TN have long been contradictory in conventional CWs. Denitrification is an anaerobic microbial process which accounts for 60–95% of TN permanently removed from CWs (Lee et al. 2009). Although denitrification was efficient in non-aerated CWs, the poor nitrification caused by limited oxygen rate supply always resulted in low TN removal rate (Figure 10.4). In many studies, nitrification was usually greatly enhanced by high DO concentration in continuously aerated CWs (Ong et al. 2010); however, TN removal is still far from satisfactory due to fast depletion of the influent carbon source and lack of favorable anaerobic conditions for denitrification. Intermittent artificial aeration (4 hours per day) in the study by Fan et al. (2013) achieved a nearly

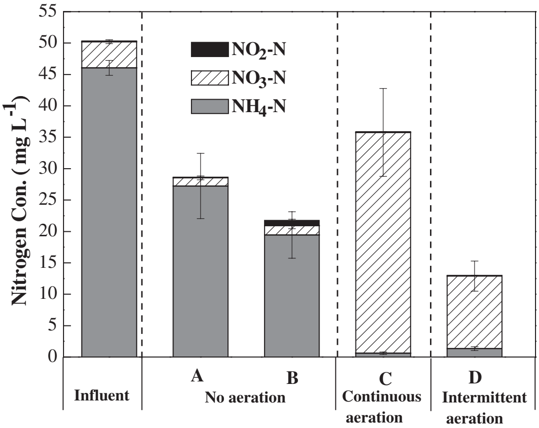

Figure 10.4. NH_4^+-N, NO_3-N and NO_2-N concentration in influent and effluent of the different wetland reactors

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Table 10.4. Removal of pollutants in CWs with different feeding operation

CWs type	*Feeding operation*	*Pollutant purification efficiency*	*References*
Vertical flow CWs	Continuous feeding	COD: 92%; NH_4^+-N: 63%; TP: 87%	Jia et al. (2010)
Horizontal flow CWs	Continuous feeding	NH_4^+-N: 71–85%	Caselles-Osorio and García (2007)
Horizontal flow CWs	Continuous feeding	NH_4^+-N: 87.7–95.9%	Zhang et al. (2012)
Vertical flow CWs	Intermittent feeding	COD: 96%; NH_4^+-N: 93%; TP: 92%	Jia et al. (2010)
Horizontal flow CWs	Intermittent feeding	NH_4^+-N: 80–99%	Caselles-Osorio and García (2007)
Horizontal flow CWs	Batch (another intermittent feeding)	NH_4^+-N: 89.6–95.8%	Zhang et al. (2012)
Vertical flow CWs	Intermittent feeding	Nitrification efficiency: 96%	Green et al. (1998)

complete nitrification. Moreover, alternate aerobic and anaerobic conditions were well developed for nitrification and denitrification. NH_4^+-N could be nitrified in the aerobic zone and then processed via denitrification in anaerobic zone, leading to high removal of NH_4^+-N and TN simultaneously.

According to Fan et al. (2013), much more nitrifying bacteria and other viable bacteria was detected in intermittently aerated SFCWs. The images indicated that there was approximately (16.5 ± 4, $n = 8$)% of AOB and (3 ± 1, $n = 8$)% of NOB in SFCW A, while few AOB and no NOB were detected in SFCW B. In non-aerated SFCWs, the low DO concentration seriously limited the growth of nitrifying bacteria, and the high NH_4^+-N concentration and TN concentration in effluent confirmed the FISH results. The FISH results could further explain the high removal of NH_4^+-N and TN. These results suggest that intermittent aeration was a reliable option to achieve high nitrogen removal in VFCWs.

10.4.1.2 Intermittent Operation Protocol

Oxygen transfer into the CWs substrate can be achieved by different ways as (i) diluted oxygen present in wastewater, (ii) convection due to batch loading and (iii) diffusion processes (Green et al. 1998). The primary aeration process is gas diffusion, which takes place between doses and during the rest periods. Diffusion and convection processes depend on the feed operation. So we can adopt the

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operation of intermittently draw and fill which improve the redox conditions of the CWs. It is both low cost and simple.

Compared to continue feeding operation, intermittently operated CWs involve alternate drawing and filling. During the cycle, a passive air pump worked on a fill and draw sequence where oxygen depleted air is removed from the CWs and fresh air is introduced. During the draw phase (when effluent is drained from the system), fresh air flows from the atmosphere (the higher pressure zone) into the system (the lower pressure zone), so we can supposed that each volume of effluent drained is displaced by an equal volume of fresh air; during the fill phase (when treated water accumulates in the lower layers), "exhausted" air (having low oxygen concentration) flows to the atmosphere (Green et al. 1998), thus improving the oxygen required for nutrients and organic matters oxidation in order to receive better purification efficiency.

Jia et al. (2010) studied the influences of intermittent operation and different length of drying time on contaminant removal in VFCWs, and found that the intermittent operation caused more oxidizing conditions in the microcosm wetlands and thus greatly enhanced the removal of ammonium (more than 90%). There were also many studies about intermittent operation and continuous feeding. Some studies found higher oxygen-demanding pollutants removal efficiency in CWs with intermittent operation (Table 10.4).

10.4.2 Development of Hybrid CWs

As previously introduced, CWs can be divided into SFCWs and SSFCWs, however, single CWs failed to achieve high pollutant removal efficiency, for example, single-stage CWs cannot achieve high removal of total nitrogen due to their inability to provide both aerobic and anaerobic conditions at the same time. Therefore, various types of CWs may be combined with each other to exploit specific advantages of the individual systems.

Hybrid systems (also sometimes called combined systems) comprise most frequently VF and HF systems. By incorporating aeration, anaerobic and anoxic phases, it is possible to produce an effluent which is low in BOD and has a much lower total nitrogen concentration due to its entire nitrification and partial denitrification. The systems are often arranged in the following three manners: (i) VF-HF systems, (ii) HF-VF systems, and (iii) other systems:

(i) VF-HF systems: Many of these systems are derived from original hybrid systems developed by Seidel at the Max Planck Institute in Krefeld, Germany, which consists two stages of several parallel VF beds followed by two or three HF beds in series (Figure 10.5) (Seidel 1965). In the 1990s and early 2000s, VF–HF systems were built in many European countries, e.g. in Norway (Mæhlum and Stålnacke 1999). This type was getting more attention in most European countries.

(ii) HF-VF systems: In mid-1990s, HF–VF hybrid systems were introduced. The large HF bed is placed first to remove organics and suspended solids and to provide denitrification. An intermittently loaded small VF bed is

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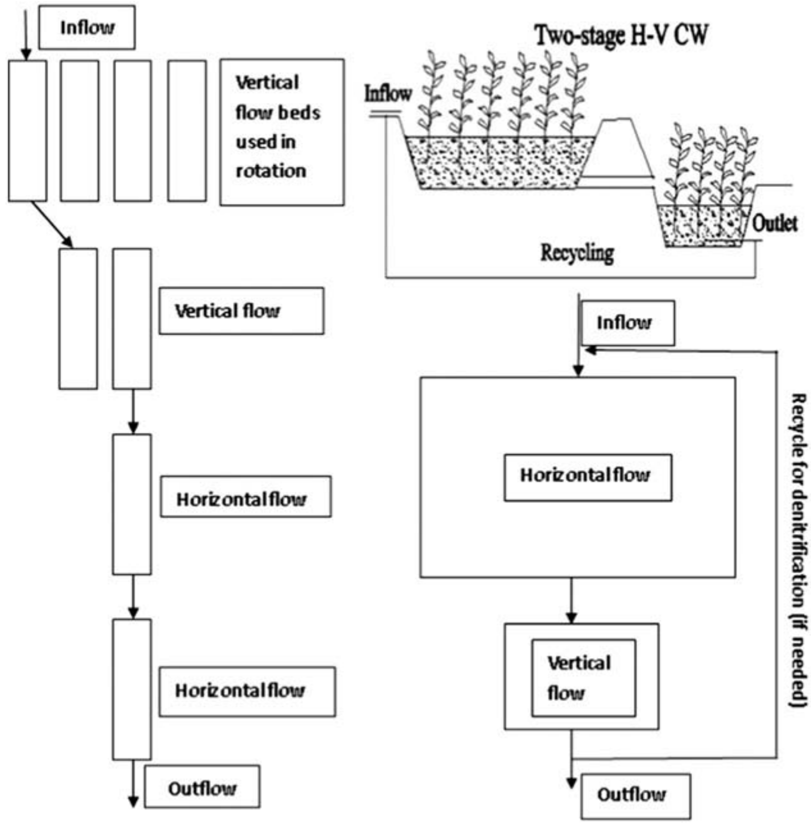

Figure 10.5. Typical hybrid systems used in wastewater treatment

designed for further removal of organics and SS and to nitrify ammonia to nitrate. However, in order to remove total nitrogen, the nitrified effluent from the VF bed must be recycled to the sedimentation tank.

(iii) Other types of hybrid systems: recently, hybrid CWs comprise more than two types of CWs and quite often include a FWS CWs and other sewage treatment reactors, such as subsurface horizontal flow CWs-surface free CWs (HF-FWS), CWs-pond, anaerobic baffled reactor (ABR)-CW, hybrid tidal flow CWs and so on. Compared with single CWs, hybrid CWs or other combined systems could enhance the wastewater purification efficiency, and these effects had been demonstrated in many studies (Table 10.5).

10.4.3 Allocation of Various Plants

Plants selection and allocation of the wetland ecosystem play a crucial role in its purifying process, as well as in the growth status of plants. Plants with better growth and more reasonable collocation have better purification ability. Wetland plant types include: floating plants, emergent aquatic plants, submerged plants,

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Table 10.5. Removal of pollutants in various types CWs

	Efficiency (%) in concentration (mg/L)			
CW type	*COD*	*NH^{4+}-N*	*TN*	*References*
FWS	—	55.1	41.2	Vymazal (2007)
SSHF	—	48.3	42.3	Vymazal (2007)
SSVF	—	84.2	44.6	Vymazal (2007)
SSHF-SSVF	94	86	60	Fabio and Nicola (2007)
SSVF-SSHF	82	89	—	Herrera Melián et al. (2010)
SSVF-SSHF-SSVF	98	86	—	Saeeda et al. (2012)

other types of plants (Peterson and Teal 1995). Characteristics of different plant types can be utilized to build mix hydrophytes wetland. Floating plants have strong vitality, rapid growth, high biomass and seasonal dormancy, thus they can be co-bred with emergent aquatic plants, which adapt to the environment easily and possess developed root system, huge nitrogen and phosphorus absorption. By comparison, submerged plants living under water surface call for cleaner water environment. Their growth status is easily affected by the light amount beneath water surface while they can cope with climate change in some degree. Nitrogen and phosphorus absorption ability of submerged plants is the least in these three types, only 700 $\text{kgN} \cdot \text{ha}^{-1} \cdot \text{a}^{-1}$ and <100 $\text{kgP} \cdot \text{ha}^{-1} \cdot \text{a}^{-1}$, as emergent aquatic plants absorb 200~2500 $\text{kgN} \cdot \text{ha}^{-1} \cdot \text{a}^{-1}$ and 30~500 $\text{kg P} \cdot \text{ha}^{-1} \cdot \text{a}^{-1}$, floating plants show more absorption: about 2000 $\text{kg N} \cdot \text{ha}^{-1} \cdot \text{a}^{-1}$ and 350 $\text{kg P} \cdot \text{ha}^{-1} \cdot \text{a}^{-1}$ (Gumbricht 1993; Brix 1994, 1997). The comparative result of accumulation ability of toxic and harmful substances (such as lead, cadmium, mercury, arsenic, chromium, calcium, nickel, copper, zinc, iron, manganese, etc.) is different: submerged plants > floating plants > aquatic plants (Ye et al. 2001).

The purifying function of CWs is closely related with the selection and configuration of plants, as well as microorganisms and the soil matrix. On the basis of (1) following the principle of plant configuration, (2) applying characteristics of different plants reasonably, and (3) considering wetland function and type, we can make scientific collocation of wetland species. For example, deep root plants collocate with shallow root plants, cluster type plants collocate with scattered type plants, and nitrogen uptake dominant plants collocate with phosphorus uptake dominant plants. This will arouse better ecological effects, overcome the seasonal loss of purification caused by single configuration, and reinforce the stability of the wetland.

The following are several examples of plant collocation:

1. Inter-type collocation: Mixed planting of *water celery* (an aquatic plant) and *Potamogeton maackianus* (a submerged plant) to construct a double-layer structure of community. Both species are prominent in environmental

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adaptability and nitrogen and phosphorus adsorption capacity. The combination of these two will expand the purification ability, make full use of space, light and oxygen, as well as enhance the treatment effect.

2. Internal collocation: Mixed planting of emergent aquatic plants *Canna generalis*, *Thalia*, *Acorus calamus* in each of the three steps of HFCW system. This collocation combine ① characteristics of aquatic *Canna* whose developed root system and active oxygen secretion provide large amounts of dissolved oxygen for the first step with ② characteristics of *calamus* secreting less oxygen around roots difference, however whose nitrogen and phosphorus strong absorption ability and features of growth in a whole year create anoxic environment for the third step in favor of denitrification to improve the removal rate of TN.

In addition to the above description, the plants collocation within CWs has one more vital role that is to overcome the instability of purification efficiency caused by seasonal variation. Seasonal variation exhibits significantly in the temperate and subtropical zones, such as in the northern part of China. Significant seasonal variation makes it hard for one kind of plant to survive for a whole year, resulting in wetland purification effect decreases when seasons change. In the configuration of wetland plants in these regions, two referential allocations for sustained and stable operation are provided. One is the combination of the same type of plants. Taking floating plants as an example, they have strong vitality, rapid growth and seasonal dormancy. So, we can breed *water celery* in cold weather and *water hyacinth*, *Pistia stratiotes* or other floating plants adapted to high temperature in the summer. The other choice is to combine different types of plants. An example is the cold-resistant submerged plant *Potamogeton crispus,* which can grow under ice in winter absorbing nitrogen and phosphorus, together with emergent plants with high tolerance such as *reed*. Combination of overwintering plant such as *Potamogeton crispus* and evergreen plants such as *Acorusgramineus Soland* is also advisable.

To tackle the low performance of CWs in winter, lab-scale CWs were built by the laboratory of Shandong University, in the experimental water temperature of 0~5°C, to study the effect of water purification with *Potamogeton crispus*, compared to the reed, *Vallisneria spiralis*. Results showed that Potamogeton crispus have good growth status and relatively better removal rate in winter, with COD, NH_4^+-N, TN, TP removal efficiency were 92.45%, 93.70%, 55.62%, 92.97%, higher than that of reed system with 79.08%, 73.61%, 47.48%, 78.53% (Table 10.6).

10.5 SUSTAINABLE MAINTENANCE–PLANT RECLAMATION AND RECYCLING IN CONSTRUCTED WETLANDS

There are positive and significant linear relationships between N and P accumulations and plant biomass respectively, which imply that plant harvest could be a

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Table 10.6. Water purification effect during the whole experiment system.

Parameters	*Influent (mg/L)*	*Plant*	*Effluent (mg/L)*	*Removal (%)*
COD	61.68 ± 6.0	*none*	16.16 ± 1.8	73.79%
		reed	12.90 ± 1.8	79.08%
		Vallisneria spiralis	12.11 ± 3.3	80.36%
		Potamogeton crispus	4.66 ± 0.8	92.45%
NH_4^+-N	4.87 ± 0.06	*none*	1.35 ± 0.07	72.30%
		reed	1.28 ± 0.05	73.61%
		Vallisneria spiralis	1.49 ± 0.12	69.29%
		Potamogeton crispus	0.306 ± 0.03	93.70%
TN	14.20 ± 1.1	*none*	8.03 ± 0.3	43.47%
		reed	7.46 ± 0.4	47.48%
		Vallisneria spiralis	7.06 ± 0.7	50.31%
		Potamogeton crispus	6.30 ± 0.4	55.62%
TP	0.702 ± 0.05	*none*	0.145 ± 0.03	79.28%
		reed	0.151 ± 0.03	78.53%
		Vallisneria spiralis	0.207 ± 0.04	70.49%
		Potamogeton crispus	0.049 ± 0.009	92.97%

means of taking N and P out of wastewater. Appropriate plant cutting can also help maintain a high growth rate at all times (Perbangkhem and Polprasert 2010). If not, plant dead matter accumulated in the soils will increase the BOD, N and P of fresh water and cause blocked flood drainage and blocked inland navigation in CWs (Warneke et al. 1999; Kuschk et al. 2003). It is also reported that during the cold winter months a translocation of nutrients from stems to rhizomes occurs which results in an increase of nutrient content in the wastewater. According to these findings, we suggest that for CWs, plant harvest must be practised in order to remove organic matter and nutrients from the system. Therefore, it is necessary to combine conservation and cultivation with reasonable harvest and utilization of such aquatic vegetation. In the view of renewable energy sources, as soon as a multifunctional use of these areas is taken into consideration, the operation would be much more economic.

10.5.1 Activated Carbon from Wetland Plants

10.5.1.1 Utilization of Biomass Materials from CWs

As a kind of lignocellulosic biomass, wetland plants offer an immense potential for the production of renewable fuels and chemicals in a sustainable fashion. Extensive research is being done with biomass for energy production. However, at present, generating energy from biomass is rather expensive due to both technological limits related to lower conversion efficiencies, and logistic

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constraints. It is also well known that the use of biomass as a fuel for energy production is restricted by the fact that, as a consequence of fertilisation, biomass contains a large amount of elements such as Ca, K, Mg, Na and Si with very reactive and problematic behaviour (Ciria et al. 2005).

Meanwhile, activated carbon is a well-known material used in an increasing number of environmental applications such as water and wastewater treatment, gas filters, and so forth (Yuan and Qiu 2009). It has a very complex pore structure, large BET surface area, good catalytic activity, high chemical stability, and a variety of oxygen-containing functional groups on its surface (Tseng and Tseng 2005). These excellent features have made it an indispensable absorbent. Unfortunately, because it is derived from high-cost sources, such as wood, coal, and coconut shells, activated carbon is considered an expensive material in many countries (Attia et al. 2008). Thus, utilizing low-cost materials as adsorbent makes the adsorption process cost-effective. This has led to a search for cheap and effective substitutes. Considering these factors, new plant materials used for producing activated carbons should be hydrophytes in order to make an adsorbent with a high surface area, and they should be widely available. The well-developed porous caudex systems of these materials could also offer a good precondition for the production of effective activated carbon.

10.5.1.2 Physical and Chemical Properties of Activated Carbon from Wetland Plants

In general, preparation of activated carbon is commonly classified into physical activation and chemical activation. Since chemical activation usually takes place at a lower temperature and a shorter time, the chemical activation is lower energy cost. In chemical activation, the main activating agents used are phosphoric acid, potassium hydroxide and zinc chloride. Taking their environmental effects and chemical recovery into consideration, phosphoric acid is most preferred (Guo and Rockstraw 2006; Prahas et al. 2008). Utilization of phosphoric acid as flame retardant and activating agent for preparation of activated carbons has been well established in the literature (Zhang et al. 2008a; Chen et al. 2010; Liu et al. 2011; Ren et al. 2011). The scheme for hydrophytes-based activated carbon production with phosphoric acid activation is shown in Figure 10.6.

The withered plant, received from Nansi Lake, Shandong (China), was rinsed and dried at 105°C for 24 h. The dried sample was then crushed and sieved to a particle size fraction of 0.45–1.0 mm. 10 g of biomass was impregnated by a certain amount of H_3PO_4 at a ratio (2:1 to 3:1, g H_3PO_4: g biomass) for 8–12 h with occasional stirring. Then, the samples were heated up to 450–550°C and kept at this temperature for 60 min in a muffle furnace. After activation treatment, the samples were washed with distilled water until pH of the washed solution was steady. The activated carbons were then dried at 105°C for 8–12 h. Finally, the activated carbons were ground to obtain the particle size of 100/160 mesh and stored until required.

Surface area is one of the most important properties of activated carbons. The textural properties of the carbons were measured by N_2 adsorption/desorption at

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Figure 10.6. Scheme of activated carbon production

77 K using a surface area analyzer (SI/MP, Quantachrome, USA). The surface area (S_{BET}) was determined by using the Brunauer-Emmett-Teller (BET) method. The pore size distribution was obtained by the Density Functional Theory (DFT) method. Micropore surface area (S_{mic}), external surface area (S_{ext}) and micropore volume (V_{mic}) were calculated using the t-plot method. Total pore volume (V_{tot}) was determined from the amount of N_2 adsorbed at a P/P_0 around 0.97. Mesopore volume (V_{mes}) was calculated by $V_{tot} - V_{mic}$. Average pore diameter (D_p) was obtained from $D_p = 4V_{tot}/S_{BET}$.

Table 10.7 presents the textural characteristics of activated carbon. In general, the surface area of carbons was found to be higher than1100 m^2/g, which was relatively high compared with other solid-waste-based activated carbons. Their N_2 adsorption/desorption isotherms were a mixture of types I and IV, with a wider hysteresis loop at highly relative pressures, which revealed some mesoporosity.

Boehm's titration method (Boehm 2002) was used to quantify the amount of acidic and basic functional groups on the carbons' surfaces. The different types of functional groups were based on the assumptions that $NaHCO_3$ neutralizes carboxyl groups; Na_2CO_3 neutralizes carboxyl and lactonic groups; NaOH neutralizes carboxyl, lactonic and phenolic groups; and HCl neutralizes all basic groups. The results of Boehm's titrations for the activated carbons were shown in Figure 10.7. The activated carbons had a high acidic group content (1.5 mmol/g). In general, the relative concentrations of the acidic groups on the surface of the carbons followed the order phenol > lactone > carboxyl.

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Table 10.7. Surface areas and porosity characteristics of the activated carbons derived from different carbon precursor

Carbon precursor	Ratio ($g\,H_3PO_4/g$ biomass)	Activation		S_{BET} (m^2/g)	S_{mic} (m^2/g)	V_{mic} (cm^3/g)	V_{tot} (cm^3/g)
		T(°C)	t (min)				
Jackfruit peel (Prahas et al. 2008)	2:1	450	45	937	—	0.428	0.563
Bituminous coal (Teng et al. 1998)	2:1	500	120	517	—	—	0.301
grape seeds (Al Bahri et al. 2012)	2:1	500	120	957	706	0.54	0.73
Attalea funifera (Avelar et al. 2010)	1:1	500	360	747	—	0.324	0.543
Rice straw (Fierro et al. 2010)	1.6:1	450	60	786	—	—	1.05
Spent grain lignin (Mussatto et al. 2010)	2:1	450	120	429	346	0.155	0.303
Typha orientalis (Zhang et al. 2008b)	2.5:1	450	60	1172	370	0.618	1.621
Phragmites australis (Chen et al. 2010)	2:1	450	60	1362	379	0.172	1.271
Polygonum orientale (Wang et al. 2011)	2.4:1	450	60	1398	548	0.269	1.538
Lotus stalk (Liu et al. 2013a)	2:1	450	60	1179	510	0.289	0.823
Loosestrife (Fan et al. 2011)	2:1	450	60	1255	441	0.201	1.201
Cattail fiber (Liu et al. 2013b)	2.5:1	500	60	907	517	0.161	1.000
Trapa natans husk (Xie et al. 2011)	2.3:1	450	60	1274	477	0.187	1.087

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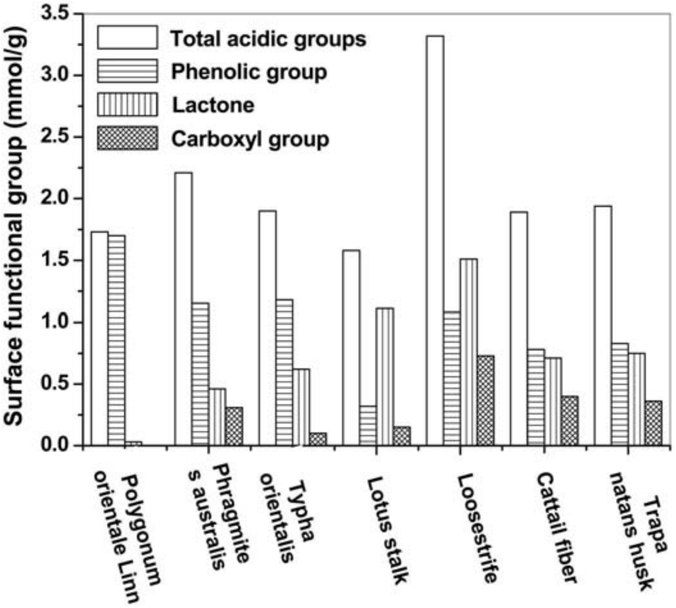

Figure 10.7. Concentrations of surface functional groups of the activated carbons derived from different carbon precursor

10.5.2 Pollutants Removal of Wetland Plants Carbon

Several physical, chemical and biological treatment techniques have been applied to remove these pollutants from wastewater, such as photochemical degradation, biological degradation, coagulation, chemical oxidation, reverse osmosis, flotation and adsorption. Among those methods, adsorption is commonly used owing to its high efficiency and ability to separate a wide range of chemical compounds, simplicity of design and economic feasibility. Currently, activated carbon is widely used as an adsorbent in wastewater treatments, since it has highly developed porosity, a large internal surface area, and relatively high mechanical strength. In previous studies (Ji et al. 2010, 2011), the pore filling mechanism has been proposed to account for the diverse adsorption affinity toward difference molecular-sized adsorbates onto porous adsorbents. Thus, low-size metal ions and large-size chlorophenols were chosen to evaluate the adsorption capacities of the produced activated carbons.

10.5.2.1 Phenolic Compounds Removal

Phenolic adsorption capacity of cattail fiber-based activated carbon. The cattail fiber-based activated carbon (CFAC) fabricated by phosphoric acid activation had large surface area ($S_{BET} = 890\ m^2/g$) and well-developed porous structures ($V_{tot} = 0.863\ cm^3/g$, $V_{mic} = 0.189\ cm^3/g$). The average pore diameter of the prepared sample was found to be 3.88 nm. According to the definition of pore

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size by International Union of Pure and Applied Chemistry (IUPAC), this indicated that the activated carbon was mesoporous ($V_{\mathrm{mic}}/V_{\mathrm{tot}} = 21.9\%$).

Surface functional groups within activated carbon give significant contribution toward its adsorption ability. From Boehm's titration, several surface functional groups' existence can be verified, which is lactones, carboxyl and phenolic groups. The results of the Boehm measurement show that the majority of the oxygen functional groups are acidic groups (1.892 mmol/g). The amount of lactone, carboxyl and phenolic groups is 0.398 mmol/g, 0.781 mmol/g and 0.713 mmol/g, respectively. Comparing to this, the basic groups are only 0.114 mmol/g.

The adsorption isotherms express the specific relationship between the concentration of an adsorbate and its accumulation onto an adsorbent surface at constant temperature under equilibrium conditions. The isotherms indicate how the adsorbate molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. In this study, equilibrium data at various temperatures (20, 30, 40°C) were modeled with the Langmuir and Freundlich models.

The Langmuir isotherm has been used by many workers to study the adsorption of a variety of compounds. The Langmuir equation is based on a theoretical model and assumes that adsorption takes place at specific homogeneous sites within the adsorbent and once a dye molecule occupies a site, no further adsorption takes place at that site. The linear form of the Langmuir isotherm equation is given as:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{k_L Q_m} \qquad \text{(Eq. 10.1)}$$

where C_e is the concentration of the dye solution (mg/L) at equilibrium, qe is the amount of adsorption (mg/g), Q_{m} and k_{L} are the Langmuir constants related to adsorption capacity (mg/g) and free energy of adsorption (L/mg), respectively. The Freundlich isotherm is an empirical equation that considers heterogeneous adsorptive energies on the adsorbent surface, the linear form of which can be given by the equation

$$\ln Q_e = \ln k_F + \frac{1}{n} \ln C_e \qquad \text{(Eq. 10.2)}$$

where k_{F} ($(\mathrm{mg/g})(\mathrm{L/mg})^{1/n}$) and n are the Freundlich constants related to the adsorption capacity and adsorption intensity, respectively. For the value $n = 1$, the partition between the two phases is independent of the concentration. A value for $1/n$ below one indicates a normal Freundlich isotherm while $1/n$ above one is indicative for a cooperative adsorption.

Table 10.8 lists the maximum monolayer adsorption capacity of various types of chlorophenols on various adsorbents. The high adsorption capacity of CFAC found in this study reveals that CFAC is a promising adsorbent for chlorophenol removal, as compared to some previous work reported in the literatures (see Table 3).

Table 10.8. Comparison of maximum monolayer adsorption capacity on various adsorbents reported in literature

Adsorbent	*T (°C)*	*C_0 (mg/L)*	*Q_m (mg/g)*	*References*
For 2, 4-dichlorophenol				
CFAC	30	25–200	135	Ren et al. (2011)
Oil palm empty fruit bunch carbon	30	50–250	27	Alam et al. (2007)
palm pith carbon	35	10–40	19	Sathishkumar et al. (2007)
Activated bamboo charcoal	25	0.5–100	45	Ma et al. (2010)
Apricot stone shell	–	10–60	339	Daifullah and Girgis (1998)
Coir pith carbon	25	60–120	76	Bhatnagar and Minocha (2009)
For 2, 4, 6-trichlorophenol				
CFAC	30	25–200	153	Ren et al. (2011)
Coconut shell-based activated carbon	30	10–100	122	Radhika and Palanivelu (2006)
Activated clay	30	30–220	123	Hameed (2007)
activated carbon fibers	25	—	257	Liu et al. (2010)
oil palm empty fruit bunch-based activated carbon	30	25–250	500	Tan et al. (2009)

Activated carbon prepared from cattail fiber (CFAC) via chemical activation using phosphoric acid was an efficient adsorbent with a relatively large surface area of 890 m^2/g. It had a high adsorption capacity for 2,4-dichlorophenol and 2,4,6-trichlorophenol from aqueous solution over a wide range of concentrations. The results above confirmed that the CFAC had the potential to be low-cost and effective adsorbent for removal of chlorophenol from water.

Enhancement of phenolic compounds removal by Mn modified-activated carbon. For specific pollutants, the adsorption capacity and selectivity of activated carbon can be tailored by modifying its pore structure and surface chemistry. One modification method is impregnation with metal-salts which form an oxide surface coating on the carbon, offering the potential to lower the regeneration temperature of used carbons and prolong their useful life. Composite adsorbents of this type have been studied and used for the removal of metals. Mn oxides have a high affinity for many heavy metals and several investigators have suggested their application in water and wastewater treatment. Impregnation of activated

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Table 10.9. Pore characteristics and surface functional groups of the carbon before and after modification

	PLAC	*PLAC-Mn*
S_{BET} (m^2/g)	1398	1278
S_{ext} (m^2/g)	850	947
S_{mic} (m^2/g)	548	331
S_{mic}/S_{BET} (%)	39.2	25.9
V_{tot} (cm^3/g)	1.538	1.496
V_{mic} (cm^3/g)	0.269	0.143
V_{mic}/V_{tot} (%)	17.5	9.6
D_p (nm)	4.4	4.7
Carboxylic (mmol/g)	1.150	1.107
Lactonic (mmol/g)	0.461	0.444
Phenolic (mmol/g)	0.315	0.203
Total acidic (mmol/g)	2.215	2.078
Total Basic (mmol/g)	0.545	0.466

carbon with Mn salts by forming oxides on the surface improves the metal adsorption capacity. Then, we have studies on the removal of dyes by Mn-modified activated carbons.

For Mn modification of Polygonum orientale Linn-based activated carbon (PLAC): 1.0 g of PLAC was added into 250 mL of an aqueous solution with 150 ppm $MnNO_3$. After agitating for 15 h, the solution was filtered and the black compound obtained was dried at 120°C for 8 h. After cooling to room temperature, the PLAC-Mn was obtained.

The structural parameters of the carbon, including the BET surface area and pore volume, were calculated and are summarized in Table 10.9. The surface, micropore surface area, as well as the micropore volume decreased slightly after modification with $Mn(NO_3)_2$. However, the external surface area increased from 850 to 947 m^2/g. This may result from the sedimentation of Mn oxides, as its oxidation process could enlarge the pores and consequently form mesopores. Boehm titrations can further elucidate the chemistry of the carbon surface. Impregnation with $Mn(NO_3)_2$ modified the chemical environment of the carbon surface and made the carbon more acidic.

The constant values calculated from the Langmuir and Freundlich isotherms are provided in Table 10.10. The experimental data of 2,4-dichlorophenol adsorption onto PLAC could be fit well by both the Langmuir and Freundlich isotherm models, while a better fit to the Langmuir equation was statistically confirmed by giving greater R^2 values closer to unity (0.999). However, the experimental data exhibited better agreement with the Freundlich model. Therefore, the Freundlich model was the most appropriate model for the adsorption of 2,4-dichlorophenol onto PLAC-Mn. The n values calculated from the Freundlich

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Table 10.10. Isotherm model constants for 2,4-dichlorophenol adsorption onto PLAC and PLAC-Mn (C0, 80 – 130 mg/L; initial pH, 5.0; adsorbent dose, 0.5 g/L; t, 120 min)

	PLAC			*PLAC-Mn*		
Isotherm constants	*10°C*	*25°C*	*40°C*	*10°C*	*25°C*	*40°C*
Langmuir						
Q_0 (mg/g)	250	220	208	257	244	240
k_L (L/mg)	0.124	0.091	0.063	0.132	0.077	0.058
R^2	0.9997	0.9994	0.9993	0.9968	0.9975	0.9916
Freundlich						
k_F (mg/g(L/mg)$^{1/n}$)	66.4	57.5	44.2	71.0	53.7	42.2
n	3.012	3.268	3.049	3.185	3.058	2.638
R^2	0.9931	0.9944	0.9968	0.9973	0.9943	0.9914

model were greater than 1, showing that the 2,4-dichlorophenol could be readily adsorbed by PLAC and PLAC-Mn at all the temperatures studied. Moreover, Q_0 obtained from PLAC-Mn was much higher than that of PLAC at 40°C, which indicated that higher temperatures could promote the oxidation and catalytic activity of Mn oxides for 2,4-dichlorophenol removal. The adsorption capacity of 2,4-dichlorophenol was improved after coating, especially at high temperature. Table 10.10 summarizes the adsorption capacity of different types of adsorbents for 2,4-dichlorophenol. The high adsorption capacity in this study revealed that PLAC-Mn is a promising adsorbent for removing 2,4-dichlorophenol from aqueous solutions.

10.5.2.2 Heavy Metal Removal

Adsorption Cd(II) by lotus stalks-based activated carbon. The textual parameters and surface properties of the lotus stalks-based activated carbon (LSAC) were calculated and summarized in Table 10.11. LSAC displayed the high S_{BET} (1503 m^2/g) and V_{tot} (1.08 cm^3/g). The results of Boehm's titrations for LSAC was showed that the relative concentrations of the acidic groups on the surface of LSAC followed the order carboxyl > phenol > lactone.

Table 10.11. Surface area, pore volume parameters and concentrations of surface functional groups of LSAC

Samples	S_{BET} (m^2/g)	S_{ext} (m^2/g)	V_{mic} (cm^3/g)	V_{tot} (cm^3/g)	*Carboxyl (mmol/g)*	*Lactone (mmol/g)*	*Phenolic (mmol/g)*
LSAC	1503	673	0.31	1.08	0.28	0.32	1.20

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Table 10.12. Isotherm parameters for Cd(II) adsorption by LSAC

	Langmuir			Freundlich		
I (mM)	Q_0 (mg/g)	k_L (L/mg)	R^2	k_F ($mg^{1-1/n}\,L^{1/n}/g$)	1/*n*	R^2
0	33.1	20.2	0.9998	17.1	0.133	0.9240
100	16.3	7.42	0.9994	5.54	0.202	0.9229
1000	11.3	9.11	0.9989	4.65	0.167	0.9166

Table 10.13. Comparison of adsorption capacity for Cd(II) with other adsorbents developed from various lignocellulosic materials

Carbon precursor	S_{BET} (m^2/g)	Q_0 (mg/g)	References
LS	1398	33.1	Liu et al. (2013c)
Olive stone	790	1.8	Kula et al. (2008)
Bagasse	980	27.5	Mohan and Singh (2002)
Apricot stone	566	33.6	Kobya et al. (2005)
Multiwalled carbon nanotubes	–	10.9	Li et al. (2003)
Ceiba pentandra hulls	521	19.6	Madhava Rao et al. (2006)
Phaseolus aureus hulls	325	15.7	Rao et al. (2009)

The parameters of Langmuir and Freundlich models fitting to the Cd(II) adsorption isotherm data are presented in Table 10.12. The results showed that experimental data were better fitted by Langmuir model than by Freundlich model, indicating the monolayer Cd(II) adsorption on the carbons' surfaces. The values of 1/n were less than 1 in all cases, indicating that Cd(II) was favorably adsorbed by the carbons. The study on the effect of ionic strength on adsorption is usually used to distinguish the inner-sphere surface complexation from the outer-sphere one in adsorption. As shown in Table 10.12, the adsorption capacities of Cd(II) for the carbons decreased with an increase of ionic strength. Such phenomenon was interpreted as outer-sphere surface complexation. Thus, some interactions such as electrostatic attraction and cation exchange were responsible for Cd(II) adsorption. A comparison of the Cd(II) maximum adsorption capacities of LSAC with activated carbon prepared from other lignocellulosic materials is given in Table 10.13. The comparison showed that LSAC had high Cd(II) adsorption capacities, suggesting that LSAC were promising adsorbents to remove Cd(II) ions from aqueous solutions. This result showed application potential of developing an

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effective low-cost adsorbent from LS by H_3PO_4 activation and an effective adsorbent to treat wastewater that contains toxic Cd(II).

Enhancement of Cr(VI) removal by Fe-modified activated carbon. Fe oxides, especially amorphous forms, have a high affinity and selectivity toward Cr (VI) oxyanions as well as anionic phosphorus and arsenic species. Impregnating iron hydroxides into activated carbon can take advantage of both the high selectivity of ferric oxides for Cr (VI) and the high surface area of activated carbon which offers adequate reactive sites for iron loading. Several researchers have recently incorporated iron hydroxides into activated carbon and thus greatly enhanced the arsenic adsorption capacity.

Preparation of Fe modified *T. natans* husk-based activated carbon (TAC): 1.0 g of TAC was mixed with 200 mL of ferrous/ferric salt solution at a certain concentration (pH adjusted to 4.0–4.5) for 12 h, followed by filtration and washing with sufficient water to remove any unloaded and/or weakly adsorbed iron. Then the iron-loaded carbon was dried at a certain temperature under natural atmospheric conditions for 10 h. The compound was then allowed to cool to room temperature. The optimal preparation conditions (metal salt type, iron concentration and drying temperature) were determined following the results of Taguchi optimization analyses.

As shown in Figure 10.8, the carbon modified by $FeSO_4$ showed much higher Cr(VI) removal than that modified by $FeCl_3$ and $Fe(NO_3)_3$, while $FeCl_3$ and $Fe(NO_3)_3$ presented similar modification results. Based on the above results, appropriate parameters for the modification protocol were established as: $FeSO_4$,

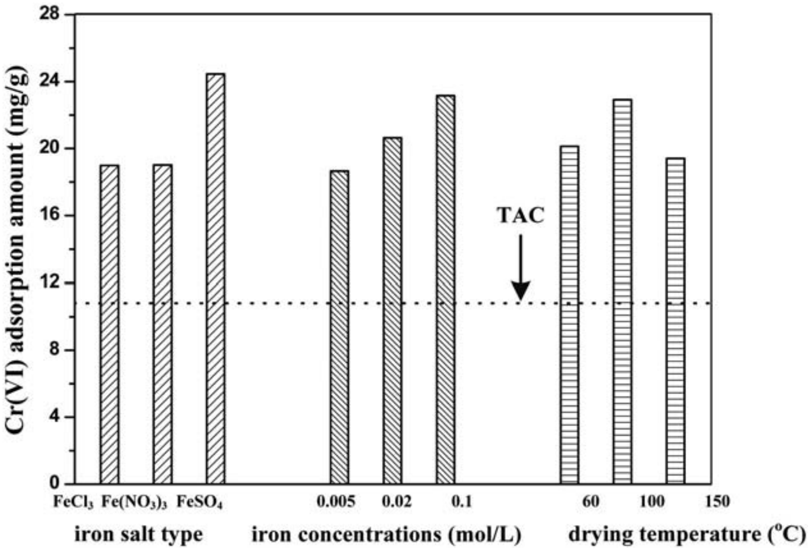

Figure 10.8. Factors that control the modification of TAC by iron salts for enhanced Cr(VI) removal

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Table 10.14. Langmuir and Freundlich isotherm parameters for the adsorption of Cr(VI) by TAC/Fe and TAC at different ionic strengths

		Langmuir			Freundlich		
Carbon	I (mol/L)	Q_m (mg/g)	k_L (L/mg)	R^2	k_F $(mg/g(L/mg)^{1/n})$	n	R^2
TAC/Fe	0	68.5	0.425	0.9945	43.4	10.3	0.9884
	0.1	65.8	0.678	0.9980	38.6	7.97	0.9968
	1.0	64.5	0.582	0.9984	37.0	6.72	0.9909
TAC	0	49.0	0.047	0.9763	5.90	2.35	0.9945
	0.1	50.2	0.035	0.9889	8.48	2.85	0.9824
	1.0	63.3	0.046	0.9798	9.45	2.58	0.9814

impregnating concentrations of 0.1 mol/L Fe and drying temperature of 100°C. The sample prepared under this condition was employed as the iron-doped TAC (TAC/Fe) for further studies, unless otherwise stated.

Adsorption isotherm experiments were conducted at solution pH 4.0 ± 0.1 with the initial Cr(VI) concentration varied from 30 to 110 mg/L. Three background electrolyte concentrations (0, 0.1 and 1.0 M NaCl) were studied to identify the effect of ionic strength on the adsorption. Two commonly used models, the Langmuir and Freundlich equations were employed to correlate the experimental data.

As-fitted Langmuir and Freundlich parameters for the Cr(VI) adsorption on TAC/Fe and TAC are given in Table 10.14. Both the Langmuir and Freundlich models correlated the adsorption isotherms on TAC/Fe and TAC quite well, with all R^2 values higher than 0.97. The good fitting results of both models implied that both chemisorption and physisorption mechanisms took place in the adsorption systems. Freundlich constant, n, were higher than 1 in all cases, indicating that hexavalent chromium is favorably adsorbed by TAC/Fe and TAC. The high adsorption capacity of this study revealed that THAC-Fe could be a promising adsorbent for Cr (VI) removal.

10.6 CONCLUSION

CWs (mainly SF and SSF wetlands) are sustainable systems. They have been designed as a widely accepted technology to deal with various kinds of wastewater for nearly 40 years. CW systems need lower cost, less operation and maintenance requirements, and little energy inputs; however, their successful application remains a challenge when facing new complex problems. Plant selection (plant adaptability, plant tolerance and pollutants removal capacity), enhancing techniques (artificial aeration, intermittent operation and CWs combination, etc.) and

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plant reclamation and recycling in CWs are important factors for the sustainable design, operation and maintenance of CWs. They also prove to be an affordable alternative in a sustainable CW wastewater treatments, especially for small communities and remote locations.

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CHAPTER 11

On-Site Treatment Systems: Biological Treatment and Nutrient Removal

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11.1 INTRODUCTION

When the collection, treatment, and discharge or reuse of wastewater occurs on or near the site where the wastewater has been generated, it is called an on-site treatment system. These systems are different from a centralized system where an extensive network of collection pipes feed a central sewage treatment plant, with the latter approach relying on energy and chemical intensive treatment methods to quickly process large volumes of wastewater. Centralized wastewater treatment has been the best option for handling wastewater in densely populated areas, but has always fallen short in areas of less dense population. It is not cost-effective to run sewage pipe for miles up and down hilly terrain. This is particularly a real case when treated wastewater from central treatment plants is then imported long distances back to the point of origin. Strategic pumping stations and thousands of connections require constant upkeeping and monitoring. In addition, some of the centralized treatment plants have a high concentration of chemicals in their treated wastewater that have adverse effects on aquatic life downstream of discharge points. Considering the increase in population, extensions of treatment plants require long periods of planning and funding for larger capacities with even further growth in mind. This ultimately affects the plants to run at lower efficiencies since they have to be constructed for projected growth and not the existing need. Onsite wastewater treatment has come a long way, especially in the last quarter century. On-site wastewater systems are typically designed to handle a few hundred to a few hundred thousand L per day. On-site technologies can range from compost privies in national forests, to high-tech membrane-filtration systems that recycle wastewater for toilet flushing in large buildings, to

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sophisticated yet elegant designs that use ecosystems, such as constructed wetlands, to treat wastewater. On-site treatment helps to reduce construction, operation and maintenance costs while conserving resources and providing an aesthetically and ecologically attractive feature for the facility. In rural areas where houses are spaced so far apart that a sewer system would be too costly to mount, or in zones around cities where the city government has not yet provided sewers to which the homes can connect, the only visible choice for these cases is onsite treatment, in which people install their own private sewage treatment plants. The increase in population beyond a reach of municipal sewer systems will force more families to rely on individual on-site wastewater treatment systems and private water supplies. At one time, an onsite wastewater system was little more than a concrete tank and a pump that would take all the waste created in a house and send it out into the woods never to be thought of again. However, with more and more concern over the protection of groundwater supplies, this type of system is being replaced with more complex and environmentally friendly systems. Newer systems actually reduce the amount of harmful bacteria in the liquid before it enters the groundwater. This provides a cost-effective and efficient method of wastewater treatment.

Onsite wastewater treatment systems (OWTSs) have evolved from the pit privies used widely throughout history to installations that can generate purified effluent that is fit for human consumption. Even though in onsite treatment, the high-quality purification of wastewater is rarely necessary, the onsite systems is pretty much effective in removing settleable solids, floatable grease and scum, nutrients, and pathogens from wastewater discharges and it is important in protecting human health and environmental resources. These onsite treatment systems remove most settleable and floatable material and function as an anaerobic bioreactor that promotes partial digestion of remaining organic matter. Septic tank effluent containing significant concentrations nutrients and pathogens, has conventionally been discharged to sand, soil or other media absorption fields (SWISs) for further treatment through adsorption, filtration, infiltration and biological processes, into underlying soils. This benefit of onsite treatment is not realized with municipal wastewater treatment, which discharges partially treated wastewater directly to rivers and coastal waters, sending wastewater either further downstream or out of the watershed entirely, and returning none to the landscape to replenish groundwater aquifers. This groundwater recharge loss decreases the quantity of groundwater available from drinking water wells. Mainly, in coastal areas, depletion of ground water resources can lead to salt-water invasion and loss of potable freshwater supplies. Because groundwater is the main source of flow to streams during dry weather, loss of recharge can also lower streamflow to levels that can no longer support healthy aquatic life.

Traditional systems work well if they are fixed in areas with proper soils and hydraulic capacities; designed to treat the incoming waste load to meet public health, surface and groundwater performance standards; installed properly; and maintained to ensure long-term performance. Unfortunately, these criteria however are often not satisfied. System densities in some areas exceed the capacity of

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even suitable soils to assimilate wastewater flows and retain and transform their contaminants. Furthermore, many systems are not designed to handle increasing wastewater flows, specifically those which are situated too close to groundwater or surface waters and others, particularly in rural areas with newly installed public water lines. Conventional onsite system installations might not be useful for minimizing nitrate contamination of groundwater, removing phosphorus compounds, and attenuating pathogenic organisms (e.g., bacteria, viruses, and etc.). Nitrate that leach into groundwater, which is used as drinking water source, is the major cause of methemoglobinemia, or blue baby syndrome, and other health problems for pregnant women. Furthermore, phosphorus and nitrate disposed into surface waters directly or through subsurface flows can encourage algal growth and eutrophication and reduce dissolved oxygen in lakes, rivers, and coastal areas. Pathogens reaching ground water or surface waters can cause human disease through recreational contact, direct consumption or ingestion of contaminated shellfish. Human excrement can transmit some enteric diseases such as cryptosporidiosis, giardiasis, salmonellosis, hepatitis A, and shigellosis. These wastewaters might also affect public health as it backs up into residences or commercial establishments because of onsite treatment system failure. In the modern age, the onsite system has comprised primarily of a septic tank and a soil absorption field, also known as a subsurface wastewater infiltration system, or SWIS. Such kinds of systems are mostly referred to as conventional systems. A septic tank is a sewage holding device made of concrete, fiberglass, polyethylene, steel, or other approved material cistern, buried in a plot, which may hold more than 1,000 gallons of wastewater. Wastewater flows from the home into the tank at one end and leaves the tank at the other.

11.2 HISTORY OF ON-SITE WASTEWATER TREATMENT SYSTEMS

Although, French are considered as the first one to use underground septic tank systems in 1870s, history resides well before it, when King Minos installed the first known water closet with a flushing device in the Knossos Palace in Crete in 1700 BC. In the intervening 3,700 years, societies and the governments that serve them have sought to improve both the removal and treatment of human wastes to reduce threats to public health and ecological resources. During the period from 800 BC to 1850 AD, the Romans, Greeks, French and British attained considerable advancement in waste removal, but removal often meant discharge to surface waters causing severe contamination of lakes, streams, rivers, and coastal areas; leading to frequent invitations to diseases like cholera and typhoid fever.

In late 1800s, the Massachusetts State Board of Health and other state health agencies had reported the connection between disease and poorly treated wastewater and hence suggested treatment of wastewater through intermittent sand filtration and land application of the resulting sludge. The 19th century has witnessed an explosion in sewage treatment technology and widespread adoption

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of centralized wastewater collection and treatment services in the United States and throughout the world. Even though, broad uses of these systems have immensely improved the public health and water quality in urban areas, homes and businesses without collection and treatment of wastewater in centralized systems often continue to depend on technologies developed more than 100 years ago. Primary treatment of wastewater using septic tanks appeared in the late 1800s, and discharge of tank effluent into gravel-lined subsurface drains became common practice during the middle of the 20th century (Kreissl 2000).

11.3 NEED OF ON-SITE TREATMENT SYSTEMS

On-site treatment systems are predominantly suitable for semi-arid and arid regions, and for regions that require riparian groundwater recharge, restoration, an increase in surface water flow, irrigation of nearby landscapes (such as golf courses) or onsite fire control storage. When water is at a premium, treatment and reuse for toilet flushing and other purposes can be cheaper if being handled on site. Several centralized facilities are part of larger communities that wish to manage sprawl, and on-site facilities are often the best choice for serving a diverse matrix of greenbelts and established areas. Onsite treatment systems can also provide safety advantages in difficult ecological conditions such as areas subject to earthquakes, slope movement, and rapid, repeated changes of grade (hilly areas).

Effective wastewater treatment avoids a variety of ailments that can be spread by exposure to pathogens (e.g., bacteria, cryptosporidiosis and viruses), nutrients (e.g., nitrates and phosphorus), personal-care products, pharmaceuticals, and household cleaning products that can be present in untreated sewages, and thus helps prevent disease. Releases of untreated sewage can intensely contaminate surface waters and groundwater used for recreation, drinking and fisheries. Untreated wastewater from failed conventional septic systems or sewage discharged directly into the environment can percolate into groundwater, contaminating drinking-water wells with pathogens. The discharge of untreated sewage to streams can spread disease through direct contact, making such streams unfit for forms of recreation that involve skin contact with the water such as swimming and boating. Rodents or insects that received primary exposure and in turn harbor the pathogens can also spread disease by indirect (secondary) contact. Discharged, untreated sewage also can damage the receiving streams' ability to support healthy and living environment of aquatic organisms and can contaminate fisheries. The contaminants present in wastewater and their potential impacts are illustrated in Table 11.1.

On-site wastewater treatment is typically considered when following conditions apply:

- **Remote sites and new developments.** When the centralized facility is distant from an existing treatment plant or sewer main, but at great expense, this remote site can still be connected to a municipal system. Many such sites

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Table 11.1. Typical pollutants of concern in effluent from onsite wastewater treatment systems

Component	*Description*
BOD (biochemical oxygen demand)	Biodegradable organic carbon compounds, in particulate and soluble forms
Solids(includes particulates)	Slowly biodegradable organic compounds, primarily carbon-based
Bacterial, viral, and protozoan pathogens	Direct or indirect body contact or injection of contaminated water or contaminants, and disease-causing agents of fecal matter can cause communicable disease. Pathogens can be transported for significant distance in ground water or surface water.
Phosphorous (P)	P is an aquatic plant nutrient which contributes to eutrophication of phosphorous limited inland surface waters. High aquatic plant and algal production during eutrophication is often accompanied by an increase in populations of decomposer bacteria and reduced dissolved oxygen levels for fish and other organisms.
Nitrogen (N)	N as organic and ammonium (NH_4^+) forms and is an aquatic plant nutrient which contribute to eutrophication and dissolved oxygen loss in surface waters, especially in estuaries, nitrogen limited lakes, and coastal embayment. Excessive nitrogen in drinking water can cause methemoglobinemia in infants and pregnancy complications. Aquatic weeds and algae can contribute trihalomethane (THM) precursors to the water column that might generate carcinogenic THMs in chlorinated drinking water.
Household chemicals	Detergents, cleansers, etc.

simply choose a septic field. In fact, new suburban developments with low-flow fixtures also responsible for increasing the concentration of solids in the wastewater, creating situations that federal plants are not designed to handle. Decentralized treatment and reuse systems serving these new developments make a lot more sense. It is also the case when topography necessitates expensive pumping and excavation.

- **Nutrient cycling.** The primary aim of wastewater treatment is to eliminate the disease-causing pathogens. During the process, nitrogen and phosphorus are removed to reduce biochemical oxygen demand (BOD) before releasing

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effluent. These nutrients can damage the environment and are major concern of wastewater treatment. They are rarely viewed as a valuable resource. Natural onsite treatment systems can change that by returning nutrients slowly and safely to depleted soil, potentially repairing decades of damage.

- **Overtaxed municipal system.** As urban sprawl continues and the population increases in rural areas, the cost of building additional sewage disposal systems increases. One of the prime reasons for annexation is to increase the tax base without increasing the cost of municipal government. The governments involved often buy into short-term tax gains at massive long-term costs for eventual infrastructure improvements to annexed communities. Although centralized systems can boast economies of scale, many are leaky, aging, and overtaxed. Older ones combine stormwater and wastewater, which can lead to combined sewer overflow - the release of raw sewage into water streams.
- **Expensive sewer fees:** Potable water remains remarkably cheap even in regions where it's scarce, but centralized wastewater treatment can represent a major sewer charge for commercial buildings in some places, potentially creating a business case for onsite treatment. In some cities, sanitation charges may be waived considerably if owners choose to treat their water on the site, and ongoing sewer fees are also avoided. On the other hand, energy use will offset cost savings, as will system maintenance. Furthermore, onsite treatment has multiple functionalities that can add further benefits to the treatment system.
- **Education and research:** One of the most convincing reasons to treat wastewater onsite is to educate students, visitors, occupants, and professionals about freshwater scarceness and treatment of sewage, though this is a minor issue. Natural onsite systems may include beautiful landscaping and water features e.g. constructed wetlands. They also require frequent testing and provide research opportunities for students and scholars alike, and they can even serve as test beds, helping develop natural treatment methods that may someday work at the district or municipal scale.

11.4 GENERAL PRINCIPLES OF ON-SITE TREATMENT SYSTEMS

In the old time, an onsite wastewater treatment system was little more than a concrete tank and a pump designed for collection of waste created in a house that would send it out into the woods, never to be thought of again. However, with more and more concerns over protection of groundwater supplies, this type of system is being replaced with eco-friendly and more complex systems. Newer systems actually help to reduce the amount of harmful bacteria in the effluent entering the groundwater. This provides an efficient and cost effective method of wastewater treatment.

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These private disposal treatment systems are typically called septic tank systems. Septic tank is nothing but a sewage holding device usually made up of steel, concrete, polyethylene, fiberglass or other approved material cistern, buried in a backyard. It can withstand more than 1,000 L of wastewater. Sewage flows from the home into the tank from one end and leaves the tank at the other. The three major primary components of a conventional system are the soil, the subsurface wastewater infiltration system (sometimes referred as a leach field or infiltration trench), and the septic tank. The subsurface wastewater infiltration system functions as the interface between the receiving ground water environment and the engineered system components. Treatment of the wastewater effluent in the soil horizons below the dispersal and infiltration components of the subsurface wastewater infiltration system determines the primary performance of conventional systems. Depending on site-specific needs, treatment options include physical, chemical, and biological processes. Most preferably used systems for the treatment and dispersal of onsite wastewater are the subsurface wastewater infiltration systems. Infiltrative surfaces are located in permeable, unsaturated natural soil or imported fill material, and so wastewater can infiltrate and percolate through the underlying soil to the ground water. Subsequently, it is treated through a variety of physical, chemical, and biochemical processes and reactions. The primary infiltrative surface is the bottom of the excavation, but the sidewalls also may play a role in infiltration. To distribute the wastewater over the infiltration surface, perforated pipe is installed. To support the pipe and spreading of the localized flow from the distribution pipes across the excavation cavity, a porous medium, typically crushed rock or gravels, is placed in the excavation below and around the distribution piping. The advantage of this porous medium is that, it helps to maintain the excavation structure and exposes the applied wastewater to more infiltrative surface while maintaining enough storage space for the wastewater within its void fractions during extreme flows with gravity systems. To prevent the introduction of backfill material into the porous medium, care is taken by laying a permeable geotextile fabric or other suitable material over the porous medium before the excavation is backfilled. For backfilling, the natural soil is typically used and the surface of the backfill is usually slightly mounded and seeded with grass.

Subsurface wastewater infiltration systems provide both dispersal and treatment of the applied wastewater. Wastewater is transported from the infiltration system through three zones in which two of these zones, the infiltration zone and vadose (unsaturated) zone, act as a fixed-film bioreactor. A few centimeters thick layer of the infiltration zone, which is the most biologically active zone and is often called as the biomat, is responsible for quick degradation of carbonaceous material in the wastewater, and if sufficient oxygen is present, subsequent nitrification occurs immediately below this zone. Free or combined forms of oxygen in the soil must satisfy the oxygen demand generated by the microorganisms degrading the materials. If sufficient oxygen is not present, then both treatment and infiltration of the wastewater will be adversely affected due to reduced or halted metabolic processes of the microorganisms. The vadose (unsaturated) zone plays an important role in re-aerating the infiltration zone by providing a significant pathway for

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oxygen diffusion. In addition, it is the zone where most sorption reactions occur because the negative moisture potential in the unsaturated zone causes percolating water to flow into the finer pores of the soil, resulting in greater contact with the soil surfaces. Finally, much of the phosphorus and pathogen removal occurs in this zone.

The major engineered component of conventional system is septic system which depends on natural processes to treat waste: gravity separates solids and liquids; soils filter the wastewater by absorbing contaminants; and bacteria break down biodegradable materials. Grass roots also play a role by taking up liquid and using nutrients. In fact, septic system works as a small underground ecosystem. A conventional type onsite treatment's major component is septic tank. A septic tank is partitioned into two compartments, with access ports at the top for inspection and service. Gravity will separate the waste into three layers:

- Heavy materials, which settle to the bottom where they are broken down into sludge by naturally occurring bacteria
- Light soaps, greases, fats and similar materials, which rise to the top and form a scum layer, and;
- Liquids with some suspended solids.

Wastewater from appliances, sinks and toilets flows from the house into the first compartment and then an equal amount of liquid is transferred from that first compartment into the second one in a gravity system; a siphon periodically activates and discharges liquid out of the second chamber and into the pipes leading to the leaching bed. For a pressure distribution system, the second chamber will be periodically pumped to the distribution system. If the tank is properly operated and pumped out regularly, only the liquid effluent leaves the tank leaving solids in the tank.

There are a huge number of processes that can reduce nitrogen and a few that can reduce phosphorus. Nitrogen is a pollutant of concern as nitrogen in the form of ammonia is toxic to certain aquatic organisms. In the atmosphere, ammonia creates an oxygen demand and low dissolved oxygen in surface waters due to its rapid oxidation to nitrate. Organic and inorganic forms of nitrogen may cause eutrophication problems in nitrogen-limited freshwater lakes, and in estuarine and coastal waters. On the other hand, phosphorus is considered as a key element that causes eutrophication of natural or impounded freshwater bodies and some estuarine waters. Most of these phosphorus removal processes are additions to other pretreatment processes that enhance the overall removal of phosphorus. The cost, the degree of nutrient removal and the difficulty in operation and maintenance quickly reduce the number of systems that are likely to be employed for onsite nutrient removal. For onsite wastewater system application, few phosphorus removal processes are well developed and have been successfully applied using chemical, physical, and biological systems. The controlled addition of chemicals such as iron, aluminum and calcium compounds with subsequent flocculation and sedimentation has had only limited success due to its poor operation and maintenance problems of mechanical equipment and excessive sludge production. Physical and chemical processes such as ion exchange and precipitation of phosphates have been tried, but with very limited success. The only other known nutrient removal approach is the use of biological treatment systems. All aerobic biological treatment systems have the natural ability to remove 10 to 20 percent of the phosphorus from wastewater, which is connected to the organic form in the biological reactors and wasted with excess sludge. Certain processes such as the sequencing batch reactor (SBR) can improve the nutrient removal by proper sequencing of aeration periods. The addition of anaerobic steps can improve phosphorus removal performance by up to an effluent limit of 1 to 2 mg P/L. In the subsequent sections of this chapter, we will focus our discussion on biological nutrient removal of onsite wastewater treatment.

11.5 BIOLOGICAL NUTRIENT REMOVAL

11.5.1 Biological Nitrogen Removal

Basically, biological nitrogen removal requires a two-step process: nitrification and denitrification. Since the original discovery of the nitrification reaction (Figure 11.1) approximately 100 years ago, there has been considerable attention given to the application of nitrifying bacteria to wastewater treatment. Nitrification is a two-step process in which, ammonium is firstly oxidized to nitrite (nitritation process) by ammonium oxidizing bacteria and later, nitrite is oxidized to nitrate (nitratation process) by nitrite oxidizing bacteria, e.g. from genera *Nitrobacter*, *Nitrococcus* and *Nitrospira* (Schmidt et al. 2003). The only organisms capable of converting the most reduced form of nitrogen (ammonium) to the most oxidised form (nitrate) are nothing but the autotrophic nitrifying bacteria.

Nitrification process reactions:

$$NH_4^+ + 3/2\,O_2 \rightarrow NO_2^- + H_2O + 2H^+ \text{ Nitritation process}$$
$$NO_2^- + 1/2\,O_2 \rightarrow NO_3^- \text{ Nitratation process}$$

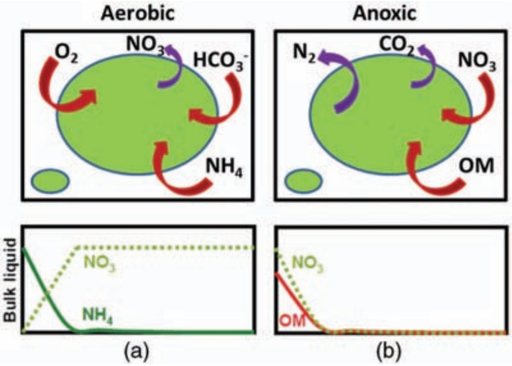

Figure 11.1. Biological nitrogen removal: nitrification process (a); and denitrification process (b). The green color in the pictures represents the biomass

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Nitrification is affected by a number of environmental factors including pH, toxicity, metals, un-ionized ammonia ($N-NH_3$), un-ionized nitrous acid (HNO_2) and reduced sulphur components (Metcalf and Eddy 2003; Ganigué et al. 2007). The alkalinity of the wastewater is the critical factor to maintain the pH in the optimum range for nitrification, because 7.13 g of alkalinity as $CaCO_3$ is consumed per gram of ammonium ($N\text{-}NH_4^+$) oxidized to nitrate ($N\text{-}NO_3^-$) (Metcalf and Eddy 2003).

Two modes of nitrate reduction can occur in biological systems: assimilating and dissimilating or denitrification (Figure 11.1b). Assimilating nitrate reduction involves the reduction of nitrate to ammonia for use in cell synthesis. Dissimilating nitrate reduction or denitrification is coupled to the respirating electron chain and involves the reduction of nitrate (the highly oxidized forms of nitrogen available for consumption by many groups of organisms) to nitrite to nitric oxide to nitrous oxide finally to gaseous nitrogen, which is far less accessible to life forms but makes up the bulk of our atmosphere. Denitrification is considered to be an anoxic process, occurring in the absence of oxygen, and requires an organic electron donor (Randall et al. 1992). In the denitrification process, the electron donor is typically one of these three following sources:

1. The organic matter of the influent:
   $C_{10}H_{19}O_3N + 10NO_3^- \rightarrow 5N_2 + 10CO_2 + 3H_2O + NH_3 + 10OH^-$
2. The organic matter produced during the endogenous decay.
3. An exogenous source such as methanol or acetate:
   $5CH_3OH + 6NO_3^- \rightarrow 3N_2 + 5CO_2 + 7H_2O + 6OH^-$
   $5CH_3COOH + 8NO_3^- \rightarrow 4N_2 + 10CO_2 + 6H_2O + 8OH^-$

Denitrification can be described as a kind of anoxic respiration. Electrons originated from e.g. organic matter, reduced sulphur compounds or molecular hydrogen are transferred to oxidized nitrogen compounds instead of oxygen in order to build up a proton motive force usable for adenosine 5'-triphosphate (ATP) generation (Schmidt et al. 2003). Dissolved oxygen can inhibit nitrate reduction by repressing the nitrate reduction enzyme (Metcalf and Eddy 2003). Denitrification is performed by various chemoorganotrophic, lithoautotrophic, phototrophic bacteria and some fungi, especially under oxygen reduced or anoxic conditions (Focht and Chang 1975; Shoun and Tanimoto 1991; Zumft 1997). Denitrification process is initiated with an increase in the medium alkalinity. One equivalent of alkalinity is produced per equivalent of $N\text{-}NO_3^-$ reduced, which equates to 3.57 g of alkalinity as $CaCO_3$ production per 1 g of $N\text{-}NO_3^-$ reduced (Metcalf and Eddy 2003).

11.5.2 Biological Phosphorus Removal

Phosphorous is one of the major nutrients responsible for the increased eutrophication of lakes and natural waters. Wastewater containing phosphorous causes increased loss of livestock, purification costs, possible lethal effect of algal toxins on drinking water and decreased recreational and conservation value of impoundments.

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In the conventional method for removing phosphate from wastewater, precipitating chemicals such as iron or aluminium salts or lime ($Ca(OH)_2$) are added to the wastewater. In general, chemicals can precipitate 70% to 95% of phosphorus and effluent total phosphorus concentrations below 0.3 mg of TP L^{-1} can be achieved, depending on the operational conditions. But these methods have the disadvantages such as generation of large amounts of sludge (an increase of sludge volume by up to 40%) and the cost of the precipitants. In addition, concentration of iron and aluminium salts in the effluent has negative ecological impact. Therefore, adding chemicals in waste treatment should be minimized (Van Loosdrecht et al. 1997).

An eco-friendly alternative to this method is the Enhanced Biological Phosphate Removal (EBPR) which is quite well documented in the literature (Jenkings and Tandoi 1991; Van Loosdrecht et al. 1997; Mino et al. 1998; Oehmen et al. 2007). In EBPR, the phosphorous in the influent wastewater is subsequently removed from the process, as it is incorporated into cell biomass and wasted in sludge. EBPR requires the combination of anaerobic and aerobic/anoxic conditions. During the anaerobic phase (Figure 11.2), Polyphosphate Accumulating Organisms (PAOs) assimilate fermentation products (i.e. Volatile Fatty Acids; VFAs) into storage products (Poly-β-hydroxyalkaonate - PHA) within the cells with the concomitant release of phosphorous from stored Poly-Phosphates (PP). VFAs are fermented products of biodegradable organic matter. They are soluble degradable organic materials that can be easily assimilated by the microorganisms. PAOs assimilate VFAs to produce intracellular PHA storage products while intracellular glycogen is converted to PHA, utilizing energy available from stored polyphosphates (Mino et al. 1998). Concurrent with the VFAs uptake is the release of orthophosphates, as well as calcium, potassium, and magnesium cations. The PHA content in the PAO increases and the glycogen and polyphosphate decrease.

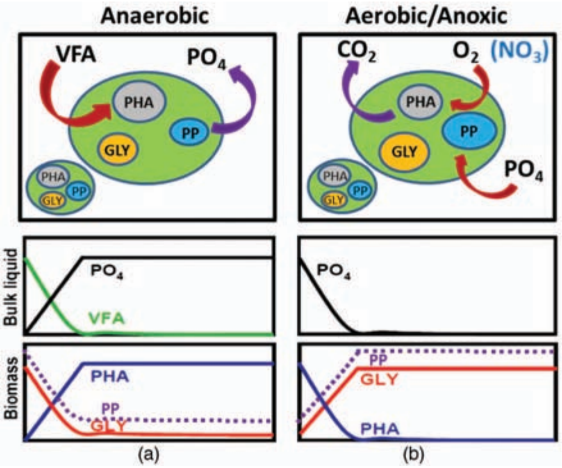

Figure 11.2. Biological phosphorus removal by PAOs. Anaerobic conditions (a); Aerobic/Anoxic conditions (b). The green color represents the biomass

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The anoxic-aerobic conditions support the oxidation of storage products leading to an increase in polyphosphate storage within the cell with concomitant production of energy (Figure 11.2). When stored PHA is metabolized, it will produce energy from oxidation and carbon for new cell growth with concomitant production of some glycogen also. This released energy is used to form PP bonds in cell storage. The soluble orthophosphate is removed from the solution and incorporated into PPs within the bacterial cell. The utilization of PHA also improves cell growth and this new biomass with high PP storage accounts for phosphorous removal. As a portion of the biomass is wasted, the stored phosphorous is removed from the biotreatment reactor for ultimate disposal with the waste sludge (Metcalf and Eddy 2003).

EBPR is affected by a number of environmental factors including pH, temperature, sludge retention time, excessive aeration, nitrite, nitrate and carbon source used by PAOs (Smolders et al. 1994; Brdjanovic et al. 1998a; Brdjanovic et al. 1998b; Brdjanovic et al. 1998c; Panswad et al. 2003; Saito et al. 2004; Oehmen et al. 2007; Puig et al. 2007). The most dominant VFA in EBPR plants is acetate, though propionate is present in substantial quantities in plants where pre-fermentation is employed. Other VFAs, such as valerate, butyrate and other VFAs may also be present, but typically in small quantities (Oehmen et al. 2007). PAOs also metabolize non-VFA organic substrates (e.g. glucose, starch, lactate and amino acids) (Cech and Hartman 1990; Randall et al. 1997). PAOs include those organisms with the anaerobic-aerobic phosphorus removal activity. The organisms with the anaerobic-anoxic phosphorus removal phenotype are called as denitrifying phosphate accumulating organisms (DPAOs). DPAOs possess similar capacities and characteristics as phosphorus removal in anaerobic-aerobic processes (Kuba et al. 1993). The only difference between the metabolism of PAOs and DPAOs is that DPAOs use nitrate instead of oxygen as an electron acceptor for phosphorus uptake. Applying DPAOs provides main advantages of savings of energy required for aeration and organic matter and lower sludge production in the overall nutrient removal process (Kuba et al. 1996).

Similar to PAOs, Glycogen-Accumulating Organisms (GAOs) take up VFAs anaerobically and convert them into storage compounds (PHA) via hydrolysis of their sole source of energy that is glycogen (Figure 11.3). However, they are not reported to contribute to P removal (Mino et al. 1998). The presence of GAOs has important consequences for the phosphorus removal capability of EBPR systems. The competitive advantage of PAOs in EBPR systems is compromised in the presence of GAOs, because GAOs use the same substrate (VFAs) under the same conditions. The supply of VFAs to EBPR systems is limited. Under this situation, the percentage of VFAs available to PAOs is reduced if a significant amount of GAOs accumulates, thereby decreasing the phosphorus removal capability of the system. Therefore, it is extremely necessary to identify operational conditions that maintain the competitive advantage necessary for the accumulation of PAOs. Special attention is given in the EBPR research on the competition between PAOs and GAOs studying the factors that influence the microbial competition in EBPR systems such as the carbon source, pH and temperature.

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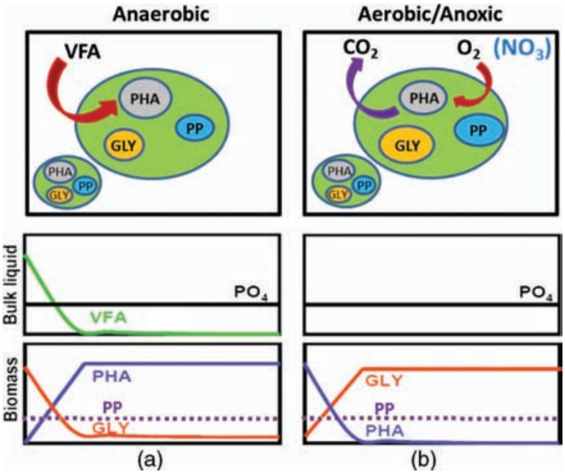

Figure 11.3. Metabolic processes of GAOs: Anaerobic conditions (a); Aerobic/ Anoxic conditions (b). The green color represents the biomass

Different carbon sources, VFAs and non-VFAs have impact on the PAO-GAO competition. While the use of acetate as a carbon source in EBPR systems has been often reported to yield robust and stable phosphorus removal performance, there are also many reported occasions where the phosphorus removal deteriorated due to what is believed to be microbial competition of GAOs with PAOs (Oehmen et al. 2007). According to recent studies, propionate may act as a more favorable substrate than acetate for successful EBPR performance in long-term operation (Pijuan et al. 2004; Oehmen et al. 2005).

Filipe et al. (2001) studied the effects of pH on the anaerobic metabolism of PAOs and GAOs, and reported that the pH control is a promising strategy for minimizing the accumulation of GAOs and increasing the reliability of biological excess phosphorus removal systems. When stoichiometry and kinetics of acetate uptake by enriched cultures of PAOs and GAOs as a function of pH was studied, it has been observed that the rate of acetate uptake by GAOs was significantly decreased when the pH of the medium was increased, but the uptake rate for PAOs was essentially independent of the pH for the range studied (6.5 to 8.0). This strongly suggests that, the growth of GAOs can be minimized if pH of the anaerobic zone of an EBPR system is controlled properly.

Temperature variation between 20°C and 35°C affects the microbial community of the EBPR system (Panswad et al. 2003). This study concludes that the PAOs are lower-range mesophiles or perhaps psychrophiles and will predominate only at 20.0°C or possibly lower. The GAOs are somewhat mid-range mesophilic organisms with optimum temperature between 25.0°C and 32.5°C. Lopez-Vazquez et al. (2007) proved that GAOs have clear advantages over PAOs for substrate uptake at a temperature higher than 20°C. Below 20°C, maximum acetate uptake rates of both microorganisms were similar. However, lower

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maintenance requirements at a temperature lower than 30°C give PAOs metabolic advantages in the PAOs-GAOs competition.

11.6 FACTORS AFFECTING NUTRIENT REMOVAL

Many factors are responsible for the growth of nutrient-removing organisms. Comparing the growth needs of autotrophic organisms, which nitrify wastewater, with those of heterotrophic bacteria, which oxidize carbonaceous biochemical oxygen demand (CBOD), can help to control both processes during the treatment. Some of the important factors affecting biological nutrient removal are discussed as below.

11.6.1 Mean Cell Residence Time (MCRT)

Mean cell residence time (also called sludge age or SRT) which measures the average length of time (in days) that microorganisms (sludge) are held in the system, is the most commonly used parameter during operation of a conventional onsite activated sludge system. If the MCRT is too short, then the biological system will not have enough bacteria to degrade the pollutants, resulting in poor effluent quality. The MCRT required depends on the constituent of wastewater and the growth rate of the microorganisms consuming it. For example, a simple carbon compound (e.g., acetate) is metabolized by fast-growing heterotrophic organisms; it often requires an MCRT of less than 1 day. Conversely, ammonia is oxidized by slow-growing bacteria, so its MCRT is much longer. Many treatment plants that remove CBOD from wastewater may have been designed for 2 to 4 days of MCRT, but for removal of ammonia, the MCRT may need to be twice as long, depending on temperature and other factors. If the basin size and MLSS are constant, then the MCRT will shorten as the sludge wasting rate increases and lengthen as the wasting rate decreases.

11.6.2 Aeration Requirements

To nitrify ammonia, aeration systems designed for CBOD removal may need to be enlarged by 30 to 50% to provide enough oxygen. Some plants accommodate the increased demand by replacing air diffusers with fine-bubble systems or other more efficient aerators, while some other incorporate denitrification (the reduction of nitrate-nitrogen to nitrogen gas) into the BNR process because denitrification can theoretically reclaim 63% of the oxygen needed for nitrification. However, because denitrification typically only reduces about half of the nitrate-nitrogen in the wastewater (denitrification effluent typically contains 6 to 8 mg/L of nitrate-nitrogen), the actual amount of oxygen reclaimed may be closer to 30 to 40%.

11.6.3 Food to Microorganism Ratio

The food to microorganism (F:M) ratio measures the amount of food (BOD) available for the amount of mixed-liquor volatile suspended solids (MLVSS) present in the aeration basin. *F* is typically based on primary effluent, if the treatment plant has primary clarifiers; otherwise *F* is based on the raw

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wastewater's BOD load. The *M* for a conventional activated sludge system is typically based on the entire aeration basin's MLVSS. Most conventional activated sludge systems are designed for F:M ratios ranging from 0.2 to 0.4 (WEF 1998). In BNR systems with several cells, the selector may be configured to encourage the growth of non-filamentous (floc-forming) organisms or the selector may be configured to encourage the growth of *Acinetobacter* organisms to increase the denitrification rate. In either case, the F:M ratio of each selector zone is important. When calculating the F:M ratio for a BNR system, *F* is based on the secondary influent BOD. If the reactors are operated in series, then the first cell's *M* is based on its volume and MLVSS concentration and, the second cell's *M* is based on the combined volume of the first and second cells, and so on. One recommendation is that the BNR systems have at least three cells to create a high substrate concentration in the initial minutes of contact. For a plug-flow reactor, F:M ratios of 6.0, 3.0, and 1.5 mg/d of BOD per 1.0 mg of MLVSS for the first, second, and third cells, respectively, have been recommended. However, if the F:M ratio is too high (more than 8.0 mg/d of BOD per 1.0 mg of MLVSS), then a viscous, non-filamentous organism could dominate the reactor.

11.6.4 Wastewater Characteristics

Nowadays, wastewater treatment plants typically are having complicated models designed for a perplexing array of wastewater characteristics. In fact, it has been reported that nearly 40 wastewater constituents are considered "important" when designing wastewater treatment facilities (Metcalf and Eddy 2003). Fortunately, operators of BNR facilities only need a fundamental understanding of the relationship between wastewater characteristics and plant operations to optimize plant performance.

One of the key characteristics is the amount of inert TSS in biological treatment influent ($\mathrm{iTSS}_{2\mathrm{INF}}$). A high concentration of inert TSS will increase the percentage of nonbiodegradable solids in the MLSS, so a longer MCRT will be needed to treat the wastewater sufficiently. To calculate $\mathrm{iTSS}_{2\mathrm{INF}}$,

$$\mathrm{iTSS}_{2\mathrm{INF}} = \mathrm{TSS}_{2\mathrm{INF}} - \mathrm{VSS}_{2\mathrm{INF}}$$

where $\mathrm{TSS}_{2\mathrm{INF}}$ = total suspended solids in secondary influent, and $\mathrm{VSS}_{2\mathrm{INF}}$ = volatile suspended solids (VSS) in secondary influent.

BOD's constituents are an important factor. The soluble BOD measurement, for example will indicate how much material is readily biodegradable. Soluble BOD typically is usually measured based on a 5-day BOD test in which wastewater is passed through a 0.45-μm filter whereas, a 1-day BOD test will provide an estimate of readily biodegradable BOD - including the simple carbon compounds that are available for rapid bio-assimilation. In a conventional activated sludge system, 5 mg of nitrogen and 1 mg of phosphorus will typically be used for every 100 mg of BOD removed. In a BPR process, for every 100 mg of BOD removed, 3 to 5 mg of phosphorus may be used. If the BPR process is operated to remove total phosphorus, then a secondary influent BOD to total phosphorus ratio of 20 : 1 or

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more may be needed to ensure that the treated effluent will contain less than 1.0 mg/L of phosphorus. The required BOD to TP ratio depends on process type and effluent goals. Processes that do not nitrify and denitrify (e.g., the anaerobic/oxic (A/O) process) may require a BOD to TP ratio of 15 : 1, while those with full nitrification and denitrification may require a BOD to TP ratio of 25 : 1 or more.

11.6.5 Sludge Settleability and Foam

Usually, many BNR federal facilities operate at high MCRTs (more than 8 days) to fully nitrify and allow for denitrification, resulting in sludge-settleability or foam problems. Wastewater constituents (e.g., soap, oil, and grease) and streams recycled from solids handling processes can exacerbate these problems. Spray nozzles to spread antifoaming chemicals is useful to avoid this problem. Before returning activated sludge (RAS) flows are raised to increase the basin MLSS concentration, plant staff should evaluate the solids loading (g/m^2 d) on the secondary clarifiers to determine if the capacity is adequate. Larger RAS pumps may be needed to obtain the higher MLSS concentration often desired in a BNR system.

11.6.6 Hydraulic Retention Time

Hydraulic retention time (HRT) required in maintaining BNR depends on the size of the reactor, which in turn depends on the MCRT necessary for growth. For the known reactor size, the HRT can be calculated by dividing the volume of the reactor (V) by the secondary influent flow ($Q_{2\mathrm{INF}}$): The result is a nominal value used to relate basin size to plant flow. The nominal value is typically used because internal recycle streams do not affect most of the reactions.

11.6.7 Return Flows

Conventional activated sludge systems typically have only one return flow: return activated sludge (RAS). Biological nutrient removal processes, on the other hand, may have more return flows [e.g., mixed liquor recycles (MLR)]. The RAS pumping rates are typically 30 to 100% of the influent flow (Q). The MLR pumping rates may be 100 to 400% of the influent flow, depending on such factors as the target effluent nitrate concentration. They also may be transferred from an aerobic or oxic zone [Mixed-liquor recycle from the oxic zone (MLROX)] or from an anoxic zone [Mixed-liquor recycle from the anoxic zone (MLRAX)]. The source of the MLR and which zone receives it often distinguishes one BNR process from another.

11.6.8 Alkalinity and pH

To control the pH and alkalinity, BNR systems also may need some chemical additives (e.g., hydrated lime, soda ash, or caustic soda). Because alkalinity is consumed during nitrification, the chemicals can help maintain the minimum alkalinity level needed (typically, 60 to 100 mg/L of alkalinity as calcium carbonate). Low alkalinity not only lowers pH but may limit the growth of nitrifying organisms because they lack enough inorganic carbon to produce new cells.

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11.6.9 Effect of Anaerobic/Aerobic Contact Time on PAOs

Anaerobic/aerobic contact times are one of the most important operation factors influencing PAO selection and phosphorus removal efficiency. The nature and amount of intercellular storage energy in two different types of PAOs that were developed from acetate-fed and glucose-fed sequential batch reactors (SBRs) was studied by Wang and Park (1998). When acetate-fed, PAO cells contained 20–23% PHB-P or phosphorus as PHB; when glucose-fed they contained 10–15% glycogen-P or phosphorus as glycogen. A longer anaerobic contact time resulted in a secondary phosphorus release that was not associated with internal cellular energy synthesis, but a longer aerobic contact time resulted in a depletion of cellular energy. PAOs with lower cellular energy may not be able to compete with other microorganisms in the biological phosphorus removal system. In order to avoid overdesign and optimize removal efficiency, Wang and Park (1998) recommend that anaerobic contact time be based on the VFA uptake rate or the fermentation rate. Aerobic contact time should be based on the amount of internal energy (VFA) stored during the anaerobic stage and the target effluent concentration.

11.6.10 Impact of Sidestreams

Many BNR plants find that the impact of in-plant sidestreams can have a dramatic impact on plant performance. If not properly managed, these sidestreams can add additional loads on the liquid train operation and reduce the effectiveness of the treatment. Solids handling systems such as dewatering equipment, sludge thickening and digestion processes are usually the most problematic. For example, the filtrate of anaerobically digested sludge can contain 500 to 1000 mg/L of ammonia and 60 to 200 mg/L of orthophosphate. Even though the volume of these sidestreams are often only a fraction of the influent flow to the plant, their mass load can add significant concentrations of phosphorus and ammonia to the plant. To minimize these effects, sidestream treatment is often required at BNR plants.

11.7 OPERATIONAL ISSUES ASSOCIATED WITH BNR PROCESSES

BNR processes are very difficult to control and operate than conventional activated sludge processes. To reduce the difficulty of operation, operators should be thoroughly trained on the mechanisms of sampling and monitoring, analytical test kits, nutrient removal, and detecting operational issues. On-line sensors and monitoring devices are important to continuously monitor variables such as DO, alkalinity, pH, ammonia, nitrate and phosphorus. Measuring these variables is important for adjusting optimizing anaerobic and anoxic zones, recycle rates, and for generally monitoring the efficiency of the process.

Although BNR plants can be designed and operated to remove nutrients to an efficient level, it is still necessary to provide chemical backup systems for phosphorus removal. The failure of a clarifier mechanism, blower, recycle pump,

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or VFA fermenter are examples of situations where supplementary chemical backup can be required to comply with permit limits. Supplementary dosages of metal salts can have a beneficial effect on biological phosphorus removal of BNR systems. However, an excessive addition of chemicals can also have an inhibitory effect on the biological uptake. Control of the BNR system and of supplementary chemical feeds is essential for cost and optimization of biological phosphorus removal.

Bacterial cells absorb the biologically removed phosphorus. The first stage of sludge treatment (thickening) should be aerobic, so the phosphorus is retained with the thickened sludge. Under anaerobic conditions, the phosphorus is released to the liquid phase. After subsequent dewatering, the return filtrate concentrate may have to be treated chemically to remove the phosphorus before being returned to the plant. An investigation of the design and operational difficulties encountered in BNR WWTPs in the United Kingdom (UK) was conducted by Cooper et al. (1995). Control of sludge age, recycle streams and oxygen input are established difficulties associated with nitrifying activated-sludge systems.

11.7.1 BOD-Nutrient Ratios

A ratio of at least 20∶1 of BOD/P is required in the anaerobic zone for a good release of phosphorus, and 7.5 mg/L of VFAs are required to release 1 mg/L of phosphorus. Weak wastewater (BOD/P ratio < 20∶1) creates conditions of insufficient substrate to initiate phosphorus release in the anaerobic zone. A common solution for insufficient VFAs in the influent wastewater is a supplemental VFA source (acetic acid or propionic acid) fed into the anaerobic zone. Some facilities utilize onsite fermenters, which are capable of producing high VFA concentrations that are injected into the anaerobic zone. Fermenters have a retention period of 3 to 5 days depending on temperature and can decrease waste gas in the digesters. It would be an advantage to reduce the amount of gas at plants.

11.7.2 Storm Water Impacts

Many WWTPs where it receives stormwater and wastewater combined, wet weather flows can reach 2.5-3.0 times the dry-weather flow. It can exceed the hydraulic capacity of the plant, and reduce the amount of substrate utilized by the PAOs in the anaerobic zone. Equalization tanks can regulate the flow to the BNR system. The equalization tanks can also provide a buffer for the return of high ammonia and phosphorus waste streams to the sludge processing facility.

11.7.3 Solids Issues

Water Research Centre (1995), on behalf of a group of water companies, conducted pilot studies. It revealed that both mainstream processes and side-stream processes were capable of producing effluent phosphorus concentrations of less than 1.0 mg/L. In a BNR process, the phosphorus is bound with the sludge and its content in the biosolids is approximately 5%. Therefore, it is important to keep suspended solids in the effluent to a minimum. Good solids retention is

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essential in the clarifier. To meet the stringent limit of less than 1 mg/L, tertiary filtration may be required. Control of dissolved oxygen concentrations is very important to achieve effective denitrification and phosphorus removal; though, this can create oxygen-deficient zones, which promotes proliferation of filaments. Filamentous sludge organisms manifest themselves as a floating scum or stable foam. These foams get trapped behind baffle walls of the reactors and can stabilize to dramatic levels, passing into the final clarifier and contaminating the effluent. Baffle walls separate the reactor zones and prevent back-mixing between zones. Sub-surface baffles could be designed as cascades between reactors to ensure that scums and foams are transported to the final clarifier. An effective scum removal system is needed in the final clarifier, as it is important that these scums and foams are transported out of the sludge inventory.

11.8 TREATMENT PROCESSES AND SYSTEMS

Onsite wastewater treatment systems are often the best choice for wastewater treatment in many areas, from public health, environmental, and economic standpoints provided that these systems are properly sited, designed, installed, and maintained. Onsite wastewater treatment permits the treatment and recycles water used in homes and businesses to replenish local groundwater supplies. This benefit of onsite treatment is not realized with municipal wastewater treatment, in which partially treated wastewater is discharged directly to rivers and coastal waters, sending wastewater either further downstream or out of the watershed entirely, and not returning to the landscape to replenish groundwater aquifers. This loss of groundwater recharge reduces the amount of groundwater available for drinking water wells. This is more problematic in coastal areas where depletion of ground water resources can lead to salt-water intrusion and loss of potable freshwater supplies. Because groundwater is the main source of flow to streams during dry weather, loss of recharge can also lower stream flow to levels that can no longer support healthy aquatic life. The two major classes of onsite wastewater treatment systems are explained here and are termed conventional treatment systems and advanced treatment, or innovative and alternative systems.

11.8.1 Conventional Treatment Systems

The term ‘conventional’ defines the standard gravity flow design, which consists of a septic tank, a distribution box, and a drainfield. Conventional systems function very well on sites with few constraints as they mainly rely on the native soils to treat bacteria, dilute other waste that is not treated. Conventional systems are the least expensive to build and maintain, and are remarkably efficient for low-density sites with sufficient space for setbacks and dilution, good soil conditions, and deep water table. Where soil conditions are not ideal for the infiltration and treatment of wastewater, or where the land area available is insufficient to handle large water loads, reliance on native soils for treatment of wastewater can be a severe

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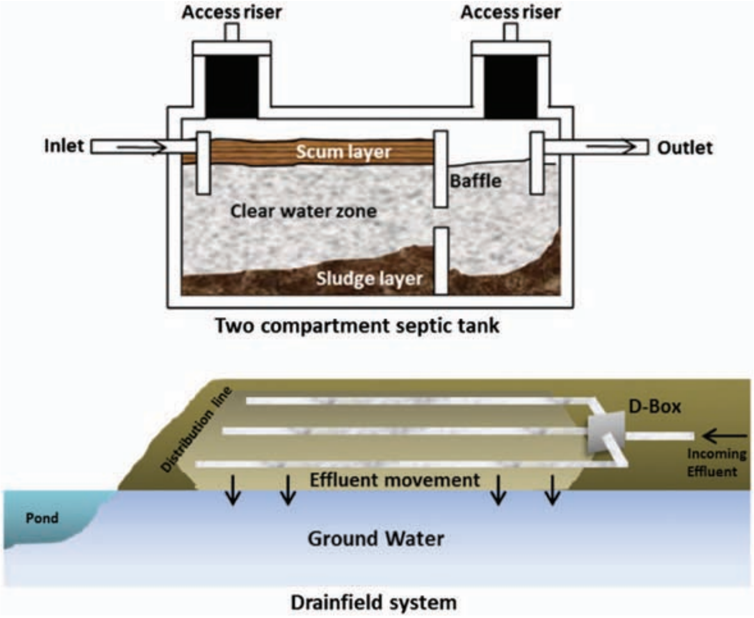

Figure 11.4. Components of conventional onsite treatment system

limitation. Primary treatment (settling of solids and fats, oils, and greases) of wastewater that takes place in an onsite system is the exact same step found in municipal sewer treatment plants, but done on a much smaller scale. A typical conventional system is presented in Figure 11.4.

11.8.1.1 The Septic Tank

The main objective of the septic tank is to temporarily retain and store wastewater to allow solids, and fats, oils, and greases (FOG) to separate before the wastewater flows to the drainfield. The tank is generally designed to provide a 2-day retention time for wastewater settling to occur. Heavy solids settle to the bottom forming a layer of sludge, while floating scum layer contains light solids and FOG. The minimum tank size for a single family home is typically 4000 L but different types of tanks can vary in size, configuration, and materials, i.e. from steel drums to concrete cylinders. Tanks are most commonly constructed out of concrete though fiberglass tanks are regularly used on lots with limited access to heavy equipment. The interior of tanks may also vary, but mostly containing either one or two compartments. Single compartment tanks equipped with a divider at the outlet end to keep floating FOG from leaving the tank and entering the drainfield. The tank shown in the figure is a typical two-compartment tank, split by a divider; the first compartment contains 2/3 of the tank volume while the second contains 1/3. These systems are particularly larger than single compartment tanks, with a capacity of 1,500 gallons. Wastewater flows from the first to the second

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compartment through a gap in the baffle at a height that should correspond with the clear zone, or the most clarified water in the tank and additional separation of solids and FOG occurs in the second compartment. The two compartment configurations combined with a larger storage volume for settling and storing waste, make sure that the greatest possible amount of separation of solids and FOG takes place before the wastewater leaves the tank to be distributed to the drainfield. The components of a septic tank are illustrated in Figure 11.4.

11.8.1.2 The Distribution Box

The distribution box is the connection between the septic tank and the drainfield, and serves to distribute the wastewater evenly amongst the drainfield lines. Distribution of the wastewater is very crucial in maintaining the longevity of the drainfield. Localized saturation of a drainfield line may occur if only a small portion of the drainfield is actually used due to poor distribution. Organic matter and solids may build up faster than they are broken down by soil microbes clogging soil pores, causing the drainfield to fail prematurely. A typical D-box is pre-cast with multiple holes, as shown in the figure, to allow for use in various system configurations. D-box shown here has three pipes; one delivering wastewater from the primary treatment tank, and two to distribute effluent to the two drainfield lines or trenches.

11.8.1.3 The Drainfield

Drainfields serve to disperse wastewater to the soil environment, where it is expected that beneficial soil microorganisms will kill pathogens. The size of the drainfield will depend on the anticipated volume of water to be produced in the home and the soil conditions at the site. For example, in Rhode Island, the drainfield may be one of three basic types: (i) Trenches, (ii) Leaching Chambers, or (iii) Eljen In-drains. In situations where required separation to groundwater cannot be met, modifications to the conventional drainfield, such as mounding or filling may be approved for use.

Trench Drainfield: A trench type drainfield is comprised of two or more parallel trenches containing a perforated PVC pipe surrounded by washed crushed stone. The crushed stone is covered by geotextile fabric to ensure that fine soil particles do not fill voids between the stones, and the native soil is used to fill the trench to the ground surface. Wastewater flows from the distribution box into the drainfield PVC pipes, to the crushed stone, and then to the soil environment.

Leaching Chambers: These are perforated, bottomless, concrete boxes surrounded by crushed stone on the sides and bottom and generally installed in a series of three or more units, depending on the anticipated volume of wastewater. Liquid effluent flows from the septic tank into the chamber, where it seeps out the side walls and bottom. Galleys and flow diffusers are the two types of leaching chambers commonly used in the state. Deep galleys are $4' \times 4' \times 4'$ units, and may be installed as deep as 10 feet below ground, depending on the site characteristics and system design. In contrast, flow diffusers are shallow units,

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typically installed about one to two feet below the ground surface and are 8′ × 4′ × 2′ in size.

Eljen In-drains: These are gravelless trenches containing prefabricated units of geotextile fabric and cuspated plastic spacing cores. This type of drainfield was one of the first alternative drainfield technologies, but now is considered to be a conventional drainfield option. These units are bordered on the sides and beneath by six inches of specific sand media, and are covered with native soil. To prevent fine soil particles from clogging the filter fabric pores, a layer of protective fabric is placed on top of the units prior to covering with soil.

18.8.1.4 Mounded and Filled Systems

Mounded and filled systems are common solutions to overcome shallow depth to ground water table, ledge, or other restrictive features, where site conditions allow for the use of conventional onsite wastewater treatment technologies. Adding fill to a site is a means to increase the distance to such features, as well as addressing other requirements such as the cover of components or drainfield fill-perimeter. The onsite treatment system components are installed within the mound of fill. Mounds are often contained within a retaining wall. It should be noted that these systems alter the drainage patterns of a site and the surrounding area. There are two types of mound systems. A Type I Mound is an OWTS consisting of a series of perforated pipes on a rock bed above the natural soil surface. These perforated laterals receive wastewater effluent from a septic tank through a distribution box. The effluent is transmitted into the rock bed and natural soil for final treatment and disposal. A Type II Mound is an OWTS that is raised above the natural soil surface in a specific graded, clean sand media. Perforated laterals, under pressure, receive wastewater effluent from a septic tank. These laterals distribute the effluent over a gravel bed and sand media. Gravel is laid over the sand layer or chambers to assist in the distribution of the effluent over the entire surface of the sand layer and provide a brief storage layer for the effluent as it is pumped onto the mound. The covering soil, loamy sand, must be porous to provide good aerobic conditions in the sand layer. It is important to note that most bacteria require air to digest sewage so using a clay soil for covering material would limit air movement into the mound causing anaerobic (without air) conditions and greatly reduce the effectiveness of the sand layer.

11.8.1.5 Constructed Wetlands

Constructed wetland systems are used to treat septic tank effluent. The wetlands use a combination of soil, microorganisms and plants to naturally treat wastewater. There are two main types of wetland systems as illustrated in Figure 11.5, Free Surface Flow and Subsurface Flow wetlands (White et al. 2001). Free Surface Flow Wetlands have exposed water surfaces, where the water and wastewater are exposed to the atmosphere. A Free Surface Flow Wetland looks and acts like a natural marsh area. The plants in the wetland, such as bull rush and cattails are chosen for their filtration capabilities. There is a soil layer at the bottom of the

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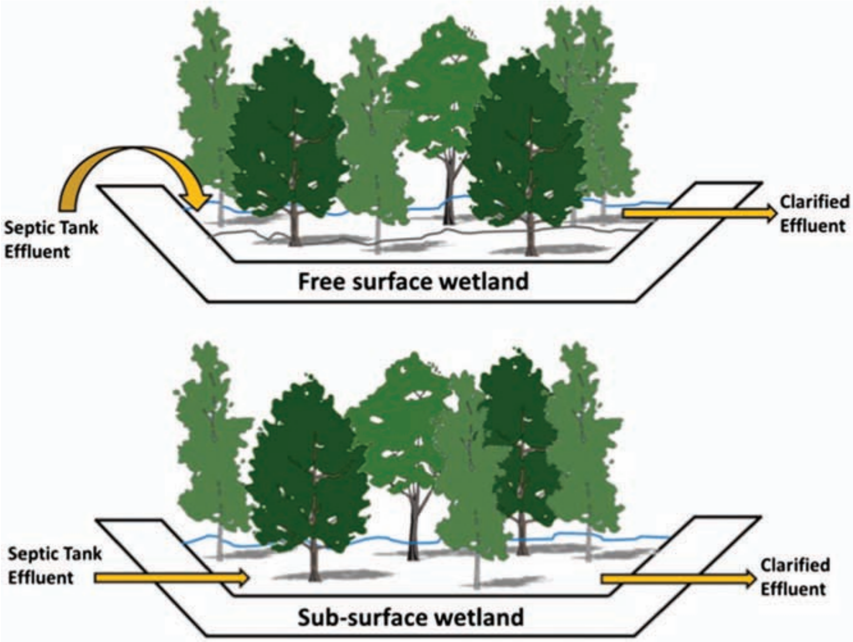

Figure 11.5. Constructed wetland systems

wetland that helps to treat the wastewater, as a soil absorption system. In Subsurface Flow Wetland, the water flows below the surface through the bed media. This means that the water surface is not exposed to the atmosphere. By not exposing the water surface to the atmosphere, the wetlands reduce odor and standing water for the breeding of mosquitoes. Subsurface Flow Wetlands are constructed to clarify wastewater. (See Table 11.2)

11.8.2 Advanced Treatment Systems

Advanced treatment systems are different from conventional onsite treatment systems in a variety of ways, but the principal difference is that they further purify the effluent before it is disposed. Advanced systems combine carefully designed treatment steps and create conditions to facilitate a consistently high degree of treatment. Usually, advanced treatment systems control the flow by using pumps and timers to avoid overloading the treatment and final disposal components during periods of high water usage, which could occur during a morning session of activity.

The advanced treatment system helps in additional reduction of the strength of the wastewater, or the fats, solids, oils, and greases suspended in the wastewater. It may also contribute the reduction in the pathogens and/or nutrients in the effluent depending on the configuration and design of the system. Systems working for nitrogen reduction generally recirculate the effluent back into the septic tank where raw and treated effluent are mixed, creating conditions that facilitate the nitrogen removal by beneficial bacteria. Advanced treatment systems

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Table 11.2. Comparison of mound system and constructed wetland system

	Advantages	*Disadvantages*
Mound System	Space efficient compared to conventional rock lateral systems; May be used in areas with high bedrock, groundwater, or restrictive clay soil near the surface; Allows home building in areas unsuitable for below grade systems and detergents are not harmful to this system	Periodic flushing of the distribution network is required; Must be installed on relatively level lots; System may be expensive; System may be difficult to design; Regular inspection of the pumps and controls necessary to maintain the system in proper working condition; Water softener wastes, common household chemicals
	Can be installed at shallower depths and requires less topsoil cover and on irregular lot shapes and sizes; Space requirements are nearly half those of a conventional septic tank system; Installation sites are left in their natural condition; Provides alternating dosing and resting cycles	Electric components are necessary, Design and installation may be difficult; Some low-pressure pipe systems may gradually accumulate solids at the dead-ends of the lateral lines; Therefore, maintenance is required, installers with experience with such systems should be sought
Constructed Wetlands	Wetland systems can be constructed inexpensively; Potential for homeowner construction	Efficiency varies with weather conditions; Insects or animals may carry pathogenic organisms to locations where human contact is possible; Less desirable for residential use except where no other options are available to deal with an existing problem.

are designed as a logical sequence of treatment components to achieve certain level of treatment, specified by local, state, or regional governing agencies. Since not all technologies can achieve effective nutrient and/or pathogen reduction, technologies are originally chosen based on the required level of treatment. Treatment systems attain the best results when receiving wastewater with certain chemical and microbiological characteristics, and so the components are selected and combined with this in mind. Site limitations may also dictate the potential use of technologies. For instance, on a small group with existing homes and failed septic systems, the advanced treatment systems with the smallest footprints are most preferably used as replacement systems. Advanced treatment systems normally require semi-annual or annual maintenance in order to function properly and should be accomplished by a trained and qualified service provider.

11.8.2.1 Primary Treatment

Primary treatment separates solids, fats, oils, and greases and is a crucial step in the treatment process, which eliminates portions of the waste that cannot be easily broken down by bacteria living in the system. If it is not removed then it could clog the pores raising problems in subsequent steps of the treatment train. This is the same process as in a conventional two-compartment tank.

An advanced treatment system assists to decrease solids and fats, oils and grease concentrations in the effluent, and may also reduce nutrient concentrations. This step can be added to the system in two different ways:

1. An additional compartment within a single processing tank - the tank would have separate compartments dedicated to the initial settling and separation of solids and FOG, and then for additional treatment.
2. A separate component installed in between septic tank and drainfield option.

Treatment is achieved by transferring the effluent through any of a variety of systems. The majority of advanced treatment systems used are of three types, aerobic treatment units, media filters, and sequencing batch reactors.

11.8.2.2 Aerobic Treatment Units

Aerobic treatment units use air injection systems and blowers to build an oxygenated environment, which can maintain bacterial populations that break down organic material. This aeration produces an effluent with reduced total suspended solids (TSS) and biochemical oxygen demand (BOD) than that of conventional systems. The aeration creates agitation in wastewater, so solids are readily mixed with the bacteria, enabling organic matter digestion by bacteria. There is a step in the process in which, any settled solids and bacteria are returned back to the aerobic portion of the tank for additional process and mixing. Clarification is also one step of the process, which allows solids and bacteria to settle out of the effluent prior to distribution to the drainfield, ensuring that effluent leaving the aerobic treatment unit possess very few solids and organic matter particulates.

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11.8.2.3 Media Filters

Media filters is a lined or watertight structure having specified media, which act as a support for bacterial growth providing a basis for biochemical and physical treatment processes to occur. During the trickling process, the organisms growing on the media treat the wastewater by breaking down organic matter with simultaneous nutrient removal in the effluent. As the filter is never saturated with wastewater, the presence of air encourages the establishment of beneficial aerobic microorganisms. The media may be an absorbent such as peat or textile media or a non-absorbent like sand or plastic.

11.8.2.4 Sequencing Batch Reactors

A sequencing batch reactor is a special unit that performs both aeration and clarification in a single treatment tank. During the cycle, the wastewater enters the tank and then the full tank is aerated for biological oxidation. After a certain period of aeration, the mixing is stopped, and the solids are allowed to settle, followed by decantation of clarified effluent from the clear zone in the tank. The cycle is completed when the system develops anaerobic conditions to facilitate potential nitrogen removal.

11.8.3 Specific Biological Nutrient Removal Systems

Biological processes for the wastewater treatment have been widely implemented for classical industrial and urban wastewater. Moreover, there are many biological processes that are effective in nutrient removal. Some of the widely used nutrient removal processes are described below.

11.8.3.1 Anaerobic/Anoxic/Oxic Process

Anaerobic/anoxic/oxic process represents the sequence of zones in this process, as illustrated in Figure 11.6. This process is a combination of the modified Ludzack-Ettinger (MLE) process for nitrogen removal, and the Anaerobic/Oxic or Phoredox process for phosphorus removal. When the two processes are combined to create the Anaerobic/anoxic/oxic process, the efficiency of nitrogen removal is the same as the MLE process, but the removal of phosphorus is not as efficient, due to the recycling of nitrate to the anaerobic zone. Although the recycling to the anoxic zone results in a substantial removal of nitrate, complete removal is not possible,

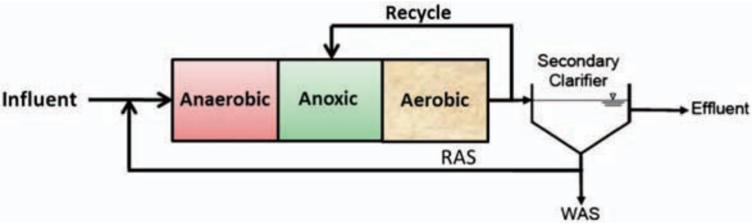

Figure 11.6. Schematic diagram of Anaerobic/anoxic/oxic process

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and some nitrate is recycled to the anaerobic zone. The impact of the nitrate on the anaerobic zone depends on the organic content of the wastewater. If the organic content is high, denitrifying organisms will oxidize the VFAs, making the VFAs unavailable for uptake by PAOs, thus reducing the release of phosphorus and the efficiency of phosphorus removal. Maintenance of a solids blanket (the settled solids) in the final clarifier has been used with this process to allow denitrification of the RAS in the solids blanket of the final clarifier to reduce nitrate recycling to the anaerobic zone. Maintenance of the solids blanket requires careful clarifier operation to prevent clumping and floating sludge. MLSS recycle rates typically range between one to two times the influent flow rate. The SRT in the anoxic zone is similar to that used in the Anaerobic/anoxic/oxic process (0.75 to 1.5 days), and the SRTs in the anoxic and aerobic zones are similar to those used in the MLE process. The HRTs are also correspondingly similar.

11.8.3.2 Modified Five-Stage Bardenpho Process

The five-stage Bardenpho process is essentially the same as the four-stage Bardenpho nitrogen removal process with the addition of an anaerobic zone divided into multi-staged compartments to achieve phosphorus removal, by minimizing nitrate recycling to the anaerobic zone. Bardenpho ® Biological Systems signify an advancement in the activated sludge process consisting of a multi-stage biological reactor. When an anaerobic zone precedes the conventional four-stage Bardenpho process, the resulting five-stage process can be used to encourage the growth of *Acinetobacter* organisms. Modified Bardenpho process resembles the anaerobic/anoxic/oxic process followed by a second anoxic and a reaeration zone. The total HRT of this process is about 22 hours, although the HRTs vary for each zone: anaerobic (2 hours), anoxic (3 hours), aerobic (12 hours), secondary anoxic (2 hours), and reaeration (1 hour). Without using excess chemicals, high levels of suspended solids, BOD, nitrogen, and phosphorus can be removal consistently. Influent is mixed with activated sludge, returned from the final clarifier, in the fermentation stage. After contact, the liquid is transferred to an anoxic zone where it is mixed with nitrates from the nitrification zone. Oxygen, which is added in the nitrification zone, converts BOD to carbon dioxide, and ammonia to nitrate. In the second anoxic zone, nitrate is reduced to nitrogen gas. The final stage of the process is a reaeration zone in which the dissolved oxygen concentration in the mixed liquor is increased to prevent phosphorus from being released in the last clarifier. A typical Modified Five-stage Bardenpho Process is presented in Figure 11.7.

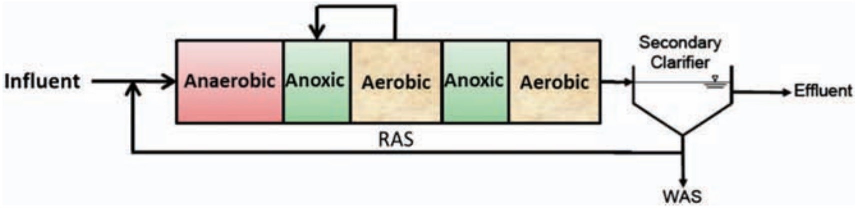

Figure 11.7. Schematic diagram of Modified 5-stage Bardenpho process

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Process Description

Fermentation Stage: Activated sludge containing a variety of organisms is returned to the fermentation stage from the clarifier. This sludge is mixed with the plant influent to produce the suitable stress condition that allows maximum possible phosphorus removal from the wastewater biologically in the following aerobic stages. Organism stress occurs in the absence of dissolved oxygen and nitrates.

First Anoxic Stage: Nitrate-rich mixed liquor from the third stage is recycled to the first anoxic stage where, it is mixed with conditioned sludge from the fermentation stage without oxygen. Bacteria reduce the nitrate to gaseous nitrogen by utilizing BOD in the influent. Approximately two-third of the influent nitrogen is removed in the first anoxic stage.

Nitrification Stage: In the nitrification stage oxygen is introduced to oxidize BOD and ammonia. BOD is converted to new cell mass and carbon dioxide, while ammonia is converted to nitrate. Mixed liquor with the nitrate contents is recycled back to the first anoxic stage where the additional uptake of phosphorus by the organisms occurs.

Second Anoxic Stage: Nitrate, not recycled to the first anoxic stage, is introduced to the second anoxic stage where it is reduced to nitrogen gas which enables a low effluent nitrate concentration.

Reaeration Stage: When maintained in an aerobic environment, the Bardenpho system mixed liquor contains 5% to 6% phosphorus. If the sludge is permitted to become septic, phosphorus could be released in the final clarifier. Subjecting the sludge to reaeration introduces additional oxygen to the mixed liquor, ensuring that it remains aerobic, thus retaining phosphorus.

Bardenpho Process is somewhat similar to a conventional activated sludge process. Raw or settled wastewater is mixed with return settled sludge when it enters the biological reactor. This mixture then flows to a clarifier where bio-solids are separated from the treated wastewater and are recycled to a reactor basin. Few part of the sludge is wasted in this process, removing extra cell growth generated during processing and it also removes phosphorus from the system. The advantages of this process are as follows: no expensive chemicals and low effluent concentrations of BOD, phosphorus and nitrogen. Reliability has been demonstrated at installations obtaining an AWT 5-5-3-1 effluent (BOD, SS, N, P). Operating costs are lower than the conventional nutrient removal processes. In addition, the stable sludge handling is easy and can be disposed of directly. The operation flow of Bardenpho System is similar to conventional activated sludge plants, and the flowsheet is simple, with few control parameters to measure and adjust, so the staff does not require retraining. This system is also compatible with the Carrousel ® Biological Oxidation Systems which is typically used as the nitrification stage in the Bardenpho Process. These systems provide the advantages which include lower energy cost and construction, and improve performance and control. Existing Carrousel System can also be upgraded to a Bardenpho Process as per the changes in regulations, requiring strict control of nitrogen and phosphorus.

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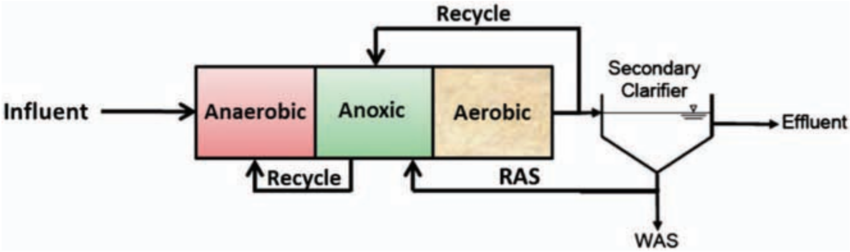

Figure 11.8. Schematic diagram of University of Cape Town (UCT) process

11.8.3.3 University of Cape Town, South Africa (UCT) Process

Marais and his co-workers determined the detrimental effects of nitrate entering the anaerobic zone on the performance of biological phosphorus removal processes (Randall et al. 1992). They developed a modification of the three-stage Phoredox process that eliminated the recycle of nitrate in the RAS to the anaerobic zone. This process, which they named the University of Cape Town (UCT) process, consists of anaerobic, anoxic, and aerobic zones, with the RAS directed to the anoxic zone for denitrification, as illustrated in Figure 11.8. Nitrified mixed liquor from the aerobic zone is also directed to the anoxic zone to increase nitrogen removal through denitrification. Denitrified MLSS from the end of the anoxic zone is recycled to the anaerobic zone to provide the microorganisms needed there for phosphorus removal to occur.

The wastewater influent flows directly into the anaerobic zone, which provides a source of organic matter to the anaerobic zone. Because the RAS is not recycled to the anaerobic zone, longer HRTs (1-2 hours) are needed to achieve the desired solids retention time. Anoxic and anaerobic SRT and HRTs are similar to those used in the MLE process. Anoxic and mixed liquor recycle rates are typically double the influent flow rate.

11.8.3.4 Modified University of Cape Town, South Africa (MUCT) Process

The MUCT process was designed to improve the UCT process and is unique in that the anoxic zone is divided into two cells, as illustrated in Figure 11.9. The

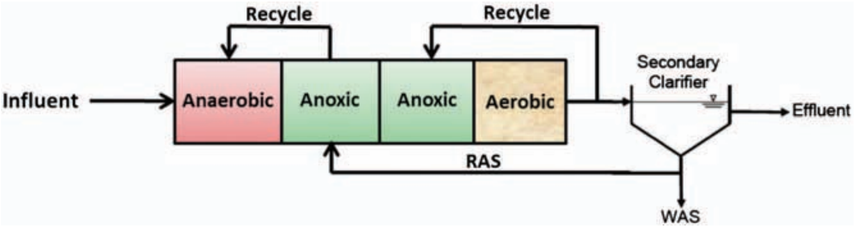

Figure 11.9. Schematic diagram of Modified UCT process

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upstream anoxic cell is reserved specifically for receiving and denitrifying the RAS. The second anoxic cell receives and denitrifies the mixed liquor from the aerobic zone. Primary treated influent is mixed with denitrified anoxic recycle from the second anoxic cell and is routed into the anaerobic zone, where multi-staged compartments are used to minimize nitrate recycling to the anaerobic zone. Flow from the anaerobic zone then enters the first and second anoxic cells, and onto the aerobic zone where nitrification occurs. The nitrified aerobic effluent is recycled back to the second cell anoxic zone for denitrification. This discharge of the aerobic recycle to the second cell of the anoxic zone limits the amount of nitrate returned to the first anaerobic cell, which improves nitrogen and phosphorus removal performance compared to the traditional UCT process.

The disadvantage of the UCT and MUCT processes is that the influent flows directly into the anaerobic zone, which can result in unstable conditions when high flow rate occur, or when the wastewater contains high levels of dissolved oxygen or low substrate levels.

11.8.3.5 Virginia Initiative Plant (VIP) Process

The VIP process was developed in the late-1980s for Hampton Roads Sanitation District, Hampton Roads, Virginia (Daigger et al. 1987). This process is said to be an improvement over the UCT Process because all zones consist of at least two completely mixed cells in series. The VIP process consists of anaerobic, anoxic, and aerobic zones, with the RAS mixed with the nitrified mixed liquor from the aerobic zone and is directed to the anoxic zone for denitrification, as illustrated in Figure 11.10. Denitrified mixed liquor from the end of the anoxic zone is recycled to the anaerobic zone to provide the microorganisms required in the anaerobic zone. The wastewater influent flows directly into the anaerobic zone, which provides a source of organic substrate to the anaerobic zone. This process is designed as high-rate, and all zones consist of at least two cells in a series. A short SRT is used to maximize phosphorus removal.

The disadvantage of the VIP process is the same as the UCT and MUCT processes, in that the influent flows directly into the anaerobic zone, which can result in unstable conditions when high flow rates occur, or when the wastewater

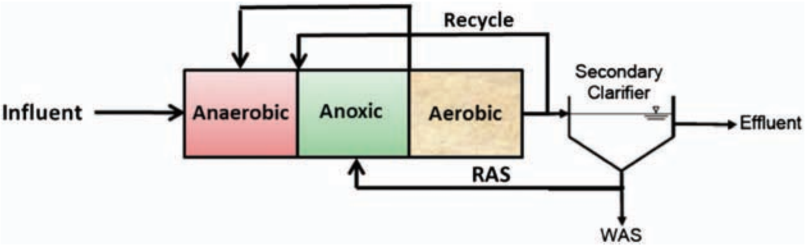

Figure 11.10. Schematic diagram of Virginia Initiative Plant (VIP) process

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contains high levels of dissolved oxygen or low substrate levels. A four-month bench-scale study was conducted to assess the nitrogen and phosphorus removal efficiencies of the VIP process. This study was performed because the VIP process was thought to be ideal for wastewater facilities in Florida that reuse treated effluent by land irrigation. The results indicated that the VIP process was successful in meeting the effluent limits for wastewater reuse applications but was unsuccessful in meeting more stringent limits set for wastewater treatment facilities that discharge into surface waters.

11.8.3.6 The Orange Water and Sewer Authority (OWASA) Process

The OWASA process was developed in the late-1980s for phosphorus removal at the Mason Farm WWTP for the Orange Water and Sewer Authority, Chapel Hill, North Carolina. This process consists of anaerobic, anoxic, and aerobic zones. The anaerobic zone is provided in a sidestream reactor, as illustrated in Figure 11.11. The primary settled wastewater flows to the aerobic zone where BOD is reduced and ammonia is converted to nitrate or nitrite, then to the anoxic zone for denitrification, and finally to another aerobic zone for stripping of the nitrogen gas generated by denitrification. RAS, to provide the microorganisms, and a substrate source are combined in the anaerobic zone.

Primary sludge fermentation has been shown to be a good source of VFAs and has been used to enhance a number of BNR processes. A portion of the raw wastewater is routed through the sludge fermenter. The fermented sludge is combined with the RAS in the anaerobic zone to facilitate phosphorus release. Phosphorus uptake occurs in the aerobic zone, and concentrations in the aerobic effluent are typically less than 1.0 mg/L (Kalb 1993).

Since the OWASA process was developed for phosphorus removal, it is not optimized for nitrogen removal. There is no mechanism to use carbon substrate in the influent to enhance denitrification in the anoxic zone. Therefore, a supplemental substrate must be added to the anoxic zone to ensure low total nitrogen in the secondary effluent. The fermented sludge that provides the VFA source to the anaerobic zone can also be fed to the anoxic zone to enhance denitrification. Poor denitrification can also impact phosphorus removal by allowing excess nitrate in the RAS to enter the anaerobic zone. If the organic content is high in the presence of nitrate, the denitrifying organisms will oxidize the VFAs, making them

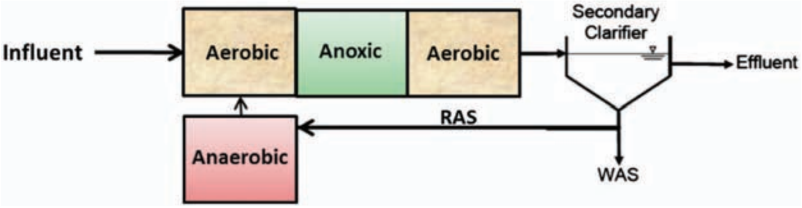

Figure 11.11. Schematic diagram of the OWASA Process

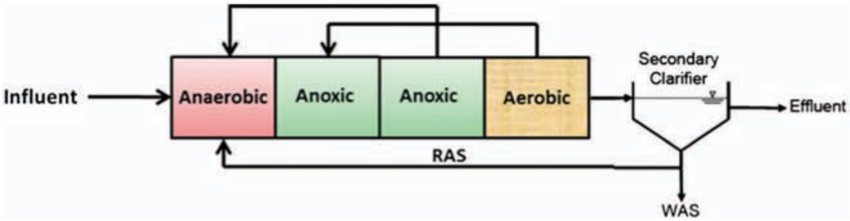

Figure 11.12. Schematic diagram of the CNC Process

unavailable for uptake by PAOs. The result is reduced phosphorus release and reduced overall phosphorus removal efficiency.

11.8.3.7 Charlotte, North Carolina (CNC) Process

The CNC process was developed by Hawkins et al. (1996) at the Mallard Creek WWTP, Charlotte, North Carolina, for Charlotte-Mecklenburg Utilities. The process was developed to overcome some of the problems encountered in the three zones of the current design of BNR processes used for phosphorus and nitrogen removal. Like the OWASA process, anaerobic, anoxic, and aerobic zones are used, with the anaerobic zone as a sidestream reactor, as illustrated in Figure 11.12. The primary clarifier effluent flows into the anoxic zone, which is used for denitrification and reduction of BOD. Flow proceeds to the aerobic zone, where BOD and ammonia are oxidized, and phosphorus uptake occurs. RAS and mixed liquor recycle streams are directed to the anoxic zone to enhance BOD reduction and denitrification. The two recycle streams are independent and can be varied to optimize the treatment. This part of the process is similar to the MLE process. It also incorporates improvements to the anoxic zone similar to those used in the VIP and MUCT processes, where a multiple cell anoxic zone is used to minimize nitrate recycling to the anaerobic zone. Denitrified mixed liquor from the anoxic zone is recycled to the anaerobic zone and combined with a supplemental substrate, such as acetic acid.

The detention time in the aerobic zone is dictated by the time required to oxidize ammonia to nitrate, and a 6-day SRT is typical. The resulting HRT varies between 4-10 hours to achieve a low soluble BOD concentration. The detention time in the anoxic zone is adjusted according to the nitrate concentration recycled to the anoxic zone and the desired effluent nitrate concentration. The detention time in the anaerobic zone is typically between 0.5-1.5 hours, and it is used as a microbial selector to optimize phosphorus uptake in the aerobic zone.

All these BNR processes are popular due to lower sludge production, the fertilizer value of the bio-P sludge and the use of wastewater components as process chemicals. These processes are specifically designed as per the treatment need. Hence, as compared to other treatments, one particular treatment may have its own limitations. The advantages and limitations of each process are depicted in Table 11.3.

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Table 11.3. Comparison of Biological nutrient removal systems

	Advantages	*Disadvantages*
Anaerobic/anoxic/oxic process	• Provides alkalinity for nitrification; • Removes both nitrogen and phosphorus; • Operation is relatively simple; • Produces good settling sludge, • Saves energy	• Needs higher BOD/P ratio; • Nitrogen removal is limited by internal recycle ratio; • RAS containing nitrate is recycled to anaerobic zone, thus affecting phosphorus-removal capability
Modified 5-stage Bardenpho process	• Produces good settling sludge; • Can achieve 3 to 5 mg/L TN in unfiltered effluent	• Requires larger tank volumes; • Less efficient phosphorus removal
UCT	• Produces good settling sludge; • Good nitrogen removal; • For weaker wastewater, process can achieve improved phosphorus removal; • Nitrate loading on anaerobic zone is reduced, thus increasing phosphorus removal capability	Requires additional recycling system; More complex operation
MUCT	• Moderate reactor volume; • Alkalinity recovery; • Good phosphorus removal; • Good nitrogen removal; • Good solids settleability; • Multiple anoxic cells to improve performance; • Reduced oxygen requirement; • Simple control	• An additional mixed liquor recycling step is required; • High level of nitrogen removal not generally possible

(Continued)

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Table 11.3. Comparison of Biological nutrient removal systems (Continued)

	Advantages	*Disadvantages*
VIP	• Produces good settling sludge; • Requires lower BOD/P ratio than UCT; • Nitrate loading in anaerobic zone is reduced, thus increasing phosphorus removal capability	• More equipment required for staged operation; • Requires additional recycling system; • More complex operation
OWASA	• Sidestream anaerobic zone; • Good phosphorus removal	• Phosphorus removal adversely impacted if nitrification occurs; • Not configured to optimize nitrogen removal
CNC	• Multiple anoxic cells to improve performance; • Sidestream anaerobic zone; • Good nitrogen removal; • Good phosphorus removal	• External VFA source is required; • An additional mixed liquor recycling step is required

11.9 ON-SITE TREATMENT SYSTEM SELECTION

The key to selecting, sizing, and installing the system is to identify the desired level of performance and ensuring that the effluent quality at the performance boundaries meets the expected performance requirements. To install a properly-sized and effective system, a thorough site evaluation is important. This should require a number of tasks such as digging test pits and testing the soil. The scale of the system depends on the population size, and the largest possible size of the residence will be assumed. It can also be estimated by the number of rooms in the home at final completion (i.e. after the basement is finished). Sometimes high flushing rates can cause backflow which leads to system failure by backing up of sewage in the home, and further contamination problems need to be faced.

The actual size of the system is also dependent on the local site conditions. For example, a field located in a silt loam requires a much greater area than one based on a sand area. Practices in water conservation will not save the money on the installation of the system; however, less water coming into the system will increase the life span of the system with improved treatment. Furthermore, it decreases the chance of groundwater contamination and sewage backflow. On the other side, if the fixtures like multiple head showers or jet tubs are installed, consumption of water will be large that can intensely increase the water volume entering a system over a short period of time. This can create problems with the system, as the material is flushed from the system to the field. If these types of fixtures are preferred, additional capacity in the septic tank and field should be added.

A suitable onsite wastewater treatment system concept for a given receiver site-proposed location of the system, down gradient soils used for treatment and regional geohydrologic features depends on the prevailing design conditions. Design conditions must be considered and evaluated carefully before selecting a system concept. It includes the characteristics of the wastewater to be treated, regulatory requirements, and the characteristics of the receiver site. The designer can develop an effective preliminary design concept, if sufficient knowledge of these factors is provided. Wastewater source characterization comprises wastewater composition, projections of wastewater flow, and owner requirements. The physical characteristics of the site which (including the regional geologic and hydrologic features, location of the proposed system and the soils to be used in the treatment process) decide the performance and treatment needs. To assess the capacity of the site to treat and assimilate effluent discharges, a careful and thorough site evaluation is essential. It must be sufficiently thorough to identify all possible design boundaries that might affect system design. Usually, the critical design boundaries are obvious for surface water discharging and evaporation systems. Design boundaries for subsurface wastewater infiltration system, however, are more difficult to identify because they occur in the soil profile, and there might be more than one critical design boundary.

The soil is the medium for a biological, physical, and chemical treatment of the wastewater; in addition, it acts as a porous filter medium from which the

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wastewater percolates to the groundwater in the receiving environment. Therefore, during the site evaluation, the capacity of the soil to hydraulically accept and treat the expected daily mass loadings of wastewater should be monitored. Site and soil properties must deliver adequate drainage of the saturated zone to sustain the essential unsaturated depth below the infiltrative surface; allow oxygenation of aerobic biota in the biomat and reaeration of the subsoil; and prevent effluent surfacing at down gradient locations. Hydraulic loading rates to this boundary are usually estimated from percolation tests and/or soil profile analyses. The recommended daily hydraulic loading rates typically assume septic tank effluent is to be applied to the soil. Evaluation of the wastewater receiver site is a critical step in system selection and design. The objective of the evaluation is to determine the capacity of the site to accept, disperse, and safely and effectively assimilate the wastewater discharge.

11.10 CASE STUDY

A case study of North Cary Water Reclamation Facility, North Cary, North Carolina was chosen as an example of nutrient removal technology, as the facility at this plant includes both nitrogen and phosphorous removal technologies.

11.10.1 Introduction and Permit Limits

The North Cary, North Carolina, Water Reclamation Facility (WRF) is a 50 million L per day (MLD) facility that included biological nutrient removal (BNR) as part of a 1997 expansion. This facility, which was a replacement/expansion of the 16-MLD Schreiber process on the same site, was selected as a case study because of its phased isolation ditch (PID) technology with tertiary filters.

The North Cary facility is unique in that it provides reliable nutrient removal by means of a PID process followed by tertiary filters. This entire biological process could remove phosphorus with a mean concentration of 0.38 mg/L with a COV of 64% and nitrogen removal with a mean of 3.67 mg/L with an extremely low COV of 14%. The process is flexible enough to control fluctuating flow conditions and the wastewater characteristics through the year, including the severe rain caused by Tropical Storm Alberto in June 2006. Automatic controls installed into the system provide much reliable control and operation through these operating stages. The wastewater characteristics are favorable for both nitrogen and phosphorus removal, and PID process does not require any external carbon sources as a supplement with this.

The WRF is not provided with primary settling and uses the PID technology or the BioDenipho process by Kruger. The process system uses two pairs of oxidation ditches following anaerobic selectors and finally a second anoxic zone. Each pair of ditches is operated in an aerobic/anoxic sequencing mode or phases. The effluent from the ditches goes to two clarifiers (diameter-40 m). Before discharge to Crabtree Creek, effluent is passed through an upflow Dynasand filter

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and ultraviolet disinfection unit, and aeration is also provided. The original Schreiber tank was converted into a 28 million L equalization basin in addition to a 15 million L equalization basin at the headworks area, and the stored water is drained by gravity to the influent pump station for subsequent treatment. Sludge derived after waste treatment is thickened and aerobically digested before it is transported to the South Cary WRF for dewatering and drying for final disposal. The relevant permit limits that the North Carolina Department of Environment and Natural Resources (NCDENR) established for the plant are shown in Table 11.4. Compliance limits are primarily for the monthly averages shown for carbonaceous biochemical oxygen demand (CBOD), total suspended solids (TSS), and ammonia nitrogen. Additional limits are specified for the quarterly limit for total phosphorus (TP) and for the annual maximum limit of 144,000 lb for total nitrogen (TN), which is equivalent to 3.94 milligrams per liter (mg/L) as nitrogen.

The alternating aerobic and anoxic flow pattern and process conditions occurring within the oxidation ditches is a distinguishing feature of the Bio-Denipho process. This working strategy permits nitrogen and CBOD elimination to occur within the active process volume, eliminating the need for internal recycle pumping. The operation of the mechanical process equipment and controlling the phase lengths within each ditch is coordinated by a programmable logic controller (PLC)-based system. The PLC system allows both manual and automatic control of the treatment process and also includes preprogrammed operational modes, such as the stormwater mode to address infiltration/inflow (I/I) concerns. For example, manual or automatic activation of the stormwater mode incorporates a sedimentation phase into the BioDenipho process to avoid washout of solids during severe rain events. This innovation allows reduction of the required size of the secondary clarifiers or eliminates the requirement for redundant clarifiers.

Table 11.4. NCDENR permit limits

Parameter	*Summer limits (mg/L)*	*Winter limits (mg/L)*	*Quarterly limits (mg/L)*	*Annual limits*
CBOD	4.1	8.2	—	—
TSS	30	30	—	—
NH_3-N	0.5	1.0	—	
TN	—	—	—	144,000 lb (max)[a]
TP	—	—	2.0	—
Coliforms	—	—	200[b]/100 mL	—

Notes: NH_3-N = ammonia nitrogen

[a] Equivalent to 3.94 mg/L as TN for 48 MLD

[b] Unit: Colony forming units

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Table 11.5. Facility design data

Units	*Number*	*Volume*
Anaerobic selectors	4 each train	0.372 ML × 4 = 1.488 ML
Oxidation ditch	2 each train	6 ML × 2 = 12 ML
Secondary anoxic zone	3 each train	0.444 ML × 3 = 1.332 ML
Reaeration zone	1 each train	0.444 ML
Clarifiers	2 each	130 ft diameter

Note: ML = million liters

11.10.2 Plant Design and Process Parameters

To ensure economical and efficient treatment, the system is also equipped with automatic dissolved oxygen (DO) control to control the aeration equipment, in which the DO probes regularly monitor and report residual DO levels within the oxidation ditches to the PLC panel that controls the aeration equipment to meet the current oxygen demand without exceeding it. This eliminates costly and wasteful over-aeration that can compromise process stability and operational budgets. Table 11.5 present relevant design data for the facility and Table 11.6 presents operational results for the October 2005 to September 2006 period. Table 11.7 presents plant monthly average plant process parameters. The sludge residence time (SRT) for an oxidation ditch was 12 days at 12°C.

11.10.3 Plant Performance

During the period of October 2005 through September 2006, overall ammoniacal nitrogen oxidation was complete, with a mean of 0.06 mg/L and a 31% coefficient of variation (COV) for non-tropical storm months. Even during June 2006 when the plant's service area was subjected to nearly 8 inches of rain in a 24-hour period from Tropical Storm Alberto, the plant still managed to meet the monthly limit of 0.5 mg/L for ammoniacal nitrogen.

Phosphorus removal was completely by biological means and worked well, with a monthly mean of 0.38 mg/L and a COV of 64%. This removal was sufficient to meet the facility's quarterly limit of 2 mg/L. The total nitrogen (TN) removal was also excellent, with the effluent mean 3.7 mg/L with a COV of 14% on a monthly average basis, including the period with heavy precipitation caused by the tropical storm.

11.10.4 Reliability Factors

The North Cary plant performance was effective and reliable for entirely biological phosphorus and nitrogen removal. The COVs were 102% for ammoniacal nitrogen at the mean concentration of 0.08 mg/L, 64% for total phosphorus at the mean concentration of 0.38 mg/L, and 14% for total nitrogen at the mean

Table 11.6. Influent and effluent averages

	Parameter (mg/L)	Avg.	Max. month	Max. vs. Avg.	Max. week	Samplemethod/ frequency
	Flow (MGD)	7.0	8.71	24%	10.8	–
Influent	TP	7.7	9.2	20%	11.1	Composite, 3x/week
	BOD	244	271	11%	296	Composite, 5x/week
	TSS	366	418	14%	594	Composite, 5x/week
	NH_4-N	45.5	49. 4	8%	53.5	Composite, 5x/week
	TKN	56.4	62.2	10%	65.6	Composite, 3x/week
Effluent	TP	0.38	1.06	180%	1.45	Composite, 3x/week
	BOD	0.8	1.26	50%	1.84	Composite, 5x/week
	TSS	1.0	1.47	45%	2.28	Composite, 5x/week
	NH_4-N	0.08	0.34	316%	1.03	Composite, 5x/week
	TN	3.67	4.46	21%	5.87	Composite, 3x/week

Note: Max. = Maximum; Avg. = Average; TKN = Total Kjeldahl nitrogen; BOD = Biochemical oxygen demand

concentration of 3.67 mg/L. The following points summarize the factors affecting the reliability of the North Cary WRF:

- The BioDenipho process operated at North Cary is a flexible process with regard to varying flow rate and strength of wastewater. The reliability is achieved through well-controlled oxidation of ammonia and subsequent denitrification in two distinct anoxic steps. The anoxic cycle phase in the ditch can be adjusted from 60 to 90 minutes, for example, during a low-flow period, and can be reversed during a high-flow period. The rotors can maintain the DO concentration from 1 to 1.5 mg/L in the ditch, while mixers keep the organisms in suspension during the anoxic phase. This flexibility to control mixing separately from aeration is one of the keys to this plant's reliability. The low DO in the ditch effluent ensures decent denitrification in the second anoxic step to achieve the desired nitrogen level in effluent and furthermore, no external carbon source is needed to meet the permit limit.

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Table 11.7. Monthly averages for plant process parameters

Month	*MLSS (mg/L)*	*Sludge age (days)*	*HRT (hours)*	*Temperature (°C)*
Jan 2005	2,665	13.1	28	23
Feb 2005	2,628	13.8	29	20
Mar 2005	2,736	13.0	26	19
Apr 2005	2,672	13.3	27	18
May 2005	2,720	12.8	27	16
Jun 2005	2,692	13.3	29	18
Jul 2005	2,661	12.6	27	19
Aug 2005	2,625	13.5	28	21
Sept 2005	2,700	11.3	21	24
Oct 2005	2,713	12.3	25	26
Nov 2005	2,709	12.6	25	27
Dec 2005	2,685	12.1	24	26

Notes: HRT = hydraulic retention time; MLSS = mixed liquor suspended solids

- An automated control system is another key reliability factor, consisting of sensors and DOES controllers operating with the PLC and associated supervisory control and data acquisition (SCADA) system. Based on the preset control logic, the exact phasing decision is made which is site-specific and fully automated. These online monitoring and automatic controls also make training easy but require continuous maintenance by the plant personnel.
- A key reliability factor for phosphorus removal by biological means is the feed point of the influent. The influent is fed to the second anaerobic selector and return activated sludge is fed to the first selector ensuring that the returning nitrate from the clarifier will be denitrified in the first selector zone. Therefore, second to fourth selector zones become anaerobic and allow full energy exchange for polyphosphate accumulating organisms (PAOs). The wastewater exhibited a favorable ratio of BOD to TP, greater than 30 as an average, proving the reliable plant performance through this process (WEF 1998).
- A key reliability factor for nitrogen removal is the three phases of anoxic cycles. The first is in the anaerobic selector before the ditch, the second is following the ditch, followed by the third in the anoxic zone after the ditch. These multiple opportunities to denitrify in the presence of BOD in the wastewater are unique and enable good nitrogen removal. The wastewater exhibited a favorable BOD/TKN ratio of 5 as an average, which is adequate for good denitrification (U.S. EPA 1993).
- The reason behind the less power consumption is the maximum use of nitrate during the anoxic phase and the prevention of over-aeration during the oxic phase. Pumping of oxidized effluent to 3 to 4 times the discharge (Q) is not required to reach the same level of denitrification.

- Tertiary filters used are pretty much effective in suspended solids removal.
- Recycle loads are minimized; aerobic digestion occurs onsite, and the digested sludge is shipped away for processing at another facility.
- Wet-weather flows are handled in two ways: The equalization basins have a total of 9 MG storage that is equal to 75% of the influent design flow; the PID has a storm mode in the process control, which switches to a sedimentation phase which prevents the solids washout. These kind of facility assisted to manage high flows during the June 2006 Tropical Storm Alberto that brought high flows to the plant. All the storage volume was used, and the PID went into the storm mode for a short duration but all flows and complied with the permit.

11.11 SUMMARY

Onsite wastewater treatment systems provide alternative options to centralized treatment system, if these federal systems are far away from the treatment site and when the sewage treatment facility is severely limited. The typical conventional onsite treatment systems like septic tank with distribution box, drainfield with leaching chambers can be applied, whereas more advanced systems such as aerobic treatment units, media filters and sequential batch reactors can be employed depending upon the demands. More specific biological nutrient removal technologies such as Modified Five-stage Bardenpho Process, UCT and modified UCT Process, Virginia Initiative Plant (VIP) Process, OWASA Process and Charlotte, North Carolina (CNC) Process can retrieve both nitrogen and phosphorous nutrients. These processes are affected by many environmental factors such as wastewater characteristics, cell residence time, aeration, food to microorganism ratio, pH etc., and during the processing these factors should be considered for effective nutrient removal. BNR processes are very difficult to control and operate than conventional activated sludge processes. On-line sensors and monitoring devices are important to continuously monitor variables such as DO, alkalinity, pH, ammonia, nitrate and phosphorus to control aerobic, anaerobic conditions, which is important to reduce the operational issues associated with nutrient removal.

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CHAPTER 12

Anammox: A Sustainable Technology for Nitrogen Removal and Water Recycling

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12.1 INTRODUCTION

Human activities such as fossil fuel combustion, extensive use of nitrogen fertilizers in agriculture, wastewater discharge from various industries and livestock farming etc. are altering the global nitrogen cycle and accelerating the nitrogen pollutant in the environment. Nitrogen (inorganic) pollution in aquatic ecosystems causes three major environmental problems, namely acidification of freshwater ecosystems, eutrophication of aquatic ecosystems and impairment of the ability of aquatic animals to survive, grow and reproduce (Camargo and Alonso 2006). Nitrogen compounds such as nitrite and nitrate also have adverse effects on human health. Methemoglobinemia, a conversion of haemoglobin to methemoglobin, is the most common direct effect on human, especially infants, due to ingested nitrates and nitrites from polluted drinking water (Camargo and Alonso 2006).

Due to the aforementioned reasons nitrogen removal from water and wastewater has become a worldwide emerging concern and therefore, stringent nutrient discharge regulations have been implemented in most of the countries to regulate the wastewater treatment plant effluent and its possible re-usability.

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For example, in Taiwan the maximum discharge limit of ammonia nitrogen for new industries has been set at 20 mg/L. For existing industries, the maximum ammonia nitrogen discharge limit is 75 mg/L (for the first stage), which has been implemented from 1 July 2013. For the second stage, this limit would be reduced to 30 mg/L from 1 January 2017 (EPA Taiwan 2013).

Nitrogen from water and wastewater can be removed by physical (air stripping), chemical (ion-exchange and breakpoint chlorination) and biological (nitrification-denitrification) methods (O'Farrell et al. 1972; Pressley et al. 1972; Zhu et al. 2008). Biological approaches are considered to be the most efficient and economical for removing nitrogen compounds from wastewater (Zhu et al. 2008). In general, nitrogen removal from wastewater is accomplished by conventional biological nitrogen removal method i.e. nitrification followed by denitrification process, where ammonium nitrogen (NH_4^+-N) is biologically transformed to a series of nitrogen intermediates before being converted to the nitrogen gas ($NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$). Anaerobic ammonium oxidation (Anammox) is a recently identified short-cut method to convert ammonium nitrogen to nitrogen gas using nitrite as an electron acceptor. The anammox process seems to be more promising than nitrification-denitrification in terms of its efficiency, low-cost and eco-friendly nature. Anammox reaction is carried out by a specialized group of lithoautotrophic microorganisms belong to the bacterial phylum *Planctomycetes.* In this Chapter, developments in the anammox process since its discovery are discussed, including identification of responsible microbes and their physiology, potential process inhibitors, reactor types used and application to treat different wastewater.

12.2 HISTORY OF ANAMMOX

In the context of this chapter, nitrification, denitrification and anammox are the three main processes of the nitrogen cycle, which have been applied to remove nitrogen from different wastewaters. Denitrification and nitrification processes were discovered in 1882 and 1890, respectively (Strous and Jetten 2004). The nitrogen cycle was generally believed to be completed after the discoveries of nitrification (aerobic oxidation of NH_4^+ to NO_2^- followed by oxidation of NO_2^- to NO_3^-) and denitrification (reduction of NO_3^- to N_2 gas). However, there were few reports suggesting the possibilities of ammonium oxidation under anaerobic condition.

The first assumption about the oxidation of ammonium under anaerobic conditions in the ocean was made in 1941 (Hamm and Thompson 1941). In 1965, Richards observed the disappearance of ammonia under anoxic conditions and proposed the possibilities of ammonia oxidation with nitrate. Later, Broda (1977) also suggested that oxidation of ammonia using either nitrite or nitrate as electron acceptor is possible based on thermodynamic calculations. Broda (1977) predicted that two kinds of lithotrophs were missing in nature, which could oxidize

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ammonia using either nitrite or nitrate as the electron acceptor. However, it took another two decades to experimentally confirm the predictions of Broda (1977). In 1995, the first evidence of anaerobic ammonia oxidation in a denitrifying pilot plant at Gist-Brocades (the Netherlands) treating wastewater from a yeast factory was reported by Mulder et al. (1995). Arnold Mulder gave the term "Anammox" for this unique and potential ammonia oxidation process (Kuenen 2008). In the same year, Van de Graaf et al. (1995) designed tracer experiments using $^{15}NH_4^+$ and $^{14}NO_2^-$ as tracers in fluidized bed reactor (FBR) to demonstrate the utilization of nitrite as the electron acceptor. They found the end product of the reaction was nitrogen gas composed by $^{14-15}N_2$. This confirmed that two nitrogen atoms came from $^{15}NH_4^+$ and $^{14}NO_2^-$ and anammox bacteria use nitrite as electron acceptor not nitrate. Based on the amazing discovery of anammox bacteria, the nitrogen cycle is revised as shown in Figure 12.1.

Since the discovery of anammox bacteria, many researchers have studied the process and bacterial species involved in anammox. Now, cell constitution, physiology and reaction mechanism of anammox bacteria are well known. So far, five Anammox genera (Kuenenia, Brocadia, Anammoxoglobus, Jettenia and Scalindua) and eleven anammox species (Table 12.1) have been isolated and identified in the bacterial order 'Brocadiales' of the phylum Planctomycetes (Kartal et al. 2012).

However, these anammox species are not available as a pure culture and therefore, they all have given *Candidatus* (*Ca.*) status i.e well characterized but uncultivable as a pure species. These species have been found and enriched from wastewater treatment systems, marine environments, and fresh water. The anammox bacteria *Ca.* Brocadia caroliniensis (the 10th anammox species) was isolated from sludges of nitrification-denitrification systems treating liquid swine manure, and this anammox species was deposited in the Agricultural Research Service Culture Collection (NRRL) at Peoria, Illinois, USA, with accession number NRRL B-50286 (Vanotti et al. 2011; Magri et al. 2012). Recently, a new marine

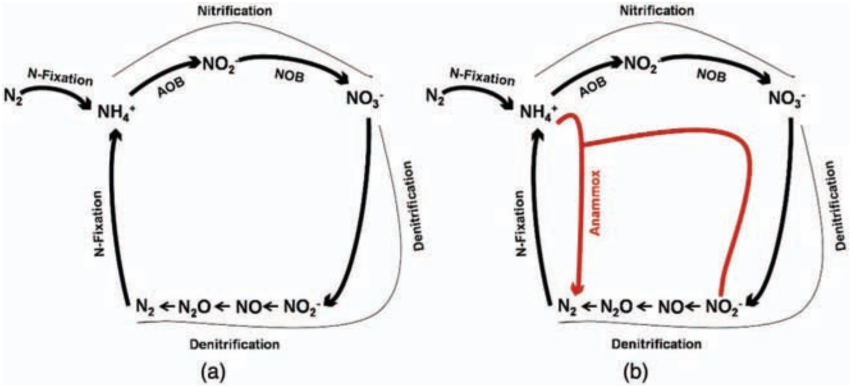

Figure 12.1. Simplified form of nitrogen cycle: (a) before and (b) after the discovery of anammox process

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Table 12.1. Anammox bacterial species identified so far from the order of 'Brocadiales'

Genus	*Species*	*References*
Kuenenia	*Ca.* K. stuttgartiensis	Strous et al. (2006)
Brocadia	*Ca.* B. anammoxidans	Strous et al.(1999a)
Brocadia	*Ca.* B. fulgida	Kartal et al. (2008)
Brocadia	*Ca.* B. Sinica	Oshiki et al. (2011)
Brocadia	*Ca.* B. caroliniensis	Vanotti et al. (2011)
Anammoxoglobus	*Ca.* A. propionicus	Kartal et al. (2007)
Jettenia	*Ca.* J. asiatica	Quan et al. (2008)
Scalindua	*Ca.* S. brodae	Schmid et al. (2003)
Scalindua	*Ca.* S. wagneri	Schmid et al. (2003)
Scalindua	*Ca.* S. Sorokinii	Woebken et al. (2008)
Scalindua	*Ca.* S. profunda	Van de Vossenberg et al. (2013)

anammox bacterium (the 11th anammox species), tentatively named "*Ca.* Scalindua profunda" has been identified (Van de Vossenberg et al. 2013). Interestingly, only about 50% of the metagenome assembly of *Ca.* Scalindua profunda could be matched to the metagenome assembly of K. Stuttgartiensis (Van de Vossenberg et al. 2013).

The well accepted and known stoichiometry of the anammox process is shown in Eq. 12.1 (Kuenen 2008). Many important conclusions can be drawn from the stoichiometry Eq. 12.1. For example, anammox bacteria use inorganic carbon (carbon dioxide) under anaerobic conditions to produce cell biomass ($CH_2O_{0.5}N_{0.15}$). In this case, biomass yield is very low; nitrite serves dual functions in the anammox process: an electron acceptor to oxidize ammonium and an electron donor to reduce bicarbonate (carbon dioxide), and complete conversion of nitrogen to nitrogen gas is not possible by the anammox process as part of nitrogen converted to nitrate.

$$NH_4^+ + 1.32\,NO_2^- + 0.66\,HCO_3^- + 0.13\,H^+ \longrightarrow 0.066\,CH_2\,O_{0.5}\,N_{0.15} + 1.02\,N_2 + 0.26\,NO_3^- + 2.03\,H_2O \qquad \text{(Eq. 12.1)}$$

The fact that many researchers have shown interests in the anammox process in the recent past can be evidenced by the number of papers published since the discovery of anammox bacteria (Figure 12.2) (Source: Web of Knowledge 2012). There are many reasons, which make this process more attractive. Some of them are listed below:

1. It is anaerobic process so no aeration cost and overall up to 60% power saving
2. No need of organic carbon source (reducing agent)

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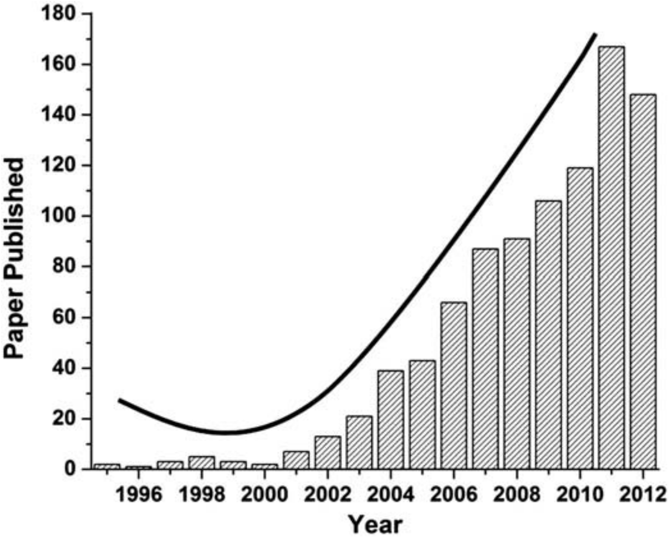

Figure 12.2. Number of research papers published each year since the discovery of anammox process

3. Less production of sludge saves sludge treatment cost
4. Less space required (up to 50%)
5. Eco-friendly (up to 90% reduction in CO_2 emission; theoretically no N_2O emission)

12.3 MICROBIAL PHYSIOLOGY AND REQUIREMENTS FOR GROWTH

12.3.1 Cell Structure and Mechanism

Microscopic examination of anammox bacteria revealed many unusual characteristics. They are coccoid bacteria and varied in cell size with an average diameter ranging between 800 and 1,100 nm (Van Niftrik et al. 2008a). Anammox bacteria from Anammoxoglobus genus (*Ca*. A. propionicus) have the largest cell size with an average cell diameter of 1,100 nm. The bacterial cells of the Scalindua genus (*Ca*. S. Brodae) have slightly larger cell size than Kuenenia and Brocadia genus. The average cell diameter of *Ca*. S. Brodae has been reported to be 950 nm. Anammox bacterial cells of the Kuenenia (*Ca*. K. stuttgartiensis) and Brocadia (*Ca*. B. fulgida) genus have the smallest cell size with an average cell diameter of 800 nm (Van Niftrik et al. 2008a).

The cell wall of anammox bacteria lacks peptidoglycan and has proteinaceous cell wall (Strous et al. 2006; Van Niftrik et al. 2008b). The cytoplasm of a cell is compartmentalized into three individual bilayer membranes. The outermost membrane is in direct contact with a thin cell wall and has been defined as

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cytoplasmic membrane. The second membrane defined as intracytoplasmic membrane. The third anammoxosome membrane surrounds an organelle or vacuole called anammoxosome (Lindsay et al. 2001; Strous et al. 2006; Van Niftrik et al. 2008b). The bilayer anammoxosome membrane is a predominantly curved configuration to increase the surface to volume ratio, which contributes to catabolic process (Van Niftrik et al. 2008b).

Paryphoplasm compartment, a unique feature of all planctomycete is a peripheral ribosome-free region of the cytoplasm. Paryphoplasm compartment is bounded and defined by the cytoplasmic membrane on its outer side and by intracytoplasmic membrane on its inner side. Riboplasm compartment is a cytoplasm containing DNA, ribosomes and glycogen granules. It is bounded by intracytoplasmic membrane on its outer side and by anammoxosome membrane on its inner side (Lindsay et al. 2001; Van Niftrik et al. 2008b).

The innermost compartment is anammoxosome, which is covered by anammoxosome membrane. Interestingly, the anammoxosome comprises 50–70% of the total cell volume and is believed to be the place where anaerobic oxidation of NH_4^+ to N_2 occurs (Jetten et al. 1998; Kuenen 2008). The anammoxosome compartment is enriched with ladderane lipids (or ladderanes), which are very tightly packed. This tightly packing of ladderanes makes it impermeable for non-polar compounds. The presence and packing of ladderanes is another unique feature as it is only found in anammox bacteria. Anammox bacterial cell is rich in heme protein (approximately 20% of cellular protein mass) and therefore, its culture is characteristically brown-red in color (Kartal et al. 2008). Figure 12.3

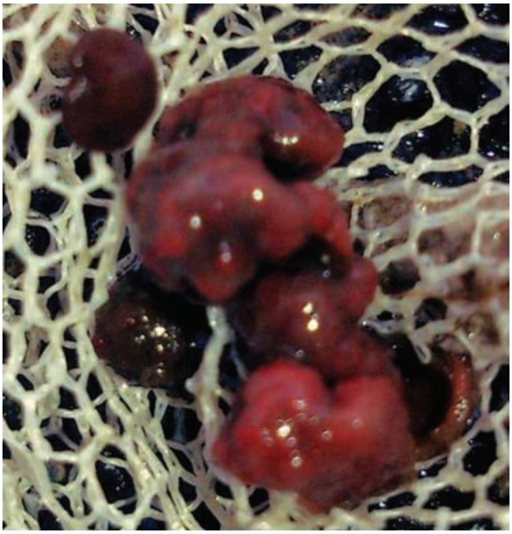

Figure 12.3. Picture of anammox granules collected from the wastewater treatment plant located in Taiwan

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shows the brown-red color anammox cell granules collected from a landfill leachate wastewater treatment plant in Taiwan.

The specific mechanism of anammox bacteria to oxidize ammonium nitrogen to nitrogen gas under anaerobic conditions is quite unique due to the following two reasons: (1) it is difficult to oxidize ammonium in the absence of molecular oxygen but carried out by anammox bacteria; and (2) two very toxic compounds i.e. hydrazine (N_2H_2) and hydroxylamine (NH_2OH) are intermediates of the anammox process (Kuenen 2008; Kartal et al. 2011). Initially, a three-step pathway based on in-vitro marker experiments was proposed by Van de Graaf et al. (1997).

This three-step pathway involved (1) a four-electron reduction of nitrite, followed by (2) the condensation of NH_2OH and ammonium to make N_2H_2, and finally (3) the oxidation of N_2H_2 to nitrogen gas. They suggested that NH_2OH was presumably derived from nitrite. In their experiments, N_2H_2 was not consumed by anammox bacteria until the complete utilization of NH_2OH. However, the intermediates i.e. N_2H_2 and NH_2OH of this pathway have not been demonstrated in anammox cells under physiological relevant conditions (Kartal et al. 2012).

Later, a complete genome assembly of *Ca*. K. Stuttgartiensis is identified and a three-step mechanism of anammox bacteria is re-explained (Strous et al. 2006; Kartal et al. 2011; Van Niftrik and Jetten 2012). In the first step, nitrite is reduced to nitric oxide (NO) by a specific nitrite reductase (NirS) enzyme present in anammox bacteria (Eq. 12.2). NO is identified as an essential intermediate in anammox metabolism. In the second step, NO and ammonium are combined by hydrazine synthase enzyme to form a highly reactive N_2H_2 intermediate (Eq. 12.3). In the final step, N_2H_2 is oxidized by hydrazine dehydrogenase (HDH) enzyme to nitrogen gas (Eq. 12.4) and provide four electrons for nitrite reduction (Eq. 12.2 and 12.3). Eq. (12.5) shows the overall equation for the anammox process.

$$NO_2^- + 2\,H^+ + e^- = NO + H_2O(E_0' = +0.38\ \text{V}) \qquad \text{(Eq. 12.2)}$$

$$NO + NH_4^+ + 2\,H^+ + 3e = N_2H_4 + H_2O(E_0' = +0.06\ \text{V}) \qquad \text{(Eq. 12.3)}$$

$$N_2H_4 = N_2 + 4H^+ + 4e(E_0' = -0.75\ \text{V}) \qquad \text{(Eq. 12.4)}$$

$$NH_4^+ + NO_2^- = N_2 + 2H_2O(\Delta G = -357\ \text{kJ mol}^{-1}) \qquad \text{(Eq. 12.5)}$$

12.3.2 Growth Conditions: Substrates, Temperature, pH

Similar to other microorganisms, anammox bacteria also have physical (such as temperature and pH) and chemical (such as substrates for carbon and nitrogen source) requirements for their growth and metabolism. Since, the growth rate of anammox bacteria is very low, it was difficult to cultivate in reactors in the early stage of anammox discovery. As microorganisms grow at faster rate under the specific environmental conditions, the growth physiology of anammox bacteria

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has been studied by various research groups (Strous et al. 1998, 1999b; Egli et al. 2001; Van der Star et al. 2008a, b; Oshiki et al. 2011; Awata et al. 2013). The specific growth rate of anammox bacteria is very low and varied from 0.002 to 0.0041 h^{-1}. The bacterial sp. *Ca.* B. sinica is the fastest growing anammox species compared to other anammox species as it has the lowest doubling time of 7 d than *Ca.* B. anammoxidans (11 d) and *Ca.* K. stuttgartiensis (8.3–11 d) (Oshiki et al. 2011). The biomass yield of anammox bacteria is very low (Eq. 12.1) due to their low growth rate. The biomass yield of *Ca.* B. anammoxidans is reported to be 0.07 mmol C/mmol N (Strous et al. 1999b).

Anammox bacteria are chemoautotrophic bacteria and use CO_2 as the main inorganic carbon source to oxidize ammonium to nitrogen gas using nitrite as the electron acceptor. Therefore, a sufficient amount of inorganic carbon is required to grow anammox bacteria and maintain anammox activity (Kimura et al. 2011a). Liao et al. (2008) studied the effect of bicarbonate on the anammox process in the sequencing batch reactor (SBR). They observed an increase in anammox activity as the influent bicarbonate concentration increased from 1.0 to 1.5 g/L. However, anammox activity inhibited at a higher bicarbonate concentration (2.0 g/L), probably due to the increased free ammonia (FA) concentration (Liao et al. 2008). Kimura et al. (2011a) used anammox sludge entrapped in a gel carrier and indicated that an influent inorganic carbon to NH_4^+-N ratio of 0.2 is ideal for the anammox process.

Ammonium and nitrite are the two substrates for anammox bacteria. Ideally the activities and growth of microorganism increase with increasing substrate concentrations. However, a very high concentration may cause substrate inhibition and inhibit the growth and activities of microorganism. Though, the toxicity of ammonium is not reported, the toxicity of nitrite is varied from 7–25 mM (Awata et al. 2013). Strous et al. (1999b) exposed the anammox biomass culture to concentrations up to 70 mM of ammonium in a SBR. During one week of observation, no negative effect of ammonium on the anammox activity was observed. Dapena-Mora et al. (2007) studied the ammonium inhibition in batch tests and found that IC_{50} value (concentration at which 50% inhibition occurs) of ammonium was 770 mg/L. However, later reports confirmed that FA and not the ionized form of ammonia is the real inhibitor for anammox bacteria (Tang et al. 2010a; Jaroszynski et al. 2011; Fernandez et al. 2012).

The detail of nitrite toxicity on anammox bacteria is discussed in 12.5.1. The affinity constants (K_s) for ammonium and nitrite of *Ca.* B. anammoxidans have been estimated to be <5 μM and <5 μM, respectively (Strous et al. 1999b). In case of *Ca.* K. Stuttgartiensis, the K_s values obtained were between 0.2–3 μM for nitrite (Van der Star et al. 2008a, b). On the other hand, K_s values for ammonium (28 ± 4 μM) and nitrite (86 ± 4 μM) reported for *Ca.* B. sinica were much higher than those of *Ca.* B. anammoxidans and *Ca.* K. Stuttgartiensis (Oshiki et al. 2011). Recently, K_s values of *Ca.* Scalindua sp. for ammonium and nitrite have been estimated. The K_s value of *Ca.* Scalindua sp. for nitrite was very low (0.45 μM), while K_s value for ammonium (3 μM) was comparable to those of *Ca.* B. anammoxidans and *Ca.* K. Stuttgartiensis (Awata et al. 2013). In a recent study,

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the K_s values of *Ca*. Brocadia sp. dominated granular and flocculent culture for ammonium were very high (0.64 ± 0.13 and 0.53 ± 0.05 mM, respectively) compared to those reported earlier (Puyol et al. 2013). The K_s values for nitrite were also very high (0.35 ± 0.09 and 0.37 ± 0.04 mM for granular and flocculent anammox culture dominated by *Ca*. Brocadia sp., respectively) in this study (Puyol et al. 2013).

Temperature is an important physical parameter for the growth of microorganisms and the optimum value varies from one species to another. The effect of temperature on the growth-rate of anammox bacteria can be expressed by the van't Hoff-Arrhenius equation as shown in Eq. 12.6, which suggests that the growth-rate of bacteria increases with temperature (Tchobanoglous and Burton 1991).

$$\mu = \mu_{20} \times \theta^{T-20} \qquad \text{(Eq. 12.6)}$$

where, μ is the growth rate coefficient (d^{-1}); μ_{20} is the value of μ at 20°C(d^{-1}); θ is the dimensionless temperature coefficient; and T is temperature (°C).

The optimum temperature range for the growth of anammox bacteria is reported to be between 30 and 40°C (Strous et al. 1999b; Egli et al. 2001). In case of *Ca*. B. anammoxidans and *Ca*. K. Stuttgartiensis, the optimum temperatures are 40 and 37°C, respectively (Strous et al. 1999b). However, lower and higher temperature can inhibit the activity of anammox bacteria. At higher temperature (above 45°C) anammox bacteria can lose its activity due to biomass lysis (Dosta et al. 2008). At lower temperature (below 15°C), the activities of metabolic enzymes of anammox bacteria reduce, which causes nitrite accumulation and inhibition (Dosta et al. 2008). The sludge, which had two anammox species i.e. *Ca*. K. Stuttgartiensis and *Ca*. B. anammoxidans, taken from a lab scale SBR treating optoelectronic wastewater was evaluated for its specific anammox activity (SAA) at two different temperatures (Daverey et al. 2013a). The SAA was found to be higher at 33.5°C (0.153 g N/g VSS/d) than 25°C (0.132 g N/g VSS/d), though the nitrogen conversion rate was not affected (Daverey et al. 2013a). However, much greater effects on the nitrogen conversion rate were observed at temperatures lower than 25°C. In an anaerobic filtrated reactor, the nitrogen conversion rate was decreased from 11.5 kg-N/m^3/d at 37 °C to 8.1 kg-N/m^3/d at 20–22 °C (Isaka et al. 2007). The effect was more severe in a SBR, where more than 50% decrease in nitrogen conversion rate was observed when the temperature changed from 30 °C to 20 °C (Vazquez-Padin et al. 2009). In a cylindrical continuous reactor, Isaka et al. (2008) studied the effect of temperature on the nitrogen conversion efficiency of anammox bacteria entrapped in a gel carrier. They observed a decrease in nitrogen conversion rate from 6.2 kg-N/m^3/d at 32°C to 2.8 and 0.36 kg-N/m^3/d at 22 and 6.3 °C, respectively. In an up-flow anaerobic sludge blanket (UASB) treating low strength wastewater, the nitrogen removal rate (NRR) of anammox bacteria was decreased to about 60% when temperature decreased from 30°C to 16°C. Interestingly, no major change in the abundance of anammox bacteria was observed by PCR assay (Ma et al. 2013). In view of overall energy saving, it is

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important to study in detail about the cultivation and higher nitrogen conversion efficiency of anammox bacteria at lower temperatures.

The pH is a critical parameter, which affects the growth and metabolic activities of anammox bacteria. The pH plays an important role in the anammox process as the concentrations of potential anammox inhibitors i.e. FA and free nitrous acid (FNA) depend on pH. Moreover, an increase of the pH in the anammox reactor may occur as hydrogen ions are consumed in the anammox process (Eq. 12.1). Therefore, it is important to know the optimum pH for a stable operation of the anammox process. The anammox bacteria can grow at pH between 6 and 9 (Awata et al. 2013) while the physiological pH range of *Ca.* B. anammoxidans is between 6.7 and 8.3 (Strous et al. 1999b). However, a slightly wider physiological pH range (6.5 and 9) of *Ca.* K. stuttgartiensis with an optimum pH of 8 was observed by Egli et al. (2001).

12.4 INTEGRATION OF ANAMMOX PROCESS WITH OTHER NITROGEN REMOVAL PROCESSES

As discussed in section 12.3.2., anammox bacteria require nitrite as an electron acceptor to carry out the required reaction (Eq. 12.1). In general, nitrite is not present in real wastewater. For example, Table 12.2 shows the characteristics of different wastewaters and it is quite evident that electron acceptor (nitrite) for anammox reaction is absent in these wastewaters. The spiking of nitrite to remove ammonium nitrogen from these wastewaters by the anammox process is not an economical option. The absence of nitrite in wastewater limits the direct application of the anammox process. Therefore, the anammox process needs to be

Table 12.2. Nature of different wastewaters

Parameter[1]	*ADLSW*[2]	*SASD*[3]	*Leachate*[4]	*OEW*[5]	*OEW*[6]	*MSGIW*[7]	*DW*[8]
COD	387	—	554	100	13.5	2250	225
TKN	662	—	—	572	3799	—	—
NH_4^+-N	519	619	634	567	3712	1750	56.3
NO_2^--N	<1	4.7	—	—	—	—	0.32
NO_3^--N	3.5	0.2	3	7	—	—	1.23
PO_4^{3-}-P	30	0.6	4	0.7	—	—	—
pH	7.4	7.37	7.9	9.4	9.7	6.0	—

[1]all units are in mg/L, except pH; [2]Anaerobic digester liquor of swine wastewater (Daverey et al. 2013b); [3]Supernatant of activated sludge digestion (Fux et al. 2002); [4]Landfill Leachate (Wang et al. 2010); [5]Optoelectronic industrial wastewater (Daverey et al. 2012); [6]Optoelectronic industrial wastewater (Daverey et al. 2013a); [7]Mono sodium glutamate industrial wastewater (Shen et al. 2012); [8]Domestic wastewater (Gu et al. 2012)

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combined with other processes such partial nitrification for its practical application.

12.4.1 SHARON-Anammox or Two-Staged Partial Nitrification-Anammox Process

SHARON (an acronym for Single reactor High activity Ammonia Removal Over Nitrite) process was developed at Delft University of Technology for ammonia removal from high strength wastewater (Hellinga et al. 1998). The purpose of SHARON process development was to reduce requirements for oxygen and external carbon in conventional nitrification-denitrification process. This can be explained by the stoichiometry equations (Eq. 12.7–12.10) of nitrification and denitrification.

Eq. 12.7 shows nitrification (nitritation + nitratation) reaction, which requires two moles of oxygen to oxidized one mole of ammonium. In SHARON process, only nitritation reaction [carried out by aerobic ammonium-oxidizing bacteria (AOB)] occurs while nitratation [carried out by aerobic nitrite oxidizers (NOB)] is inhibited by selective washout of NOB by controlling dissolved oxygen (DO), pH and temperature of the reactor. Nitritation reaction (partial nitrification) requires 1.5 mole of oxygen to oxidize one mole of ammonia into nitrite (Eq. 12.8). This can save 25% of oxygen requirement in the nitrification step. Eq. 12.9 (conventional denitrification reaction) shows that the reduction of one mole of nitrate to nitrogen gas needs 5 moles of methanol (organic carbon). On the other hand, Eq. 12.10 shows that the reduction of one mole of nitrite (provided by SHARON reactor) to nitrogen gas needs 3 moles of methanol. This can save 40% of organic carbon requirement in the denitrification step (Jung et al. 2007). SHARON process has been used successfully for nitrogen removal by nitrification/denitrification with nitrite as an intermediate (Van Kempen et al. 2001).

The first application of SHARON process combined with an anammox reactor, i.e. a two-staged partial nitrification-anammox process was successfully tested to treat sludge digester effluent (Van Dongen et al. 2001a, b). Figure 12.4 shows the schematic diagram of the combined SHARON-Anammox process.

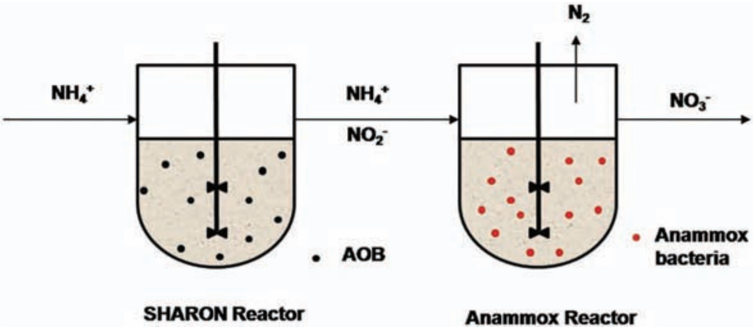

Figure 12.4. Schematic representation of a SHARON-Anammox process

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+ \tag{Eq. 12.7}$$

$$NH_4^+ + 1.5O_2 \rightarrow NO_2^- + H_2O + 2H^+ \tag{Eq. 12.8}$$

$$6NO_3^- + 5CH_3OH + CO_2 \rightarrow 3N_2 + 6HCO_3 + 7H_2O \tag{Eq. 12.9}$$

$$6NO_2^- + 3CH_3OH + 3CO_2 \rightarrow 3N_2 + 6HCO_3 + 3H_2O \tag{Eq. 12.10}$$

SHARON process needs to convert more than 50% of ammonium to nitrite since the ideal molar ratio of NH_4^+:NO_2 in influent for anammox reactor is 1:1.32 (Eq. 12.1). Van Dongen et al. (2001b) had operated SHARON process in a CSTR without biomass retention under continuous aeration with HRT of 1 day. They achieved 53% conversion of ammonia in the sludge liquor to nitrite. The effluent of SHARON process was used as influent of the anammox process, which was operated as a granular sludge in SBR. More than 80% of the ammonia was converted into nitrogen gas in their experiment (Van Dongen et al. 2001b). This process saves a lot of treatment cost compared to the conventional biological method and physical-chemical techniques. Compared to conventional nitrification-denitrification process high savings on aeration energy (up to 63%) and cost (up to 100%) of extra carbon source addition could be saved, with negligible sludge production in two staged SHARON-Anammox system (Van Dongen et al. 2001b; Volcke et al. 2005). The overall cost for treating sludge digester effluent using the two staged SHARON-Anammox system was estimated to be 0.7–1.1 €/kg N removed. While the costs of conventional biological methods and physical-chemical techniques were estimated to be 2.3–4.5 €/kg N removed and 4.5–11.3 €/kg N removed, respectively (Van Dongen et al. 2001a). The combined SHARON-Anammox process has also been used to treat landfill leachate (Akgul et al. 2013).

12.4.2 CANON

Apart from SHARON, the shortcoming of nitrite requirement for anammox process can be overcome by combing partial nitrification and anammox in a single reactor. This process has been named CANON, an acronym for Completely Autotrophic Nitrogen Removal over Nitrite (Dijkman and Strous 1999; Strous 2000). The CANON process, an integration of partial nitrification and anammox in a single reactor is called by several names such as OLAND (Oxygen-Limited Autotrophic Nitrification Denitrification) (Pynaert et al. 2004) and SNAP (Single-stage Nitrogen removal using Anammox and Partial nitrification) (Furukawa et al. 2005) by different research groups. CANON process takes the advantage of co-operation between two autotrophic bacteria i.e. AOB and anammox bacteria under oxygen limiting conditions that simultaneously perform two sequential reactions (partial nitrification, Eq. 12.8 and anammox, Eq. 12.1) in a single reactor (Strous 2000; Sliekers et al. 2002). In this process, first ammonia is converted

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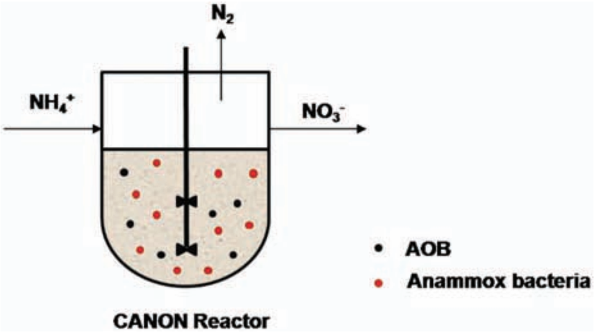

Figure 12.5. Schematic representation of CANON process

partially to nitrite (Eq. 12.8) by AOB, which consume oxygen and create anoxic conditions. Subsequently, anammox bacteria convert ammonia and nitrite to nitrogen gas (Eq. 12.1). The combined stoichiometry of CANON without considering the cell synthesis is presented in Eq. 12.11 (Strous 2000) Figure 12.5 shows the schematic diagram of CANON process. The CANON process consumes 63% less oxygen and 100% less reducing agent (organic carbon source) in comparison with the conventional nitrification-denitrification process (Third et al. 2005). It also saves 50% less space and investment costs (reactor manufacturing, electricity to run reactor etc.) compared to the SHARON-Anammox process and conventional nitrification-denitrification process.

$$1NH_3 + 0.85O_2 \rightarrow 0.11NO_3^- + 0.44N_2 + 1.43H_2O + 0.14H^+ \quad \text{(Eq. 12.11)}$$

The DO, temperature, pH, and concentrations of ammonium and nitrite are the most important factors to be controlled and monitored for the successful start-up and operation of CANON process. The key is to avoid the growth of NOB in the reactor and to protect anammox bacteria from high dissolved oxygen (DO) and nitrite exposure. The presence of NOB in the CANON reactor may destabilize the process by competing with anammox bacteria for the same substrate, nitrite, and by competing with AOB for oxygen (Third et al. 2001).

Third et al. (2001) studied the lower limit of ammonium loading rate for a successful operation of CANON process. In their experiment, about 92% of the total nitrogen was removed by CANON system when operated at ammonium loading rate of 0.1 kg-N/m^3/d. However, when the loading rate was below 0.1 kg-N/m^3/d, NOB was grown in the reactor and destabilized the CANON reaction. The total nitrogen removal efficiency decreased to 57% (Third et al. 2001). Similar observations were found in the SBR treating optoelectronic wastewater (Daverey et al. 2013a). The total nitrogen removal efficiencies of SBR operated as CANON were varied between 40–60% when the reactor was operated at influent ammonium loading rate of 0.033 kg/m^3/d. Accumulation of nitrate

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was observed along with high ammonium nitrogen removal efficiency (60–95%), which indicated the presence of NOB in the SBR (Daverey et al. 2013a). However, this ammonium limitation effect on CANON is reversible (Third et al. 2001; Daverey et al. 2013a). The high nitrite concentration (>100 mg/LN) is inhibitory to anammox bacteria (Strous 1999; Daverey et al. 2013a) and therefore accumulation of nitrite should be avoided in the CANON reactor.

DO is another important parameter, which can be used to wash out NOB for stable operation of CANON process. AOB can easily outcompete NOB under DO limiting conditions because the half-saturation constant of AOB (0.3 mg/L) is lower than that of NOB (1.1 mg/L) (Wang and Yang 2004; Zhang et al. 2008). As high DO can inhibit anammox bacteria, it is advisable that, for a stable operation of CANON process, DO should be maintained below 0.5 mg/L (Daverey et al. 2013a). A slightly higher pH (about 8) than neutral is suitable for both AOB and anammox bacteria, while it suppresses the growth of NOB (Hellinga et al. 1998). Similarly, higher temperature (above 35 °C) is suitable for anammox bacteria (Strous et al. 1999b; Dosta et al. 2008) and AOB (Hellinga et al. 1998), and is suitable to out-compete NOB from the CANON reactor. CANON process has been used successfully to remove nitrogen from digested manure (Joss et al. 2009), effluent water from municipal sludge dewatering plants (Kampschreur et al. 2009), anaerobically pre-treated swine slurry (Figueroa et al. 2012) and optoelectronic wastewater (Daverey et al. 2013a).

12.4.3 SNAD

Table 12.2 shows that many ammonium rich wastewaters (anaerobic digester liquor of swine wastewater, landfill leachate, optoelectronic industrial wastewater, monosodium glutamate industrial wastewater, domestic wastewater) also contain COD. However, CANON, the most efficient and economical nitrogen removal process could not remove COD from the wastewater. Moreover, about 11% of inorganic ammonium nitrogen remains untreated as nitrate in the CANON process (Eq. 12.11). To overcome these two limitations a new process named SNAD (Simultaneous partial Nitrification, Anammox and Denitrification) has been developed (Chen et al. 2009). Figure 12.6 shows the schematic representation of a SNAD reactor system. SNAD is an integration of partial nitrification (Eq. 12.8), anammox (Eq. 12.1) and denitrification (Eq. 12.9) in a single reactor. In other words, it is a CANON reactor with denitrifying bacteria. Three bacterial communities i.e. AOB, anammox and denitrifying bacteria co-exist in the same reactor under oxygen limiting conditions for simultaneous removal of inorganic nitrogen and organic carbon. In this process, first two reactions are same as CANON (Eq. 12.8 and 12.1), which produce about 11% nitrate (Eq. 12.11). Subsequently, denitrifying bacteria reduce nitrate produced by CANON process to nitrogen gas by using organic carbon (COD) as reducing agent in the SNAD reactor. Reduction of nitrate to nitrogen gas by denitrifying bacteria is a multi-step process (Figure 12.1). In the first step of denitrification, nitrate is reduced to nitrite followed by reduction of nitrite to nitric oxide, which subsequently reduced to nitrous oxide. Finally, nitrous oxide is reduced to nitrogen gas.

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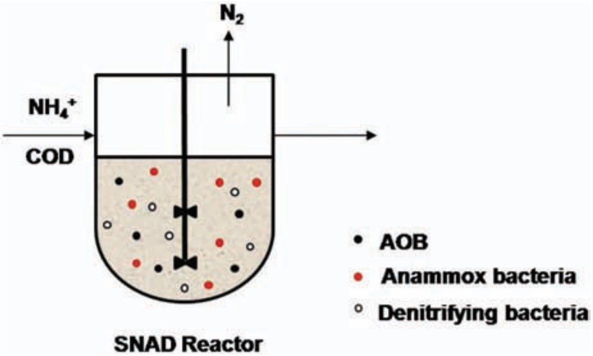

Figure 12.6. Schematic representation of SNAD process

However, the biggest issue for coupling CANON and denitrification is the competition between anammox and denitrifying bacteria for the same substrate, nitrite (Kumar and Lin 2010). The presence of NOB in the reactor can further complicate the competition for substrate (nitrite). Though, the NOB can be washed out from the reactor by following the same strategies (lower DO, higher temperature and pH, higher ammonium loading rates) as discussed in CANON process (12.4.2). The maximum growth rates of fast growing denitrifying bacteria are hundred times higher than the growth rate of anammox bacteria, while the growth yield of denitrifying bacteria (yield coefficient of heterotrophs; $Y = 0.3\ \mathrm{g\,VSS/g\,NH_4^+\text{-}N}$) is much higher than nitrifying and anammox bacteria ($Y = 0.066 \pm 0.01\ \mathrm{g\,VSS/g\,NH_4^+\text{-}N}$) (Strous et al. 1998; Kumar and Lin 2010).

Despite these issues, SNAD process has been successfully developed in a single, oxygen-limited reactor for simultaneous ammonia and COD removal by many authors (Chen et al. 2009; Wang et al. 2010; Lan et al. 2011; Daverey et al. 2012; Daverey et al. 2013b). Scanning electron microscopy (SEM) observation, polymerase chain reaction (PCR) analysis and fluorescence in situ hybridizations (FISH) analysis revealed the existence of AOB, anammox bacteria and heterotrophic denitrifying bacteria in SNAD process (Chen et al. 2009; Wang et al. 2010). So far, this process has been used to treat leachate wastewater (Wang et al. 2010), optoelectronic industrial wastewater (Daverey et al. 2012), fertilizer industry effluent, (Keluskar et al. 2013) and anaerobic digester liquor of swine wastewater (Daverey et al. 2013b).

In Taiwan, SNAD process has been reported in a full-scale landfill-leachate treatment plant (Wang et al. 2010). Based on nitrogen mass balance approach the performance of SNAD process in the full-scale bioreactor has been analyzed. In this full-scale reactor, the total nitrogen removal by combined partial nitrification and anammox reaction was 68%. Heterotrophic denitrification contributed to 8% of total nitrogen removal with 23% of COD removal (Wang et al. 2010). The sludge from this full-scale landfill-leachate treatment plant has been successfully re-cultivated in lab scale SBRs and has been tested for selected wastewaters (Lan et al. 2011; Wang et al. 2011; Daverey et al. 2012; Daverey et al. 2013b).

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12.5 INHIBITORS

12.5.1 Nitrite

Nitrite is one of the substrates for anammox bacteria. Anammox bacteria utilize nitrite as an electron acceptor to oxidize ammonium to nitrogen gas. Several studies suggested that nitrite is one of the most potential inhibitors for the anammox process (Strous et al. 1999b; Egli et al. 2001; Dapena-Mora et al. 2007; Kimura et al. 2010; Lotti et al. 2012a) and therefore, it should be carefully monitored during the process for stable performance. However, different levels of nitrite inhibition at various nitrite concentrations have been reported in the literature (Table 12.3). The IC_{50} (concentration of nitrite which causes 50% inhibition of anammox activity) values of nitrite reported by Dapena-Mora et al. (2007), Lotti et al. (2012a), and Scaglione et al. (2012) were 350, 400 and 172 mg/L N, respectively. While Strous et al. (1999b) and Egli et al. (2001) observed complete loss of anammox activities at nitrite concentrations of 100 and

Table 12.3. Inhibitory effects of nitrite on anammox processes

References	*Nitrite concentration (mg/L NO_2^--N)*	*Inhibition Effect*[1]	*Threshold concentration (mg/L NO_2^--N)*
Strous et al. (1999b)	100	Complete inhibition	100
Egli et al. (2001)	185	Complete inhibition	—
Dapena-Mora et al. (2007)	350	50% inhibition	—
Jung et al. (2007)	70	Activity decreased	—
Isaka et al. (2007)	>280	Activity decreased	280
Bettazzi et al. (2010)	>30 (long exposure)	Activity decreased	30
Bettazzi et al. (2010)	75 (spiked)	28% inhibition	60
Kimura et al. (2010)	750	90% inhibition	—
Kimura et al. (2010)	330;430	25% inhibition; 37% inhibition	274
Tang et al. (2010a)	280	10% inhibition	220
Lotti et al. (2012a)	400	50% inhibition	—
Scaglione et al. (2012)	172 (24 h exposure)	50% inhibition	—
Scaglione et al. (2012)	500 (3–4 h exposure)	<40% inhibition	—

[1] Effect mentioned as either inhibition in anammox activity or total nitrogen removal efficiency

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185 mg/L N, respectively. The nitrite inhibition threshold values were also varied in different studies (Table 12.3). For example, threshold values of nitrite inhibition reported by Bettazzi et al. (2010) and Isaka et al. (2007) were 30 and 280 mg/L N, respectively.

Initial studies concluded that nitrite inhibition on anammox bacteria was irreversible and toxic (Sliekers et al. 2003; Egli et al. 2001; Wett 2007). However, recent reports suggest that the adverse effect of nitrite on anammox is completely reversible, and the effect is inhibitory rather than toxic (Kimura et al. 2010; Lotti et al. 2012a; Jin et al. 2013). Kimura et al. (2010) studied the effect of nitrite inhibition on the anammox process by using anammox bacteria entrapped in gel carriers. In CSTR, anammox activity was decreased to 90% within 7 d when influent nitrite concentration was increased from 400 to 750 mg/L N. However, complete recovery of anammox activity was reported by the authors within 3 d after decreasing the nitrite concentration from 750 mg/L N to less than 274 mg/L N (Kimura et al. 2010). Lotti et al. (2012a) studied the nitrite inhibition on the anammox process in manometric batch tests. The anammox process was exposed to a very high nitrite concentration of 1000 mg/L N for 24 h. The anammox activity was reported to be fully recovered within 2 days by decreasing nitrite concentration through biomass washing (Lotti et al. 2012a). Recently, Jin et al. (2013) also reported the recovery of an anammox process after nitrite inhibition within 5 d by changing influent nitrite/ammonia ratio 1.8 to 1 and concluded that nitrite inhibition is non-toxic and reversible.

The most plausible reasons for different levels and nature (reversible/irreversible) of nitrite inhibition on anammox reported in literature could be the use of different biomass such as anammox species, source of seed sludge etc. and operational conditions such as temperature, pH, nitrogen loading rate, reactor configuration etc. (Cho et al. 2010; Jin et al. 2012).

12.5.2 FA and FNA

Free ammonia (FA; NH_3) and free nitrous acid (FNA; HNO_2) are the unionized or unprotonated form of ammonium and nitrite, respectively. Since only unionized forms (FA and FNA) can diffuse through the cell membrane (Anthonisen et al. 1976), it is proposed that they are the real inhibitors of the anammox process rather than ionized form (NH_4^+ and NO_2^-, respectively) (Waki et al. 2007; Tang et al. 2010a; Fernandez et al. 2012). FA and FNA rather than their ionized forms are also well known inhibitors of nitrifying bacteria (Anthonisen et al. 1976; Vadivelu et al. 2007) and poly-phosphate accumulating denitrifiers (Zhou et al. 2007). Inside the cell, FA and FNA interfere with the transmembrane pH gradient required for ATP synthesis by decreasing intracellular pH, which may cause cell death (Anthonisen et al. 1976; Sudarno et al. 2011).

Inhibition of anammox reaction is observed with FA levels of 13–90 mg/L N (Waki et al. 2007), while the IC_{50} value of FA is reported to be 38 mg/L N in short-term batch tests (Fernandez et al. 2012). However, long-term tests in the

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SBR showed that nitrogen removal efficiencies decreased to zero at 35–40 mg/L N concentrations of FA (Fernandez et al. 2012). Therefore, it is suggested that anammox processes should be operated at less than 20–25 mg/L N of FA to maintain a stable operation (Fernandez et al. 2012). Though, the lowest FA toxicity threshold concentration during start-up period of anammox is reported to be 1.7 mg/L N (Jung et al. 2007), few studies have been reported that anammox bacteria can tolerate higher concentration of FA. In an up-flow biofilm reactor, inhibitory effect on the anammox bacteria was observed at FA concentrations of 57–187 mg/L (Tang et al. 2010a). While in another up-flow fixed-bed reactor using Kaldnes biofilm carriers the anammox bacteria was able to tolerate up to 150 mg/L of FA concentration and only 10% decrease in anammox activity was observed at FA concentration of 190 mg/L (Aktan et al. 2012). However, the NRR was decreased when FA concentrations exceeded 2 mg/L N in a bench scale moving bed bioreactor and the IC_{50} value of FA was reported to be 40 mg/L N in this reactor (Jaroszynski et al. 2012).

In case of FNA, the reported toxicity level on anammox bacteria is very low and it depends on the nature of biomass. Fernandez et al. (2012) studied the effect of FNA on SAA using biofilm and flocculent biomass. The IC_{50} value of FNA was reported to be less than 11 mg/L N with the threshold inhibitory concentration of 6.6 mg/L N using biofilm biomass. While, in case of flocculent biomass more severe inhibition was observed by the authors as up to 30% decrease in SAA observed at 4.4 mg/L N of FNA (Fernandez et al. 2012). Contrary to this, Lotti et al. (2012a) concluded that nitrite is the true inhibitor of anammox bacteria rather than FNA.

Nevertheless, these studies suggest that FA and FNA could cause serious inhibition to the anammox process and, therefore, their concentrations should be monitored carefully for a stable anammox operation. Anthonisen et al. (1976) derived chemical equations to calculate the concentrations of FA and FNA (Eq. 12.12 and 12.13, respectively), which suggests that the concentrations of FA and FNA are temperature and pH dependent and could be controlled by maintaining these parameters at a certain range.

$$\mathrm{FA}(\mathrm{NH_3\ mg\,L^{-1}})\,\frac{17}{14}\times\frac{[\mathrm{NH_3\text{-}N}+\mathrm{NH_4^+\text{-}N}]\times 10^{\mathrm{pH}}}{e^{\left[\frac{6344}{273+T}\right]}+10^{\mathrm{pH}}} \qquad \text{(Eq. 12.12)}$$

$$\mathrm{FNA}(\mathrm{HNO_2\ mg\,L^{-1}})\,\frac{46}{14}\times\frac{[\mathrm{HNO_2\text{-}N}+\mathrm{NO_2\text{-}N}]}{e^{\left[\frac{2300}{273+T}\right]}+10^{\mathrm{pH}}} \qquad \text{(Eq. 12.13)}$$

12.5.3 Dissolve Oxygen (DO)

Anammox bacteria oxidize ammonium under anaerobic conditions. The presence of oxygen could be toxic to anammox bacteria and therefore, DO is a critical parameter for the cultivation of anammox bacteria. Different anammox species

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have different tolerance level of oxygen. For example, the DO tolerance level of *Ca*. B. anammoxidans is <1 μM, while it is higher (<63 μM) for *Ca*. B. sinica (Oshiki et al. 2011). The IC_{50} value for DO was reported to be 63 μM for *Ca*. B. sinica (Oshiki et al. 2011). However, the inhibition due to DO is reversible at low concentrations, while irreversible at higher concentrations (Strous et al. 1999b; Egli et al. 2001; Daverey et al. 2013a). Egli et al. (2001) observed an irreversible inhibition of the anammox process at higher oxygen concentrations (>18% air saturation). In an another study, the decreased anammox activity at DO concentration of 5 mg/L was recovered when the influent DO concentration decreased to less than 1 mg/L (Kimura et al. 2011b). Jung et al. (2007) suggested that DO should be kept below 0.2 mg/L for anammox bacteria cultivation.

12.5.4 Heavy Metals

Heavy metals are often found in wastewater systems including nitrogen-rich wastewater such as leachate, swine wastewater, etc. It is well known that heavy metals are inhibitory and even toxic to many microorganisms at high concentrations. However, very few studies have been reported on inhibition of the anammox process by heavy metals.

Van de Graaf et al. (1995) observed a complete inhibition of anammox by mercuric chloride ($HgCl_2$) at 271 mg/L. Lotti et al. (2012b) studied the short-term effect of copper and zinc on anammox activity. The IC_{50} values of copper and zinc reported by them were 1.9 and 3.9 mg/L, respectively. Recently, Yang et al. (2013a) studied the short- and long-term effect of Cu(II) on anammox mixed culture. They reported much higher IC_{50} value of Cu(II) (12.9 mg/L) than Lotti et al. (2012b) in short-term tests. The long-term exposure of Cu(II) on anammox had severe inhibition. About 94% loss in anammox activity was observed at 5 mg/L of Cu(II) concentration in a long-term experiment. Further studies need to be conducted to evaluate the effect of other heavy metals and their inhibition mechanism.

12.5.5 Antibiotics

Antibiotics are often found in different wastewaters such as municipal, livestock such as swine wastewater, aquaculture and pharmaceutical industries. Antibiotics are well-known inhibitors of many bacteria and, therefore, there inhibition or toxicity on anammox bacteria needs to be studied in detail. Few studies have been focused on the inhibition of the anammox process by selected antibiotics such as chloramphenicol, penicillins, ampicillines and tetracyclines (Van de Graaf et al. 1995; Fernandez et al. 2009; Yang et al. 2013b; Zhang et al. 2013).

Anammox inhibition by chloramphenicol has been tested in the range of 100 to 1000 mg/L, while Dapena-Mora et al. (2007) did not observe any inhibition on anammox activity, others reported significant inhibition. For example, Van de Graaf et al. (1995) observed 36 and 98% inhibition on ammonia removal by anammox at 20 and 200 mg/L of chloramphenicol, respectively. In another study, 20 mg/L of chloramphenicol reduced nitrogen removal efficiency of an anammox

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SBR system by 25%, and the system took 2 months to recover (Fernandez et al. 2009).

In case of tetracycline hydrochloride, it caused 60% inhibition in SAA in an SBR at 10 mg/L (Fernandez et al. 2009). A further decrease in anammox activity and accumulation of nitrite in the SBR were observed when the concentration of tetracycline hydrochloride increased to 50 mg/L. The inhibition caused by tetracycline hydrochloride was found to be irreversible (Fernandez et al. 2009). Recent findings of Yang et al. (2013b) suggested that the IC_{50} of oxytetracycline (OTC), another kind of tetracycline in the batch tests on anammox mixed culture is 517.5 mg/L. However, long-term study in an UASB shows 90.4% of loss in anammox activity at 50 mg/L of OTC. This inhibition was found to be irreversible, and the anammox activity could only be recovered after re-seeding with fresh anammox sludge (Yang et al. 2013b). Contrary to these studies, Zhang et al. (2013) reported that the inhibition due to OTC at concentrations between 6–50 mg/L was reversible with a short recovery time (51 d).

12.5.6 Organic Compounds

Table 12.2 shows that anaerobic digester liquor of swine wastewater (Daverey et al. 2013b), landfill leachate (Wang et al. 2010); optoelectronic industrial wastewater (Daverey et al. 2012), monosodium glutamate industrial wastewater (Shen et al. 2012), and domestic wastewater (Gu et al. 2012) contain organic compounds or organic matter as COD. Since, anammox bacteria are chemoautotrophic microorganisms they use inorganic carbon (CO_2), therefore, organic matter could inhibit their activity. Inhibition of the anammox process due to organic matter is generally related to “out-competition phenomenon” by heterotrophic bacteria, which has very high growth rate compared to anammox bacteria (Jin et al. 2012).

Ni et al. (2012) found that low organic carbon concentration (100 mg COD/L) did not affect ammonia and nitrite removal efficiency of the granular anammox sludge in a reactor but total nitrogen removal increased via denitrifiers, which utilized nitrate along with organic carbon. The activities of anammox bacteria were suppressed at high concentration of organic carbon. The PCR results confirmed that the heterotrophic denitrifiers were dominated in the anammox reactor when high organic carbon (400 mg COD/L) supplemented to the reactor. A gradual reduction in anammox activity was also observed by Chamchoi et al. (2008) when organic carbon increased above 100 mg COD/L. In their experiment, anammox bacteria were deactivated at 100 mg COD/L of organic carbon. Dapena-Mora et al. (2007) observed 22 and 70% inhibition at 25 and 50 mM concentrations of acetate, respectively in batch tests.

12.6 REACTOR SYSTEMS USED FOR ANAMMOX GROWTH

Reactor configuration plays important role for the cultivation of microorganisms and therefore, a number of reactors such as FBR, SBR, membrane bioreactor

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(MBR), up-flow anaerobic sludge blanket (UASB), rotating biological contactor (RBC), etc. have been tested for the cultivation of anammox bacteria in the laboratory. The major obstacle for the cultivation of anammox bacteria in any reactor system is the slow growth rate of this microorganism. Moreover, the biomass yield is also very low and, therefore, a small fraction of biomass in the effluent is undesirable (Trigo et al. 2006). An effective retention of the biomass inside the reactor is important for successful cultivation and practical application of anammox bacteria. Therefore, different kinds of carriers and reactor configurations have been used to retain the biomass inside the reactor.

12.6.1 Fluidized Bed Reactor (FBR)

The anammox process was first identified in FBR treating effluent from methanogenic reactor operated with wastewater from baker's yeast production plant (Mulder et al. 1995). Sand particles with diameters of 0.3–0.6 mm were used as carrier material on which bacteria grew as a biofilm. Van De Graaf et al. (1995) and Strous et al. (1997b) re-cultivated the sludge taken from the reactor operated by Mulder et al. (1995) in different FBRs using sand particles as carrier. The maximum SAA of 0.021 g-N/g-VSS/d with 65% of nitrogen removal efficiency was observed by Van De Graaf et al. (1995) using synthetic wastewater at volumetric nitrogen loading rate (NLR) of 4.8 kg-N/m^3/d in the FBR. Strous et al. (1997b) reported that fixed-bed reactor and FBR are suitable reactor configurations for anammox cultivation. Sand particles were used as a carrier for FBR while sintered glass beads used as fixed-bed in the reactor. High total nitrogen removals (99%) have been reported in both reactors (Strous et al. 1997b).

12.6.2 Sequencing Batch Reactor (SBR)

The determination of several important physiological parameters (biomass yield, maximum specific growth rate, maximum specific ammonium consumption rate etc.) had been made possible by using SBR (Strous et al. 1998). The SBR has many advantages such as efficient biomass retention, homogeneous distribution of substrates, products and biomass aggregates over the reactor, reliable operation for more than 1 year, and stable conditions under substrate-limiting conditions, which make it the most suitable reactor for the growth of anammox bacteria (Strous et al. 1998). The doubling time has been effectively reduced from 30 d in FBR (Van de Graaf et al. 1996) to 11 d in SBR.

Chamchoi and Nitisoravut (2007) used three sets of SBR for anammox enrichment from conventional sludges (upflow anaerobic sludge blanket, activated sludge and anaerobic digestion sludge). Anammox activity was observed in all three SBRs after 120 d of operation. In another study, Third et al. (2005) detected the anammox activity after 105 d of SBR operation. The anammox process was successfully started up in the SBR after 101 days using a mixed aerobic activated sludge and nitrifying activated sludge (Wang et al. 2012).

Compared to these studies, Lopez et al. (2008) using SBR inoculated with three different activated sludge biomass detected the anammox bacteria by PCR analysis on day 60. This reactor took only 78 d to start-up the anammox process. The different start-up times in these studies is due to the fact that these reactors were seeded with different sludge and operated at different conditions.

Fernandez et al. (2008) studied the biofilm and granular systems to improve anammox biomass retention in the SBR inoculated with anammox sludge. High inorganic salt concentrations were used to form granular sludge in the SBR. In another SBR, zeolite particles were used as carrier material for anammox biofilm formation. Significant reduction of biomass wash-out in the effluent and consequently high biomass concentration inside the reactor was reported in both reactor systems. This study suggested that use of granular sludge or carrier in SBR further improve the biomass retention efficiency of the SBR.

12.6.3 Gas Lift Reactor

Gas-lift reactors have been reported to have a relatively high gas-liquid mass transfer of oxygen than SBR and other reactors. Therefore, few researchers evaluated the performance of gas-lift reactors to cultivate anammox bacteria (Sliekers et al. 2003; Dapena-Mora et al. 2004).

Sliekers et al. (2003) cultivated anammox bacteria and developed the CANON process in a gas lift reactor (1.8 L). Stable operation of both processes (the anammox and CANON) with high N-conversion rates has been achieved in gas-lift reactor. The gas-lift reactor was kept anoxic for the anammox process and oxygen limited for CANON process. The anammox process and the CANON process in the gas-lift reactor could achieve NRR of 8.9 and 1.5 kg-N/m^3/d, respectively.

Dapena-Mora et al. (2004) studied the stability of anammox process in a gas-lift reactor and SBR. Total nitrogen and nitrite removal efficiencies of 88% and 99%, respectively were achieved in the gas-lift reactor. Compared to this, total nitrogen and nitrite removal efficiencies of 78 and 100%, respectively were achieved in the SBR. Biomass was formed granules in both the reactors. However, at higher NLRs (above the maximum SAA of the sludge) biomass washout was observed in both the reactors. The presence of gas bubbles inside the granules was observed by optical microscopy. These bubbles provoked the floatation of biomass and responsible for the biomass washout in both the reactors. The authors suggested that biomass floatation could be reduced by increasing the shear stress, which can be increased by increasing up-flow gas flow rate in the gas-lift reactor. In case of SBR, the mechanical stirring could be more effective to eliminate the gas from the granules (Dapena-Mora et al. 2004).

12.6.4 Membrane Bioreactor (MBR)

No matter which type of reactor is used for the cultivation of anammox bacteria, floatation of the biomass occurs due to the production of nitrogen gas, which causes breakage of granules. Though SBR has efficient biomass retention, which can also be improved by using granular sludge or carrier, however, a fraction of the generated biomass is inevitably washed out with the effluent (Trigo et al. 2006).

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In the study of Dapena-Mora et al. (2004), floatation of granular biomass occurred in both reactors (gas-lift reactor and SBR) when the NLR exceeded the maximum SAA of the sludge. Fluctuations in influent also provoke the biomass flotation and finally wash-out (Trigo et al. 2006). MBR is a combination of common bioreactor and membrane filtration unit, and it can retain complete biomass. Taking the advantage of complete biomass retention in MBR, it was first used by Wyffels et al. (2004) for nitrogen removal by a two-staged partial nitrification and anammox process. The overall nitrogen removal efficiency and NRR of the system were 82% and 0.55 kg-N/m^3/d. Later, Trigo et al. (2006) installed ultrafiltration hollow fibre membrane module in an SBR for the cultivation of anammox bacteria. The NRR of up to 0.71 kg-N/m^3/d was achieved in this membrane SBR (MSBR). Wang et al. (2012) compared the anammox start-up performances from the conventional activated sludge between a MBR and SBR. A remarkably shorter start-up period was noted in the MBR (59 d) than in the SBR (101 d). The maximum NRRs of 0.345 and 0.292 kg-N/m^3/d were reported in the MBR and SBR, respectively. Tao et al. (2012) also reported that start-up of the anammox process in the MBR is more effective than in the SBR. An acceleration of SAA by 19 times was observed when a SBR modified as MBR (Tao et al. 2012).

12.6.5 Rotating Biological Contactor (RBC)

The RBC, a fixed film biological reactor is widely used in wastewater treatment. However, its application for the enrichment of anammox bacteria is very limited and mainly used to develop a single-staged partial nitrification and anammox process. Siegrist et al. (1998) observed a significant loss of ammonium nitrogen (~70%) in a nitrifying RBC treating ammonium-rich leachate from a hazardous-waste landfill site and suggested the possibilities of anammox process establishment in the RBC. Later, the sludge from this RBC was enriched in 2.25 L Schott flasks and characterized as anammox bacteria (Egli et al. 2001). Pynaert et al. (2004) developed OLAND (a single-staged partial nitrification and anammox process) in a lab scale RBC, which could able to achieve high NRR (1.8 kg-N/m^3/d). In other RBC reactors, the nitrogen removal efficiencies of OLAND processes were reported to be 89% (Pynaert et al. 2003) and 76% (Vlaeminck et al. 2009). In a study conducted by Liu et al. (2008), anammox bacteria were enriched in a non-woven RBC. A very high NRR (3.4 kg-N/m^3/d) was achieved in a very short time (100 d), which suggests that RBC is a very suitable reactor system for the enrichment of anammox bacteria.

12.6.6 Up-flow Anaerobic Sludge Blanket (UASB)

The floatation of biomass due to the production and presence of the gas bubbles inside the reactor could be overcome by using UASB. In UASB, a solid-liquid separator (a three phase separator), which is installed in the upper part of the reactor, enables the separation of gas, water and sludge under high turbulence conditions (Lettinga et al. 1984). UASB also form a very compact granular sludge, which helps biomass retention inside the reactor. Apart from this, UASB offers a

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number of advantages over other reactors (SBR, and biofilm reactors) such as high space-loading, low footprint, and resistance to shocks and toxins (Schmidt et al. 2004).

In a UASB reactor, inoculated with sludge collected from a full scale anaerobic digester, Thuan et al. (2004) observed anammox activity after 200 d. Tang et al. (2010b) observed a very high NRR of 45.24 kg-N/m^3/d after 230 d of UASB operation. The NRR was increased to 74.3–76.7 kg-N/m^3/d after operating the UASB for about 400 d (Tang et al. 2011). These authors used low substrate concentrations to avoid inhibition caused by nitrite and FA. The high SAA (5.6 kg-N/kg-VSS/d) and high biomass concentration (42.0–57.7 g-VSS/L) were obtained in this UASB, which were regarded as the key factors for this high NRR by the reactor (Tang et al. 2011).

Considering the fact that few wastewater streams are in low strength and reactor operation at higher temperature increases the overall treatment cost, UASB has been successfully used to treat low strength wastewater (<20 mg/LNH$_4^+$-N) under moderate and low temperatures (16–30°C). The NRR was maintained at 2.28 kg-N/m^3/d with HRT of 0.28 h at 16 °C, which was about 60% lesser than NRR at 30 °C (Ma et al. 2013).

12.6.7 Up-flow Biofilter (UBF)

UBF is a fixed bed biofilm reactor, in which porous media are used to immobilize microorganisms. The porous media enable the separation of gas and solids, thereby provide uniform flow through the reactor. This type of reactor has been widely used due to its large biomass attachment, high organic loadings, long sludge retention time, easily restarting and simple operation (Han et al. 2013).

Recently, UBF has been used for anammox cultivation and nitrogen removal (Tsushima et al. 2007; Tang et al. 2009; Jin et al. 2013; Chen et al. 2010). Higher NRRs by the anammox process in UBF have been reported in the literature. In a study, UBF has been operated for more than 1 year, and the highest NRR of 24.0 kg-N/m^3/d was attained in this reactor (Tsushima et al. 2007). Recently, Chen et al. (2010) developed anammox function in the UBF. This reactor has been operated for 435 day at 35 °C and the maximal NLR attained was 34.5 kg-N/m^3/d. The doubling time of anammox bacteria was between 4.3–7.4 d in this UBF.

Some other reactor systems such as EGSB (Expanded Granular Sludge Bed) have also been used for anammox cultivation (Chen et al. 2011). However, UASB has been proven the best reactor system for anammox cultivation with highest NRR attained.

12.7 APPLICATIONS OF ANAMMOX AND CANON/SNAD PROCESSES

Anammox is considered as the most cost-effective nitrogen removal technique. Very high NLR and NRR can be achieved by the anammox reactor. Though most

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of these studies conducted using synthetic wastewater in lab-scale reactors, these studies have shown the potential of the anammox process in treating nitrogen rich wastewaters. In recent years, applications of anammox or its related processes (SHARON-Anammox, CANON or SNAD) have been tested to treat real world wastewaters by many researchers in lab scale reactors (Wyffels et al. 2004; Wang et al. 2011; Daverey et al. 2012, 2013a, b; Figueroa et al. 2012). Some pilot- and full-scale anammox reactors have also been started up to study the practical applications of the anammox process (Fux et al. 2002; Innerebner et al. 2007; Van der Star et al. 2007; Chen et al. 2009; Wang et al. 2010).

However, its application in nitrogen removal from real wastewater has been reported for few kinds of wastewater, mostly landfill leachate and anaerobic digester effluent. Some of the recent applications of anammox and its related processes are summarized in Table 12.4. It could be seen from Table 12.4 that the SBR is most widely used reactor system. The NLRs achieved in treating real wastewater are much lower than those studied with synthetic wastewater.

Landfilling of municipal solid waste is still one of the main waste disposal methods around the world. The municipal solid waste in landfill undergoes biological and chemical degradation after disposal, and generates leachate, which is an inevitable consequence of this waste disposal practice. The leachate is a concentrated mixture of organic and inorganic contaminants including humic acids, ammonia nitrogen, heavy metals, xenobiotics and inorganic salts (Renou et al. 2008; Wang et al. 2010). The age of landfill has a significant effect on leachate characteristics. Generally, the old landfill leachate is characterized by its low ratio of BOD/COD and fairly high NH_3-N (Renou et al. 2008). Many researchers have been studied the treatment of leachate by the anammox process (Siegrist et al. 1998; Fux et al. 2002; Zhang and Zhou 2006); however, the COD remain untreated by the anammox process. For example, in a study landfill leachate has been treated using UASB-MBR-SHARON-Anammox system (Akgul et al. 2013). The UASB-MBR system could remove 90% of COD, but the residual COD (about 2000 mg/L) was remained untreated by the SHARON-Anammox system, which could remove 78% of NH_4^+-N. Wang et al. (2010) applied SNAD process to remove COD and nitrogen from a landfill leachate. Though authors observed 80% of NH_4^+-N removal, the COD removal was only 28%. Recently, the combination of partial nitritation-anammox system with photo-Fenton treatment or with coagulation/flocculation along with ozonation treatment has been tested for better COD and nitrogen removal from landfill leachate (Anfruns et al. 2013). The combined partial nitritation-anammox system with photo-Fenton treatment could remove above 97 and 87% of COD and total nitrogen, respectively.

Apart from landfill leachate, many industries such as food, agriculture, livestock, etc. produced concentrated wastewater streams. These wastewater streams are generally treated by using anaerobic digestion methods, which efficiently remove COD from wastewater and generate biogas. The effluent from the anaerobic digestion method is highly rich in NH_4^+-N with very low or no biodegradable COD (Strous et al. 1997b). The effluent of an anaerobic digester cannot be treated economically by conventional nitrification-denitrification

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Table 12.4. Recent applications of anammox and its related processes in the nitrogen removal from real wastewater streams reported in the literature

Wastewater	*Process*	*Anammox Reactor (volume)*	*NH_4^+-N removal efficiency (%)*[*]	*NLR ($kg/m^3/d$)*	*References*
Landfill-leachate	UASB-MBR-SHARON-Anammox configuration	CSTR (2.3 L)	78	1.13	Akgul et al. (2012)
Landfill-leachate	Anammox	UASB (4.46 L)	87.5		Zhang and Zhou (2006)
Landfill-leachate	Short-cut nitrification reactor-Anammox	UASB (8.5 L)	93	0.91	Liu et al. (2010)
Landfill-leachate	PN-Anammox	SBR (1600 L)	>90[1]	2.4	Fux et al. (2002)
Landfill-leachate	PN-Anammox-oil infiltration systems	up-flow fixed bed biofilm reactor (36 L)	60	0.06–0.11	Liang and Liu (2008)
Landfill-leachate	SNAD	CSTR (400000 L)	80	0.03–0.05	Wang et al. (2010)
Landfill-leachate	PN-Anammox-AOP	SBR (250 L)	87–89[1]	1.78 ± 0.15	Anfruns et al. (2013)
Digested sludge dewatering wastewater	OLAND	MBR (1.5 L)	82	1.1	Wyffels et al. (2004)
Optoelectronic wastewater	SNAD	SBR (2.5 L)	>85	0.23	Daverey et al. (2012)
Optoelectronic wastewater	CANON	SBR (18 L)	98	0.909	Daverey et al. (2013a)
Digester liquor of swine wastewater	SNAD	SBR (5 L)	96	0.153	Daverey et al. (2013b)
Pre-treated swine slurry	CANON	SBR (1.5 L)	78	0.49	Figueroa et al. (2012)
Swine digester Liquid	CANON	SBBR[2] (6.5 L)	-	0.26	Zhang et al. (2012)
MSGIW[3]	Anammox	SBR	69–74	0.023	Shen et al. (2012)
Livestock manure digester liquor	PN-Anammox	UASB (3 L)	79.2	2.2	Yamamoto et al. (2011)

[*] Removal efficiency of anammox reactor; [1] Total nitrogen removal efficiency; [2] Sequential batch biofilm reactor; [3] Monosodium glutamate industrial wastewater

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processes due to its low COD/NH_4^+-N. Therefore, the anammox process has been tested by many researchers for the treatment of effluent from the anaerobic digester (Table 12.4). Though digester effluent contains very low biodegradable COD, the total COD is sometimes very high (720 mg/L), which negatively affects the anammox process (Molinuevo et al. 2009; Daverey et al. 2013b). Figueroa et al. (2012) reported that the presence of COD did not affect the CANON reactor in their experiment and claimed 40–50% COD removal.

However, the NH_4^+-N and total nitrogen removal efficiency of the CANON reactor were only 78 and 75%, respectively. The SNAD process has been the most successful for treating digester effluent as it could remove 80, 96 and 76% of total nitrogen, NH_4^+-N and COD, respectively (Daverey et al. 2013b).

There are many other industries such as pharmaceutical, high technology (optoelectronic and semiconductor), petrochemical, tanning, which produce nitrogen rich wastewater streams. However, there have been few studies on the application of the anammox process to treat these kinds of wastewater (Daverey et al. 2012; Daverey et al. 2013a; Falas et al. 2012). Since, the anammox process has tremendous potential in treating nitrogen rich wastewater, its applications needs to be further explored.

12.8 SUMMARY

Anammox combined with partial nitrification has been identified as the most efficient, economical and environmentally-friendly nitrogen removal method in recent years. SNAD process has shown potential to remove the organic matter along with nitrogen and could be applied for wastewater rich in NH_4^+-N with low COD. However, more research is needed to shorten the long start-up time required for the anammox process for its feasible commercial applications. The research on its applications to treat real world wastewaters other than landfill-leachate and digester effluent should be carried out.

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CHAPTER 13

Anionic Pollutant Removal by Biomass-Based Adsorbents

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13.1 INTRODUCTION

A number of anionic pollutants, including anionic nutrients, toxic anions as well as some anionic metal complexes, get into the aquatic streams via various industrial activities, such as mining, refining ores, fertilizer production, tanneries, batteries, pulp and paper production, etc. (Chabani et al. 2007; Mohan and Pittman 2007; Yoon et al. 2009; Bhatnagar et al. 2011). These anions are of great importance since they are toxic and harmful to humans and animals even at very low concentrations (Behpour et al. 2005; Kumar et al. 2010; Bryan and van Grinsven 2013). Various regulatory bodies have set the maximum prescribed limits for the discharge of these anions in the aquatic systems. However, the anions are being added continuously to the water stream at a much higher concentration than the regulated limits by industrial and agricultural activities, thus leading to the health hazards and environmental degradation.

Conventional technologies employed for remediation of these anionic pollutants include coagulation, electrocoagulation, co-precipitation, precipitation, membrane technology, electrolytic reduction, reverse osmosis, electrodialysis, ultrafiltration, adsorption/ion exchange, etc. (McAdam and Judd 2006; Mohan and Pittman 2007; Mohapatra et al. 2009; Srinivasan and Sorial 2009). However, these conventional techniques have their own inherent limitations such as less efficiency, sensitive to operating conditions, as well as production and costly disposal of secondary sludge. Membrane technologies for treating the water are based on the principle of employing a semi-permeable membrane that prevents the passage of certain ions. However, several drawbacks, such as generation of large volumes of reject streams as well as high cost of installation and maintenance, challenge their application in large scale systems (McAdam and Judd 2006; Mohapatra et al. 2009; Srinivasan and Sorial 2009). Precipitation, coagulation, electrocoagulation and co-precipitation methods have generally been found effective in removing some anionic pollutants, but they consume large amounts of

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chemicals and increase the volume of toxic sludge (Mohapatra et al. 2009; Srinivasan and Sorial 2009).

Another powerful technology is adsorption of anionic pollutants on adsorbents. There is a wide variety of commercial adsorbents developed with high selectivity for various anionic pollutants. However, the high cost of commercial adsorbent and its loss during theregeneration process restrict its application. Since the 1990s, the utilization of low-cost renewable organic materials for adsorption of anionic species has been explored (An et al. 2010; Miretzky and Fernandez Cirelli 2010; Bhatnagar et al. 2011). Recently, attention isdiverted towards the economic and eco-friendly-biomaterials such as byproducts or the wastes from large-scale industrial operations and agricultural waste materials (Lijklema 1995; Berge et al. 2005; Wartelle and Marshall 2006; Bechmann et al. 2010; Miretzky and Fernandez Cirelli 2010). The biomass waste materials areeconomic and eco-friendly due to their renewable capacity, abundant availability, unique chemical composition, low in cost and more efficient. They seem to be a viable option for anionic pollutants remediation. Studies reveal that various biomass waste materials have been tried, such as rice bran, wheat bran, sawdust of different plants, groundnut shells, coconut shells, black gram husk, hazelnut shells, walnut shells, cotton seed hulls, waste tea leaves, sugarcane bagasse, *Rhizopusnigricans*, brewery yeast, Chinese reed, giant reed, banana, orange peels, soybean hulls, water hyacinth, sugar beet pulp, sunflower stalks, chitosan, charcoal, cotton stalks, pistachio hull, etc. (Orlando et al. 2002; Ghimire et al. 2003; Namasivayam and Holl 2005; Ansari et al. 2009; Mishra and Patel 2009; Demiral and Gündüzoğlu 2010; Yue et al. 2010; Zhang et al. 2012).

In this chapter, uptakes of anionic pollutants by these biomass-based adsorbents are evaluated in comparison with those of the commercial adsorbents. Major issues (e.g., uptake capacity, preparing methods, and regeneration properties) and future perspectives are discussed. Understanding these issues would better provide us with some information forfuture actions.

13.2 HEALTH EFFECTS AND PERMISSIBLE LIMITS OF VARIOUS ANIONS SPECIES

These anionic pollutants are frequently presented in drinking water and various types of agricultural, domestic and industrial wastewaters. Unlike most organic pollutants, the anions, such as nitrate, fluoride, phosphate occur naturally in rock-forming and ore minerals and so a range of typical background concentrations is associated in soils, sediments and waters. However, they may be considered as pollutants that affect human health and ecosystems when present in water supplies above certain levels. For example, fluoride in drinking water may be a double-edged sword depending on its concentration and total amount ingested. The presence of fluorine in drinking water is beneficial to the production and maintenance of healthy bones and teeth when its content is within permissible limits, while excessive intake of fluoride causes dental or skeletal fluorosis, which is a chronic disease manifested by mottling of teeth

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in mild cases and softening of bones and neurological damage in severe cases (Yao et al. 2009; Alagumuthu and Rajan 2010). According to World Health Organization (WHO) norms, the upper limit of fluoride concentration in drinking water is 0.5−1.0 mg/L (WHO 1984). Nitrate and phosphate withconcentrations exceeding 0.5−1.0 mg/L will stimulate the growth of organisms and algaein most ecosystems, which would result in deterioration of water quality and detriments to fish and other aquatic life. Increasing nitrate concentrations in drinking watercauses methemoglobinemia and carcinogenic nitrosamines. The U.S. Environmental Protection Agency (US EPA) and WHO set a maximum contaminant level (MCL) of 10 mg/L of NO_3^--Nin drinking water (WHO 1993; U.S. EPA 2000).

In addition to these common anionic species, the anionic complex species (chromate, arsenate/arsenite and selenate/selenite) also show some severe impacts on the aquatic streams and human health even at trace levels (Abidi 1982; Bryan and van Grinsven 2013). As shown in Table 13.1, rigid permissible limits of these pollutants in drinking water have been adopted by the U.S. EPA and WHO (WHO 1993; U.S. EPA 2000).

13.3 COMMERCIAL ADSORBENTS FOR ANIONIC POLLUTANTS REMOVAL

Commercial activated carbons and commercial resins are the main forms of commercial adsorbents applied for anions removal. Basically, the commercial resins have shown relatively higher uptake capacities for various anions (Table 13.2).

13.3.1 Commercial Activated Carbon

The biggest advantage with activated carbon adsorption is that it is widely used in drinking water treatment, and it will be easy to retrofit to target anions in the water. Also, effective regeneration of the spent carbon makes this technology economically feasible. However, activated carbon is not found to be effective for removal of anionic species. For example, the adsorption of nitrate by commercial activated carbon studied by Park and Na (2006) shows only 6.8 mg/g of uptake. Similar low nitrate uptake was reported by Mahmudov and Huang (2010). They observed that the nitrate capacities on two commercial activated carbons were only 4.2–8.0 mg/g. Yoon et al. (2009) also reported the low perchlorate uptake by GAM 025 carbon with only 2 mg/g.

Activated carbon has little affinity for anionic contaminants because there are no available functional groups on thesurface of carbon for anions' removal. In order to ensure the adsorption capacity of anionic contaminants, some commercial activated carbons are modified by surfactants. Cho et al. (2011) used the quaternary ammonium-containing polymer for thepreparation of surface modified granular activated carbon and investigated its performance for adsorption of nitrate. The maximum uptake of surface modified granular activated carbon was about 27.56 mg/g as compared with that of virgin granular activated carbon

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Table 13.1. Permissible limits and health effects of various anions species

Anionic contaminant	*Permissible limit for drinking surface water sources in China (mg/L)*	*Permissible limits in drinking water (mg/L)*			*Health and environmental hazards*
		China	*USA*	*WHO*	
Nitrate	10	10	10	10	Nitrosoamine, methanoglobinemia; eutrophication of the aquatic streams
Nitrite	–	–	1	3	Cyanosis among children, cancer of the alimentary canal
Phosphate	0.1	–	–	–	Eutrophication in near urban areas
Cyanide	0.05	0.05	0.2	0.07	Rapid breeding, tremors; Thyroid effects and nerve damage
Perchlorate	–	–	0.0245[a]	–	Inhibiting iodide uptake by the thyroid gland; aAnemia and fetal brain damage
Fluoride	1.0	1.0	4.0	1.5	Skeletal and neurological damage
Cr	0.05	0.05	0.1	0.05	Suspected human carcinogen, producing lung tumors, allergic dermatitis.
As	0.05	0.01	0.05	0.01	Carcinogenic, producing liver tumors, skin and gastrointestinal effects
Se	0.01	0.01	0.05	0.01	Degrading the water, causing deterioration and deformity in fish and wildlife

[a] US EPA set a Drinking Water Equivalent Level (DWEL) of 24.5 μg/L for perchlorate in February 2005 (U.S. EPA 2005)

Table 13.2. Applications of various commercial adsorbents for anions uptakes

Commercial adsorbents	*Anions*	*Adsorption capacity (mg/g)*	*References*
Amberlite IRA-400	Nitrate	50.76	Chabani and Bensmaili (2005)
Amberlite IRA-900		52.80	
Amberlite IRA-410		69.44	Chabani et al. (2007)
Indion NSSR resin		119	Milmile et al. (2011)
Purolite A 520E		157.1	Samatya et al. (2006)
Commercial activated carbon		6.8	Park and Na (2006)
Commercial resin	Phospahte	13.8–22.0	Park and Na (2006)
Commercial activated carbon		5.8	
Granular activated carbon	Nitrite	1.21	Ozturk and Kose (2008)
Dowex-SAR resin		37.42	Lin and Wu (1997)
SR-7 resin		80.0	Yoon et al. (2009)
GAM025 activated carbon		4.0	
SAI carbon	Perchlorate	7.25	Chen et al. (2005)
Filtrasorb F400 carbon		31.82	Mahmudov and Huang (2010)
Nuchar SA activated carbon		18.91	
Plain carbon (Fluka)	Cyanide	7.1	Adhoum and Monser (2002)
READ-F resin	Fluoride	24	Liu et al. (2007)
Amberlite XAD-4 resin		95.6	Solangi et al. (2009)
1500H resin		188.67	Rengaraj et al. (2003)
D301 resin		152.52	Shi et al. (2009)
D314 resin		120.48	
D354 resin	Cr(VI)	156.25	
Activated carbon F400		26.2–19.1	Haghseresht and Lu (1998)
Activated carbon LB 830		22.4	Han et al. (2000)
Activated carbon F400		24.5	
Amberlite IRA-400		27.1	Rivas and Munoz (2010)
IRA 958 resin	As(V)	5.5	Park et al. (2005)
IRA 900 resin		4.5	
Chelating Dow XFS-4195		51.0	Chanda et al. (1988)
Chelating Dow XFS-4195	As(III)	46.0	Chanda et al. (1988)
Varion AT600 resin	Se(VI)	1.85	Lin (2007)
Amberlit IRA 400 resin		1.55	
XAD-4-DAN chelate resin	Se(IV)	3.4	Depecker et al. (2009)

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(14.25 mg/g). In rapid small-scale column tests, cationic surfactant-tailored activated carbon had 30 times higher perchlorate capacity than virgin carbon (Parette and Cannon 2005). However, this makes it more expensive and influences the adsorptive capacity of the carbon for the other contaminants as well.

13.3.2 Commercial Resin

Ion-exchange is currently the most effective and commonly used technology for various anions removal from drinking water. Many strong basic anion-exchange (SBA) resins have been developed for this purpose. However, most of SBA resins capacity is exhausted by sulfate or other multivalent ions due to their high affinity for these ions. As a result, resins designed to have high affinity for the contaminant and less affinity for sulfate are required.

We take the nitrate specialty resins as examples. Several research projects were developed on the denitrification of drinking water by exchanging nitrate onto the macro-porous resin, IMAC HP-555 and on freezing resins, Dowex SBRP (Liang et al. 1999). Three commercial resins, Amberlite IRA-400, Amberlite IRA-900 and Amberlite IRA-410, were investigated for nitrate removal from groundwater (Chabani and Bensmaili 2005; Chabani et al. 2007) with uptakes of 50.76, 52.80 and 69.44 mg/g, respectively. However, a common difficulty related to nitrate adsorption is "Nitrate Dumping," that is, most anion exchange resins show a lower affinity for nitrate over sulfate. Recently, resins with better selectivity for nitrate than for sulfate (e.g. Duolite A 196, Amberlite IRA 996 and Purolite A 520E) were developed. The strong base nitrate selective anion exchange resin, Purolite A 520E, illustrates its extraordinary adsorption capacity (157.1 mg/g) for column-mode removal of nitrate from groundwater (Samatya et al. 2006). It was reported that an important factor affecting the selectivity of ion-exchange resins is the spacing of exchange sites on the quaternary ammonium functional group. The distance between active exchange sites on the quaternary amine functional group affects the divalent-monovalent selectivity (Guter 1984; Pakzadeh and Batista 2011). Guter (1984) reported that theaffinity of strong base anion exchangers for nitrate could be prepared by increasing the length of the functional group from trimethylamines to triethylamines or tributylamines. The selectivity of the resin for $ClO_4^-$was increased by increasing the length of the trialkyl group from methyl to hexyl (Gu and Coates 2006).

However, current commercial SBA resins suffer from poor selectivity for arsenic and fluoride (Henry et al. 2004; An et al. 2010). A polymeric ligand exchange (PLE) resin will selectively take up these anions that are stronger ligands even in the presence of competing common solutes such as sulfate and chloride (Henry et al. 2004). Some of the very first PLE resins were prepared by Helfferich (1962) by loading a transition metal (Ni or Cu) onto commercial cation exchange resins. An et al. (2010) also prepared the new PLE resins by functionalizing commercially available XAD resins with Cu(II) for uptakes of arsenate and phosphate. Generally, a PLE resin is composed of (a) a cross-linked hosting resin that can firmly bind with a transition metal such as copper and iron, and (b) metal ions that are immobilized to the functional groups of the hosting resin.

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While sharing many common features with standard ion exchangers, a PLE resin employs transition metal ions as its terminal functional groups.

13.4 BIOSORBENTSFOR ANIONIC POLLUTANTS REMOVAL

13.4.1 Modification and Functionalization of Bisorbents

Although the commercial adsorbents offer flexibility and high efficiency in design and operation and in many cases produce treated effluent suitable for reuse, their utilizations in treating anionic polluted water/wastewater are still limited due to their costs. Some commercial resins and activated carbons were used for removing anionic contaminants with low-level concentrations, for product purification and pollution control (Mohan and Pittman 2007; Mohapatra et al. 2009). However, for wastewater with relatively high concentrations, the operation costs may beunaffordable. Therefore, low-cost adsorbents can be prepared and used for this purpose.

Some adsorbents prepared from nature waste materialsare widely used for the removal of anions from water/wastewaters, especially from biomass waste materials. Basically, there are mainly two forms of biosorbents that are produced from these biomass waste materials, biomaterial-based resins and carbon-based biosorbents (e.g. activated carbon).

Biomaterial-based resins. As shown in Table 13.3, two-thirds of some biomaterials are composed of cellulose and hemicelluloses (Wartelle and Marshall 2006). Cellulose, a linear homopolymer of β-d-glucopyranose units joined with glycosidic bonds, is the most abundant natural polymer. The cellulose structure has three reactive hydroxyl groups in every constitutional anhydroglucose unit and can be used as an alternative raw material for the preparation of various functional polymers (Orlando et al. 2002). As a result, the principles of producing the biomaterials-based resins rely on the introduction of some functional groups onto the cellulose structure in these waste biomasses.

Quaternary ammonium, amine and amino groups, which universally exist in commercial anion-exchange resins, are known as the most efficient functional groups for anionic pollutants removal. Some quaternary ammonium, amine and amino compounds that can be introduced onto the waste biomasses include dimethylamine, octadecyltrimethylammonium, triethylamine, ethylenediamine, choline chloride, N-(3-chloro-2-hydroxypropyl) trimethylammonium chloride, etc (Orlando et al. 2002; Namasivayam and Holl 2005; Wartelle and Marshall 2006; Xu et al. 2010a, b; Baidas et al. 2011; Chen et al. 2011a). For example, Orlando et al. (2002) prepared the anion exchangers from agricultural residues after reaction with epichlorohydrin and dimethylamine in the presence of pyridine. Epichlorohydrin attached to the cellulose in alkaline conditions has been demonstrated to be the most likely sites for the attachment of bioactive agents such as amines and imines groups. Wartelle and Marshall (2006) produced the anion exchange resins from cellulose-containing agricultural by-products with the quaternary amine, choline chloride, and cross-linking reagent dimethyloldihydroxyethylene urea (DMDHEU).

Table 13.3. Percentages of the major components in some virgin waste biomaterials

	Component (g/100 g dry weight)				
Biomaterials	*Ash*	*Cellulose*	*Hemicellulose*	*Lignin*	*Protein*
Almond shells	2.9	40.5	19.7	27.2	1.9
Corn cob	1.3	38.4	40.7	9.1	1.8
Corn stover	6.7	39.2	29.6	8.2	6
Cottonseed hulls	1.1	48.7	18.5	22.3	3.5
Oak chips	1.8	49.7	19.1	5.4	5.6
Oat hulls	4.5	42.7	39.2	7.3	2.7
Peanut shells	2.3	45.3	8.1	32.8	4.9
Pecan shells	3.5	33.2	9.6	48.3	1.4
Rice straw	13.1	43.3	25.1	5.4	5.6
Rice hulls	21.9	34.8	6.0	17.2	3.2
Soybean hulls	3.6	67.6	13.7	4.9	10.9
Sugarcane bagasse	0.4	58.2	9.2	13.4	1.6
Almond shells	2.9	40.5	19.7	27.2	1.9
Corn cob	1.3	38.4	40.7	9.1	1.8
Corn stover	6.7	39.2	29.6	8.2	6

Source: Wartelle and Marshall (2006); reproduced with permission from Elsevier

Reactions between cellulose and DMDHEU and between DMDHEU and choline chloride occur through the dehydration and formation of ether linkages among the primary alcoholic –OH groups on cellulose, DMDHEU and choline chloride.

Additional, some biomaterials-based chelate resins are also prepared after metal impregnation. The term metal impregnation can be defined as the fine distribution of metal ions or particles on thesurface of biomaterials. These impregnated multi-valent metal ions include Fe(III), Zr(IV), La(III), Al(III), Ce(III), Sm(III), Ho(III), Sc(III), Lu(III), Nd(III), Ti(IV), and Sn(IV), etc. (Ballinas et al. 2004; Kim et al. 2006; Yao et al. 2009; Thakre et al. 2010; Paudyal et al. 2012). Paudyal et al. (2012) prepared the chelate resin from orange juice residue after impregnating with some rare earth ions. The residue was first mixed with calcium hydroxide, forming the saponified orange juice residue (SOJR), which is further loaded with rare earth metal ions (Figure 13.1). Ca^{2+} ions presence in the saponified residue undergoes cation exchange reaction with the loaded metal ions.

Biomaterial-based activated carbon. Activated carbons have a very porous structure with a large internal surface area ranging from 500 to 2000 m^2/g and hence, good adsorption capacities towards various substances. Literature surveys indicate that there are many attempts to obtain low-cost activated carbons from biomass materials (Ioannidou and Zabaniotou 2007; Hesas et al. 2013). In principal, these biomass materials-based carbons could be produced by the physical activation and chemical activation methods (Ioannidou and Zabaniotou 2007).

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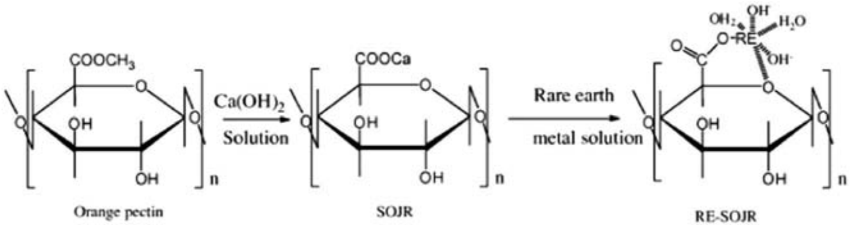

Figure 13.1. Impregnating of rare earth metal ions on SOJR (where, RE = La(III), Ho (III), Sm(III), Lu (III) and Sc(III) ions)

Source: Adapted from Paudyal et al. (2012); reproduced with permission from Elsevier

Physical activation of the biomasses is usually a two-stage process using gases such as nitrogen, steam, air, carbon dioxide or mixtures of the above(Ioannidou and Zabaniotou 2007). After the two-stage activation, the porous structure with the meso- and micro-pores is produced in these biomass-based activated carbons. Chemical activation involves a pretreatment scheme where the biomasses are impregnated with some chemicals before the activating reactions (Ioannidou and Zabaniotou 2007; Suhas et al. 2007). The common feature of these impregnationsleads to anincrease of carbonization ability and, therefore, development of a desired pore structure. The processes involve impregnation of biomass with the activating chemicals in solid or liquid form. Some widely used chemicals include NaOH (KOH), K_2CO_3, H_3PO_4, H_2SO_4 and $ZnCl_2$.

Physical and chemical activations have significantly increased the surface areas and pore volume of the biomass materials. However, the adsorption capacities of these virgin biomass carbons for anionic pollutants are still unsatisfactory, partially due to the low efficiency of porous structures for anions removal. Investigators have prepared the surface modified biomaterial carbons by impregnating with the cationic surfactants or metal ions (Cho et al. 2011; Zhang et al. 2012; Liu et al. 2013). As a result, these surfactant-loaded activated carbons, exert as both the activated carbons and anion exchange/chelate resins when eliminating anions from aqueous solution.

13.4.2 Biomass-Based Adsorbents Applied for Anionic Nutrients Removal

Wastewater discharges carrying excessive nutrients (i.e., nitrate, nitrite and phosphate ions) create a serious environmental problem worldwide. These nutrients discharged into surface waters can stimulate algae growth, resulting in eutrophication in aquatic environments (Mishra and Patel 2009). Adsorption of nitrate, nitrite and phosphate ions onto modified biomass wastes is a promising technology, which have been investigated for decades. The utilizations of various biomass-based adsorbents for nitrate, nitrite and phosphate ions removal are summarized in Table 13.4.

Nitrate. The nitrate, due to its high water solubility, is possibly the mostwidespread groundwater contaminant in the world which imposes aserious threat to

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Table 13.4. Comparative evaluation of biosorbents for removal of nitrate, nitrite and phosphate

	Biosorbents			*Biosorbents*		
Anions	*Biomass materials*	*Modifying chemicals (or physical conditions)*	*Adsorption capacity (mg/g)*	*Biomass materials*	*Modifying chemicals (or physical conditions)*	*Adsorption capacity (mg/g)*
Nitrate	Rice hull	Epichlorohydrin (EPI) and dimethylamine	75.0^{a,b}	Chinese reed	CHMAC and EPI	7.55^{f}
	Moringa hull		63.2^{a,b}	*Arundodonax* L. reed	EPI and DETA	44.61^{g}
	Lauan sawdust		47.7^{a,b}	Sugar beet pulp	Zirconium(IV)	63.0^{h}
	Coconut husk		55.2^{a,b}	Sugar beet bagasse	ZnCl (3:1); 500–700°C	9.14–27.55^{j}
	Persimmon tealeaf		48.4^{a,b}	Wheat straw charcoal	300°C;1 h	1.10^{k}
	Pine bark		65.7^{a,b}	Mustard straw	300°C; 30 min	1.30^{k}
	Sugarcane bagasse		63.2^{a,b}	Coconut	Untreated	10.2^{i}
	Wheat straw	EPI, diethylenetriamine (DETA) and triethylamine	87.21^{c}		ZnCl (2:1); 500°C	1.7^{i}
			27.5–89.8^{d}	Lignite activated carbon	Virgin carbon	14.25^{l}
		Aminated intermediate	52.8^{e}		CHMAC	27.56^{l}

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Phosphate	Wheat straw	Ethylenediamine (EDA)	22.91[d]	Coir pith	ZnCl (2:1); 700°C	5.4[s]
		DETA	22.32[d]	Activated fiber carbon	Virgin carbon	0.6[t]
		Triethylenetetramine (TETA)	20.40[d]		Hydroxyl-La doped	16.1[t]
		Aminated intermediate	45.7[e]		Hydroxyl-Fe-La doped	29.6[u]
		EPI, triethylamine and EDA	16.5–52.4[m]	Bagasse fibre	Untreated	0.25[v]
			55.8[n]		Chloroacetic acid	22.0[v]
			53.0[o]		Chloroacetic acid; $FeCl_3$	49.5[v]
	Giant reed	EPI, triethylamine and EDA	64.67[p]	Collagen Fiber	HCOOH and Fe (III)	28.5[w]
			34.13[q]		Zirconium(IV)	26.1[w]
	Cotton stalk		51.54[r]	Coconut coir pith	$Fe(NO_3)_3 \cdot 9H_2O$	23.16[x]
Nitrite	Sawdust	$FeCl_3$; Polypyrrole	14.0[y]	Carbon cloths	H_2SO_4	46.46*
		$(NH_4)_2S_2O_8$; Polyaniline	7.5[y]		Distilled water	0.23*
	Chitosan	Acetic acid; NaOH epichlorohydrin	7.5[z]	Charcoal	–	2.12**

Major references: [a]Orlando et al. (2002), [b]Orlando et al. (2003), [c]Xu et al. (2011a), [d]Xu et al. (2010b), [e]Xu et al. (2010c), [f]Namasivayam and Holl (2005), [g]Xu et al. (2012), [h]Hassan et al. (2010), [i]Bhatnagar et al. (2008), [j]Demiral and Gündüzoğlu (2010), [k]Mishra and Patel (2009), [l]Cho et al. (2011), [m]Xu et al. (2011b), [n]Xu et al. (2010a), [o]Chen et al. (2011a), [p]Xu et al. (2011c), [q]Yue et al. (2010), [r]Xu et al. (2011f), [s]Namasivayam and Sangeetha (2004), [t]Zhang et al. (2012), [u]Liu et al. (2013), [v]Carvalho et al. (2011), [w]Liao et al. (2006), [x]Krishnan and Haridas (2008), [y]Ansari et al. (2009), [z]Jing et al. (2008), *Afkhami et al. (2007), and **Mir (2010)

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water supplies. An increase in nitrate concentrations in drinking watercauses two adverse effects on human health: induction of “blue-baby syndrome” (methemoglobinemia)especially in infants, and the potential formation of carcinogenic nitrosamines (Bryan and van Grinsven 2013).

Currently, most of biosorbents applied for nitrate removal are based on amine crosslinked biomass-based resins. The promise of using these amine crosslinked biosorbents is because (1) they have the same functional groups existed in most commercial anion exchange resins and (2) they have the similar adsorption capacity for nitrate as compared with those of commercially available resins. Orlando et al. (2002) prepared some amine-based anion exchangers from different agricultural residues, e.g. lauan sawdust, sugarcane bagasse pine, bark, M. oleiferahul, coconut husk, persimmon tealeaf and rice hull. These agricultural residues anion exchangers show almost the same nitrate removal capacities (47.7–75.0 mg/g) as Amberlite IRA-900 (74.4 mg/g). Xu et al. (2012) prepared the Arundodonax L. reed based anion exchange resin (ALR-AE resin) by the amination reaction between Arundodonax L. reed, epichlorohydrin, triethylamine and diethylenetriamine. The maximum adsorption capacity for nitrate at 20°C was 44.61 mg/g (pH = 9.0). Amine groups grafted biomass wastes for nitrate adsorption were also reported in other literature (Namasivayam and Holl 2005; Xu et al. 2010b, c).

Basically, a remarkable feature for these amine grafted biosorbents is the significant increase in nitrogen content. The nitrogen contents in the agricultural residues resins prepared by Orlando et al. (2002) were in therange of 1.7–5.7%, as compared with the virgin agricultural residues of 0.3–0.9%. In the work of Gao et al. (2009), nitrogen content in wheat straw based resin (6.0%) was about 15 times higher than that in virgin straw (0.4%). This indicates that the modifying reactions proceed efficiently, and quite a number of amine groups were introduced onto the skeleton of these biomasses.

In addition to these biomass-based anion exchange resins, a PLE resin originated from sugar beet pulp was also produced by Hassan et al. (2010) for nitrate removal. The metal ion, zirconium(IV) was impregnated on the sugar beet pulp, forming the ligand exchanger. Energy dispersed X-ray (EDX)-SEM showed that Zr(IV) ions were strongly bound to the carboxylate groups of sugar beet pulp constituents, especially pectins. The maximum adsorption capacity of the Zr(IV)-loaded pulp for nitrate was 63.0 mg/g.

Some biomass-waste-based activated carbons have also been applied for the nitrate removal from water. Mishra and Patel (2009) described the capacities of physically activated wheat straw charcoal (WSC) and mustard straw charcoal (MSC) for nitrate elimination from wastewater. These carbons were prepared in a muffle furnace with heating at 300°C for 30–60 min. The calculated uptakes of WSC and MSC for nitrate were about 1.10 and 1.30 mg/g, respectively (15°C). Demiral and Gündüzoğlu (2010) eliminated the nitrate from aqueous solutions by sugar beet bagasse based activated carbon. The sugar beet bagasse was first chemically activated by $ZnCl_2$ solution and was carbonized in a vertical furnace at 700°C with specific surface area of 1826 m^2/g. The adsorption capacity

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increased from 9.14 to 27.55 mg/g with the temperature from 25 to 45°C (pH: 6.58). $ZnCl_2$ activation method was also applied byBhatnagar et al. (2008) for preparing the coconut granular activated carbon (GAC). The comparison between untreated and $ZnCl_2$ treated coconut GAC indicates that treatment with $ZnCl_2$ significantly improves the adsorption capacity of coconut GAC for nitrate from 1.7 to 10.2 mg/g. However, the uptake of nitrate by these biomass-based carbons is relatively lower as compared with those of biomass-based resins. Some attempts were made by introducing some functional groups into these carbons. For example, Cho et al. (2011) coated the lignite activated carbon with the quaternary ammonium polymer, [3-(methacryloylamino)propyl]-trimethylammonium chloride (CHMAC). The adsorption capacity of quaternary ammonium polymer-modified activated carbon for nitrate was about 27.56 mg/g, which is much higher than that of virgin activated carbon with 14.25 mg/g.

Phosphate. Phosphate in wastewaters provides an additional nutrient in the water bodies. Excess phosphate is one of the main reasons responsible for the eutrophication of receiving waters, particularly in lakes and slow-moving rivers. Eutrophication as well as the overgrowth of cyanobacteria (often calls red tide) due to the excess phosphate in recreational, industrial, and drinking water cansignificantly threaten human and ecological health. Therefore, the concentration of <0.03 mgP/L is considered as the criterion with regard to excessive algae growth in lakes and other confined water bodies, and wastewater containing phosphates must meet the discharge limit of 0.5–1.0 mgP/L. As a result, extra phosphate in water should be removed before its discharging into water bodies.

Some biomass-based resins have been applied for phosphate removal. Our groups prepared three different types of wheat straw based resins for phosphate adsorption (Xu et al. 2010a). The modified wheat straws were synthesized by grafting with three different modifying agents: ethylenediamine (EDA), diethylenetriamine (DETA) and triethylenetetramine (TETA). The experimental data of uptake capacity for phosphate were in the range of 20.40–22.91 mgP/g. A giant reed based resin was also prepared with the same method (Xu et al. 2011c). The adsorption capacity of the resin for phosphate was 54.67 mgP/g in comparison with the raw giant reed of 0.863 mgP/g. Wartelle and Marshall (2006) prepared the corn stover based resin with aquaternizing agent, CHMAC, in the presence of a strongly alkaline environment. Phosphate uptake by the quaternized corn stoverwas about 20.5 mg/g. The same groups also discussed the phosphate removal by CHMAC modified soybean hulls. The adsorption capacity for phosphate was about 19.5 mg/g. They observed that the soybean hull resin was more efficient in phosphate removal than the commercial cellulosebased resin (QA 52 resin) but not as effective as the commercial synthetic resin (Amberlite IRA-400).

Integral superficially carboxymethylated bagasse fibre doped with Fe^{2+} ions is an excellent alternative for removing phosphate from water (Carvalho et al. 2011). Thermal analyses and infrared spectroscopy show some changes incarboxymethylatedfibres after incorporation of grafted Fe^{2+} and adsorbed PO_4^{3-}. It is observed that the phosphate uptakes of bagasse fibre, carboxymethylated bagasse fibre and Fe^{2+} loaded carboxymethylated bagasse fibre are about 0.25, 22.0 and 49.2 mgP/g,

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respectively. The increased phosphate capacity on Fe^{2+} loaded carboxymethylated bagasse fibre is mostly ascribed to the Fe-P complexes formed on thesurface of the modified fibre. Liao et al. (2006) presented the adsorption behavior of phosphate by the PLE resin, metalions-loaded collagen fiber (MICF). These ligand exchangers-were prepared by loading Zr(IV) and Fe(III) onto collagen fiber. The adsorption capacity of phosphate on Zr-ICF (28.50 mg/g) was higher than that on Fe-ICF (26.10 mg/g), ascribed to the higher chelating ability of Zr(IV) with phosphate.

Biomass-based activated carbons applied for phosphate uptake was reported by Namasivayam and Sangeetha (2004). They prepared the $ZnCl_2$-treated coir pith activated carbon in a boiling solution containing zinc chloride at a weight ratio of 2:1 at 700°C. Langmuir adsorption capacity was found to be 5.1 mgP/g and got maximum in the pH range of 3–10. Uptake of phosphate by the $ZnCl_2$-treated carbon was unsatisfying because the adsorption was mainly based on porous adsorption (a small amount of existed functional groups may also contribute to the adsorption). An attempt was made by Zhang et al. (2012) using lanthanum hydroxide-doped activated carbon fiber (ACF-LaOH) to promote phosphate uptake. Lanthanum hydroxide ($La(OH)_3$) was loaded on ACF through the ultrasonic precipitation method. They calculated that the adsorption capacity of phosphate onto ACF-LaOHwas 16.1 mg/g (virgin ACF = 0.6 mg/g) and assign the mechanism toligand exchange, electrostatic interactions and Lewis acid-base interaction. The same groups also prepared the hydroxyl-iron-lanthanum doped activated carbon fiber (ACF-LaFe) for phosphate adsorption (Liu et al. 2013). The content of lanthanum and iron in ACF-LaFe determined by ICP was 189.82 mg/g and 24.67 mg/g respectively. They found that the adsorption capacity (29.4 mg/g) of ACF-LaFewas much higher than that of ACF-LaOH (16.1 mg/g); this indicates both La and Fe participate in the adsorption of phosphate.

Nitrite. Nitrite ion is one of the most important widespread contaminants of theaqueous environment and serves as a significant indicator of natural water quality. The increasing level of nitrite in surface or ground waters results mainly from theagricultural application of fertilizers as well as from many industrial processes. Nitrite ions enter the bloodstream through gills by a mechanism that normally transports chloride. Exposure to nitrite causes respiratory distress because of the loss in oxygen-carrying capacity of blood. Additional, the high concentration of nitrite in drinking water may cause struma, cancer and other diseases (Abidi 1982).

Ansari et al. (2009) dealt with the new application of polypyrrole and polyaniline electroactive polymers by coating on sawdust and then use them for removal of nitrite ions. The adsorption capacities of polypyrrole and polyaniline coated sawdust were about 14.0 and 7.5 mg/g, respectively. The cross-linked chitosan (CCTS) applied for nitrite uptake was prepared by using the crude macromolecule chitosan as the matrix material and epichlorohydrin as the crosslinked reagent under alkaline conditions (Jing et al. 2008). The maximum nitrite uptake by CCTS was only about 7.4 mg/g, which might be because of the low deacetylation degree, high crystallinity and the purity of the crosslinked chitosan they prepared. Physical adsorption is the dominant mechanism ofnitrite adsorption by CCTS since it is a porous solid with a high surface area.

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Additionally, electrostatic attraction by CCTS–NH_3^+ is also the important factor that control the nitrite adsorption.

Effect of acid treatment of carbon cloths (C-cloths) on the adsorption of nitrite ions was discussed by Afkhami et al. (2007). The C-cloths weresubmerged in a 4.0 mol/L of H_2SO_4 solution for the modification of surface functional groups and porous structures. The adsorption capacity of acid treated C-cloth for nitritewas 46.46 mg/g at 25°C and pH 7.0. This value is much higher than that obtained for distilled water treated C-cloth (2.3 mg/g). Mir (2010) presented the effect of electrolytes on the adsorption of nitrite and nitrate from aqueous solutions by activated charcoal. The adsorption of nitrite by activated charcoal was adequately explained by Freundlich and Langmuir isotherm models with parameters indicative of a beneficial adsorption. The maximum uptake of nitrite by activated charcoal was 2.12 mg/g (28.9 ± 0.4°C).

Generally, there is still limited researchonnitrite uptake by commercial adsorbents or biomass-based adsorbents. As a result, these studies are of great significance to control the nitrite level in drinking water as well as to solve the problem of the nitrite pollution in groundwater.

13.4.3 Biomass-Based Adsorbents Applied for Toxic Anions Removal

Toxic anions such as perchlorate, fluoride and cyanide ions are discharged into the aquatic environments mainly from industrial activities. Removal of these toxic anions from waters has received increasing attention in recent years because of their potential harmful impact on human health.

Perchlorate. As an emergent environmental contaminant, perchlorate has been detected in soil, surface water, as well as groundwater. Perchlorate salts, the compounds that are nonvolatile, highly soluble, and kinetically inert in water, can inhibit iodide uptake by the thyroid gland; in large doses, it is linked to anemia and fetal brain damage (Tikkanen 2006; Kumar et al. 2010). In February 2005, the US EPA established 24.5 μg/L as an official reference dose (RfD) for perchlorate in drinking water (U.S. EPA 2005).

Among several treatment technologies applied, adsorption is currently the most effective and commonly used technology for perchlorate removal from water. Baidas et al. (2011) reported a kinetic study of perchlorate by quaternary amine modified giant reed. The giant reed was reacted with epichlorohydrin to form cellulose ether and then quaternaried amine groups through cross-linking. The content of the quaternary amine charge was about 1.64 eq(+)/g which is equal to an exchange capacity of 162 mg-ClO_4/g. The adsorption capacity for perchlorate was 150.2 mg/g on the modified reed particles: this is just similar to the ClO_4^- exchange capacity calculated from content of the quaternary amine in modified reed. Quaternized biomass as an anion exchanger for the removal of perchlorate was also reported by Namasivayam and Holl (2005). They used the Chinese reed as a model biomass for the development of anion exchangers using a quaternization agent, N-(3-chloro-2-hydroxypropyl) trimethylammonium

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chloride (CHMAC). Uptake was maximized at pH 5.8 (10.07 mg/g). Peng et al. (2011) reported the modified mulberry shoot powder for perchlorate uptake. The mulberry shoot powder was modified by the cationic surfactant cetyltrimethyl ammonium bromide (CTAB). The uptake of perchlorate decreased from 15.06 to 10.68 mg/g as the temperature increased from 15 to 35°C, indicating an exothermic nature of adsorption process.

Biosorbentfrom chitosan with cationic modification has a potential for perchlorate removal from contaminated water. Xie et al. (2010) prepared the protonated cross-linked chitosan for the removal of perchlorate from aqueous solution. They observed that the maximum adsorption capacity is 45.46 mg/g at pH 4.0 (25 ± 1°C). Electrostatic attraction and physical force are the main driving forces for perchlorate adsorption by the protonated cross-linked chitosan.

Cyanide. Since cyanide is highly reactive, it will readily bind metals as a strong ligand to form complexes of variable stability. As a result, cyanide is considered as the most preferred solvent in the extraction of gold and silver ores over a century. Wastewaters generated in these operations often contain cyanide species i.e. free and metal-cyanides and cyanide related compounds at various levels. These cyanide species are classified as hazardous materials with acute and/or chronic characteristics of toxicity, which have highly adverse health effects on people, as well as other living organisms. Exposure to small amounts of cyanide can be deadly, irrespective of the route of exposure. Therefore, environmental regulations require reducing the cyanide concentration in wastewater to below 0.2 mg/L prior to discharge into the environment. But free cyanide is difficult to be removed from the aqueous by adsorbents. As a result, the adsorption of cyanide is mainly based on the uptake of metal-cyanide complexes from the cyanidation liquor (Gupta et al. 1987; Kurama and Catalsarik 2000).

Cyanide uptake using plain coconut shell activated carbonsand metal impregnated coconut shell activated carbons was discussed by Yazıcı et al. (2009). They observed that the uptake of cyanide by plain coconut shell activated carbons, copper and silver impregnation of activated carbons were 3.516, 6.032 and 16.426 mg/g, respectively. This indicates that the adsorption of cyanide is significantly enhanced via impregnation with metals. The waste brewery yeast and Aspergillus nigerwerereported to adsorb lead, copper and cadmium and their cyanide complexes (Kim et al. 2006). The adsorption of metal-cyanide complexes by Aspergillus niger follows the order asPb-CN (91.58 mg/g) > Cu-CN (33.43 mg/g) > Cd-CN (26.75 mg/g). Other metal impregnated wastes applied for cyanide uptake were reported by Soleimani and Kaghazchi (2008), Behnamfardand Salarirad (2009), and Yalcin and Arol (2002).

Fluoride. Fluoride in drinking water has significant advantages as well as detrimental effects on human health depending on its concentration (Yao et al. 2009). Biosorption is an emerging technique for fluoride-wastewater treatment utilizing abundantly available biomaterials. Various biosorbents have been developed for fluoride removal (Yao et al. 2009; Alagumuthu and Rajan 2010; Vijaya et al. 2011).

A novel biosorbentwas developed by the crosslinking of the anionic biopolymer, calcium alginate, with glutaraldehyde (Vijaya et al. 2011). The maximum uptake of

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fluoride occurred at pH 8.0 with maximum monolayer adsorption capacity of 73.5 mg/g. Chitosan coated silica (CCS) was also prepared for testing its potential in defluoridation(Vijaya and Krishnaiah 2009). FTIR results indicated that the hydroxyl and amine groups was responsible for fluoride sorption by CCS. The monolayer sorption capacity estimated using Langmuir model was 44.4 mg/g.

The profuse natural biomass, collagen fiber, has abundant functional groups and is capable of chemically reacting with many types of metal ions, which can be used as a carrier of metal ions and demonstrate as the PLE resins for defluoridation. Liao and Shi (2005) studied the adsorption behaviour of fluoride onto zirconium (IV)-impregnated collagen fiber with maximum adsorption capacity of 41.4 mg/g at 30°C. Yao et al. (2009) evaluated the application of neodymium(III)-modified chitosan as adsorbents for the removal of excess fluoride from water. The maximum adsorption capacities were between 11.41 and 22.38 mg/g. It is suggested that ligand exchange mechanism between fluoride and hydroxide coordinated on Nd(III) is held responsible for fluoride adsorption onto the adsorbent. The zirconium(IV)-loaded orange waste gel was used for the adsorption of fluoride from aqueous solution (Paudyal et al. 2012) andthe maximum sorption capacity of the gel for fluoride reached up to 22.8 mg/g, which was higher than that of zirconium(IV)-loaded Amberlite 200CT (9.5 mg/g) under the same experimental conditions.

Basically, these metal-impregnated biosorbentsare intensively used for fluoride removal from water. Some other related work reported by Ma et al. (2007), Sathish et al. (2007), (2008), Bansiwal et al. (2009), Alagumuthu and Rajan (2010), Thakre et al. (2010) are also shown in Table 13.5.

13.4.4 Biomass-Based Adsorbents Applied for Metal Complex Anions

Cr, As, and Se are metals of widespread use and frequently found in industrial wastewaters. These metal ions exist as metal complex anionic species in contaminated water. The release of liquids containing these anionic species into streams poses a threat not only to aquatic life but also to the health of human beings, throughout which they accumulate to higher concentration in food chain (Tang et al. 2003). To eliminate these toxic metal complex anions from water, some biosorbents with high selectivity can beprepared by incorporating the principle of metal complexation or exchange (Marshall and Wartelle 2004; Wartelle and Marshall 2006; Anirudhan and Unnithan 2007; Babu and Gupta 2008; Chen et al. 2011b).

Cr(VI). In the environment, chromium occurs mainly in two stable oxidation states Cr(III) and Cr(VI). The Cr(VI) state is known to be much more toxic and hazardous than Cr(III). Cr(VI) causes skin irritation resulting in ulcer formation. Over exposure to Cr(VI) leads to liver damage, pulmonary congestion, and oedema. Cr(III) is about 300 times less toxic than Cr(VI) and due to the fact that has limited hydroxide solubility, less mobility and bioavailability.

In recent reports, numerous biomass wastes were tested as alternative adsorbents to remove Cr(VI) (Babu and Gupta 2008; Wang et al. 2008; Chen et al. 2011b). Basically, uptake of Cr(VI) by these virgin biomasses was relatively high. Table 13.6

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Table 13.5. Comparative evaluation of biosorbents for theremoval of perchlorate, cyanide and fluoride

	Biosorbents			
Anions	*Biomass materials*	*Modifying chemicals (or physical conditions)*	*Adsorption capacity (mg/g)*	*References*
Perchlorate	Giant reed	EPI, triethylamine and EDA	150.2	Baidas et al. (2011)
	Chinese reed	CHMAC and EPI	10.07	Namasivayam and Holl (2005)
	Chitosan	Acetic acid; hydroxide solution; glutaraldehyde solution	45.46	Xie et al. (2010)
			37.98	Xie et al. (2009)
			34.39	
			128.78	
	Mulberry shoot	CTAB	15.06	Peng et al. (2011)
			10.68	
Cyanide	Coconut shell	Activated; HCl solution	16.39	Behnamfard and Salarirad (2009)
	Coconut shell	activated	3.516	Yazıcı et al. (2009)
		Cu impregnated	6.389	
		Ag impregnated	16.426	
	Rice husk	Untreated	0.401	
	Brewery yeast	Pb impregnated	21.76	Kim et al. (2006)
		Cu impregnated	14.36	
		Cd impregnated	9.442	
	Aspergillus niger	Pb impregnated	91.58	
		Cu impregnated	33.43	
		Cd impregnated	26.75	

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Fluoride	Alginate	Glutaraldehyde	73.6	Vijaya et al. (2011)
	Chitosan	Chitosan coated silica	44.0	Vijaya and Krishnaiah (2009)
	Chitosan	Nd(III)	11.41–22.38	Yao et al. (2009)
	Coconut shell	$ZrOCl_2$	7.51	Sathish et al. (2007)
	Coconut fiber	$ZrOCl_2$	40.02	Sathish et al. (2008)
	Collagen fiber	$Zr(SO_4)_2$	2.18–2.70	Liao and Shi (2005)
	Corn cobs powder	AlCl3	18.9	Parmar et al. (2006)
		CaCl2	15.12	
	Ground nut shell	Activated; $ZnOCl_2$	13.91	Alagumuthu and Rajan (2010)
	Orange Waste	$ZnOCl_2$ solution	22.8	Paudyal et al. (2012)
	Chitosan	$FeCl_3$; Fe_3O_4; alginate	22.49	Jagtap et al. (2009)
	Chitosan beads	La-incorporated	4.7	Bansiwal et al. (2009)

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Table 13.6. Comparative evaluation of biosorbents for removal of Cr(VI), As(V)/As(III) and Se(VI)/Se(IV)

	Biosorbents			
Anions	*Biomass materials*	*Modifying chemicals (or physical conditions)*	*Adsorption capacity (mg/g)*	*References*
Cr(VI)	Wheat bran	Untreated	40.8	Wang et al. (2008)
	Rice bran		58.9	
	Tea waste		107.8	Albadarin et al. (2013)
	Date pits		96.0	
	Maize cob		13.8	Kobya (2004)
	Sawdust		39.7	
	Banana skin	Sodium alginate; $CaCl_2$	249.6±4.2	Park et al. (2008)
	Cotton stalk	EPI, triethylamine and EDA	129.0	Xu et al. (2011d)
	Wheat straw		295.4	Xu et al. (2011e)
	Corn stalk	EPI, triethylamine and DETA	227.3	Chen et al. (2011b)
			125–203	Chen et al. (2012)
	Wheat straw		322.6	Chen et al. (2010)
	Neem leaves	HCl; copper solution	62.97	Babu and Gupta (2008)
	Sludge biomass	HCl solution	246.0	Wu et al. (2010)
	Chitosan	Sodium hydroxide; $CuSO_4$; Ag_2SO_4	1100.0	Modrzejewska et al. (2006)
	Lignin	500 K; NaOH	39.5	Demirbas (2005)
	Rubber wood	Polyacrylamide	22.6	Raji and Anirudhan (1998)
	Ucides shells	Acid-washed (HCl)	28.08	Niu and Volesky (2003)

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As(V)/As(III)	Coconut coir pith	EPI, dimethylamine	13.57 [As(V)]	Anirudhan and Unnithan (2007)
	Corn stover	CHMAC	51.75 [As(V)]	Wartelle and Marshall (2006)
	Cellulose	$CaCl_2$, and NaH_2PO_4	12.72 [As(V)]	Islam et al. (2011)
	Orange waste	Phosphorylation; iron(III)	68.25 [As(V)]; 68.25 [As(III)]	Ghimire et al. (2003)
	Chitosan	Ceramic alumina	96.5 [As(V)]; 56.5 [As(III)]	Boddu et al. (2008)
	S. xylosus	$FeCl_3$	61.34 [As(V)]; 54.35 [As(III)]	Aryal et al. (2010)
	Cellulose	Fe(III)-loaded	137.1 [As(V)]; 18.0 [As(III)]	Ballinas et al. (2004)
	Chitosan	$Fe(NO_3)_3 \cdot 9H_2O$	6.86 [As(III)]	Gang et al. (2010)
	Orange waste	$ZrOCl_2 \cdot 8H_2O$	88.0 [As(V)]; 130.0 [As(III)]	Biswas et al. (2008)
Se(VI)/Se(IV)	Soybean hulls	CHMAC	43.45 [Se(VI)	Marshall and Wartelle (2004)
	Corn stover		45.82 [Se(VI)	Wartelle and Marshall (2006)
	Ucides shells	Acid-washed (HCl)	11.8 [Se(VI)]	Niu and Volesky (2003)
	Crab shells	Power form	0.996 [Se(IV)]	Jegadeesan et al. (2003)
	Lignite coal (activated carbon)	Acid-washed	4.915 [Se(IV)]	
			5.782 [Se(IV)]	
			4.143 [Se(IV)]	
	Peanut shell	Sulphuric acid (Wet)	42.96 [Se(IV)]	El–Shafey (2007a)
		Sulphuric acid (Dry)	32.15 [Se(IV)]	
	Rice husk	Sulphuric acid (Wet)	40.92 [Se(IV)]	El–Shafey (2007b)
		Sulphuric acid (Dry)	34.13 [Se(IV)]	

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illustrates the capacities of some virgin biomass materials for Cr(VI) adsorption. Cr(VI) uptake by virgin wheat bran and rice bran was 40.8 and 58.9 mg/g, respectively (Wang et al. 2008). Albadarin et al. (2013) observed the high uptake of Cr(VI) by tea waste (107.8 mg/g) and date pits (96.0 mg/g). The uptake of anionic Cr(VI) was a complicated process; wherein electrostatic attraction, reduction, ion exchange and surface complex formation are involved. Cr(VI) was able to form surface complexes with the protonated functional groups on the virgin biomass, for instance $-NH_2$, $-OSO_3$ and $-COOH$ (Albadarin et al. 2013). They can also oxidize the secondary alcohol groupswhile being reduced to Cr(III) cations. As a result, Park et al. (2008) proposed that Cr(VI) removed by natural biomaterialswas through a "redox reaction". The mechanism consists of three steps: (i) the binding of anionic Cr(VI) to the positively-charged groups present on the biomaterial surface, (ii) the reduction of Cr(VI) to Cr(III) by adjacent electron-donor groups, and (iii) the release of the reduced Cr(III) into the aqueous phase due to electronic repulsion between the positively-charged groups and the Cr(III), or the complexation of the reduced Cr(III) with adjacent groups (Figure 13.2).

A suitable modification of these biomaterials can further increase the Cr(VI) uptakes. Chen et al. (2011b) discussed the adsorption of Cr(VI) by corn stalk based biosorbent. The biosorbentwas synthesized by introducingwith diethylenetriamine andtriethylamine onto the virgin corn stalk. Amine groups in the biosorbent significantly improved the force of electrostatic attraction between Cr(VI) and biosorbent. As a result, uptake capacity for Cr(VI) was significantly increased. The maximum adsorption capacity of modified corn stalk for Cr(VI)

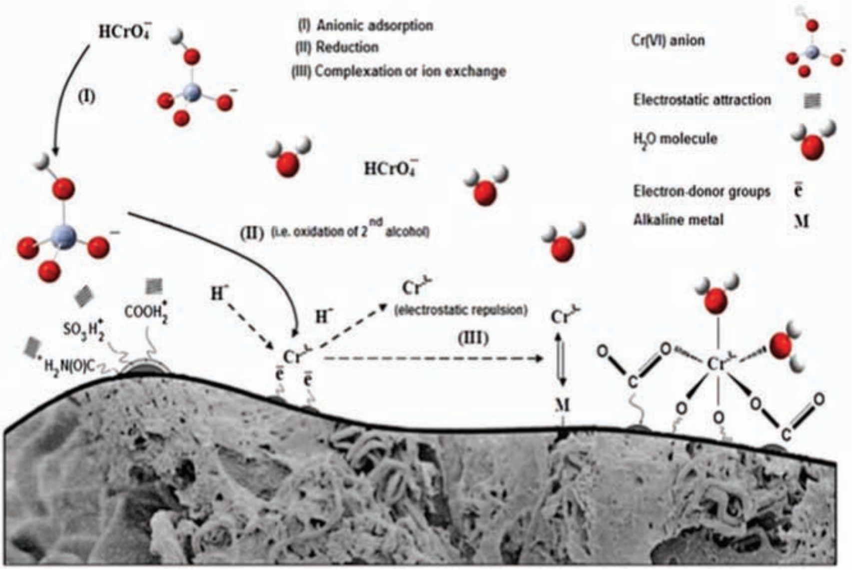

Figure 13.2. Proposed mechanism of Cr(VI) uptake by biomaterials
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was 227.3 mg/g at 40°C which was relatively higher as compared with those of some adsorbents as reported. Relevant work was also presented by our groups (Xu et al. 2011d, e; Chen et al. 2012). Park et al. (2008) developed a new alginate gel-based Cr(VI)-biosorbent from agricultural wastes. They observed that among some agricultural wastes (e.g., banana skin, green tea waste, oak leaf, walnut shell, peanut shell and rice husk), banana skin was the most efficient biomaterial to remove toxic Cr(VI) from aqueous solution. The maximum adsorption capacity was 249.6 ± 4.2 mg/g of Cr(VI) at initial pH 1.5. Mechanism of Cr(VI) biosorption by the Cr(VI)-adsorbent was its reduction into Cr(III) and binding of the reduced-Cr(III) on the surface of the adsorbent.

Some activated biomasses were reported for the removal of Cr(VI) from water. Babu and Gupta (2008) discussed the kinetic studies of the activated neem leaves for Cr(VI). Neem leave was first activated by concentrated HCl (36.5 wt%) and then was impregnated with copper solution (100 mmol/L). The maximum adsorption capacity obtained from Langmuir isotherm model was 62.97 mg/g at initial pH 2.0 and temperature 30°C. Wu et al. (2010) conducted batch experiments to remove Cr(VI) from aqueous solution using activated sludge biomass. The protonated sludge biomass was prepared by adding the raw sludge biomass into HCl solution. It is suggested that acid pretreatment of sludge biomass can successfully remove most of hydrogen–consuming substances and supply a steady acid environment for Cr(VI) removal. As a result, acid pretreatment significantly improves the Cr(VI) removal efficiency and increase Cr(VI) reducing capacity. Other relevant work reported by Raji and Anirudhan (1998), Niu and Volesky (2003), Demirbas (2005), and Modrzejewska et al. (2006), etc, is shown in Table 13.6.

As(V) and As(III). Arsenic is present in water as a result of both natural and anthropogenic activities. The most common species of arsenic in natural waters are forms of arsenite and arsenate, referred to as As(III) and As(V), respectively. Long-term drinking water exposure causes skin, lung, bladder, and kidney cancer as well as pigmentation changes, skin thickening (hyperkeratosis) neurological disorders, muscular weakness, loss of appetite, and nausea. Arsenic in natural waters is a worldwide problem which has been reported recently in the USA, China, Chile, Bangladesh, Japan and India. In water, As(V) is more prevalent in aerobic surface waters and As(III) is more likely to occur in aerobic ground waters (Behpour et al. 2005).

Some biomass by-products have proved to be useful and low-cost for the adsorption of As(V) and As(III) from water. Anirudhan and Unnithan (2007) discussed the performance of a new anion exchanger prepared from coconut coir pith for the removal of As(V) from aqueous solutions. The coconut coir pith anion exchanger (CP-AE) carrying dimethylaminohy-droxypropyl weak base functional group was synthesized by the reaction of coconut coir pith with epichlorohydrin and dimethylamine followed by treatment with hydrochloric acid. The results were analyzed using the Langmuir equation, and the uptake calculated at 20°Cwas 13.57 mg/g. Uptake of As(V) by cellulose-based anion exchange resin derived from corn stoverwas discussed by Wartelle and Marshall (2006). The virgin corn stoverwas quaternized with CHMAC with As(V) uptake of 51.75 mg/g. Islam

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et al. (2011) preparedthe cellulose-carbonated hydroxyapatite nanocomposites (CCHA) by using cellulose solution, $CaCl_2$, and NaH_2PO_4. The maximum adsorption capacity calculated from Langmuir isotherm model was up to 12.72 mg/g at temperature 45°C and pH 7.0. The thermodynamic study indicated an endothermic, spontaneous and favorable nature of As(V) adsorption by CCHA. They also ascribe the probable arsenate adsorption to the exchange of phosphate ions present in CCHA nanocomposite by the arsenate ions present in the synthetic arsenate solution.

As shown in Table 13.6, a series of chelating resins originated from these biomaterials andwere used for arsenic removal. Ghimire et al. (2003) reported the As(V) and As(III) uptake by iron(III) loaded cellulose and orange waste. The cellulose and orange waste were chemically modified by means of phosphorylation and then were further loaded with iron(III) so as to create a suitable chelating environment for As(V) and As(III). The maximum As(V) and As(III) uptake was evaluated as almost the same, i.e., 68.25 mg/g. Boddu et al. (2008) prepared a biosorbent by coating ceramic alumina with the natural biopolymer, chitosan, using a dip-coating process. The monolayer adsorption capacity of the biosorbent, as obtained from the Langmuir isotherm, was 56.50 and 96.46 mg/g for As(III) and As(V), respectively. The difference in adsorption capacity may be attributed to the stronger interaction of As(V) with the adsorbent through electrostatic forces of attraction. As(III) and As(V) biosorption using biomass *Staphylococusxylosus* pretreated with Fe(III) solutions were investigated by Aryal et al. (2010). FTIR shows that carboxyl groups were mainly responsible for Fe(III) binding, whereas As (III) and As(V) were adsorbed on the biomass surface through interaction with $-FeOH$ and $-FeOH_2^+$ groups. The maximum uptakeis calculated using Langmuir model and calculated to be 54.35 and 61.34 mg/g for As(III) and As(V), respectively.

The tea fungus, a waste produced during black tea fermentation, was examined for its capacity to uptake some ions from groundwater samples. The $FeCl_3$ pretreated tea fungal mat were exploited for removal of As(III) and As(V) from groundwater samples(Murugesan et al. 2006). $FeCl_3$-pretreated and autoclaved fungal mats remove 100% of As(III) and 77% of As(V). Other similar reports regarding to the As(III) and As(V) removal by biomass wastes are shown in Table 13.6 (Ballinas et al. 2004; Biswas et al. 2008; Gang et al. 2010).

Se(VI) and Se(IV). Selenium is a relevant element due to its important role in life processes, being recognized as an essential nutrient. On the other hand, selenium is toxic at concentrations above 1mg of selenium per kg of body weight. Selenate [Se(VI)] and selenite [Se(IV)] are two species of selenium that dominate in aqueous systems. In general, selenium species in the +4 oxidation state are more toxic than the species containing selenium in their +6 state (Tsoi and Leung 2011).

Agricultural by-products are generally poor adsorbents for uptake selenic fromsolution. Therefore, modification of these by-products is required. Soybean hulls and corn stoverwerequaternized with the CHMAC, in the presence of a strongly alkaline environment (Marshall and Wartelle 2004; Wartelle and Marshall 2006). They observed that the adsorption capacity of modified residues for Se(VI) was about 43.45 mg/g, similar to that of resin Whatman QA 52 (38.71 mg/g) but

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lower than that of Amberlite IRA-400 (71.1 mg/g). Niu and Volesky (2003) prepared the acid–washed crab shells for uptake of Se(VI). Raw crab shell material was washed with 1 N HCl for 16 h and then rinsed with distilled water until the final pH stabilized at pH 4. The residual material contained 53 ± 4% of chitin, 43 ± 3% of protein, 0.2 ± 0.1% of ash, 4 ± 0.3% of moisture and other matters. Equilibrium biosorption uptake by acid-washed crab shells was up to 11.8 mg/g at pH 3.0.

Some carbon-based biosorbents have also been used for selenic removal. Jegadeesan et al. (2003) discussed the adsorption characteristics of carbon-based adsorbents such as activated carbon and chitin for the removal of Se(IV). Chitin (R-$NHCOCH_3$) was obtained in powder form, which was prepared from crab shells. Adsorption capacities of the adsorbents were reported with the order of chitin (0.996 mg/g, pH = 4.0) < activated carbon (4.143 mg/g, pH = 4.0). The carbonaceous sorbents (carbonized wet product and dry product) were prepared from peanut shell and rice husk by sulphuric acid treatment for Se(IV) removal (El-Shafey 2007a; El-Shafey 2007b). Adsorption was found to fit the Langmuir equation, and sorption capacity for the wet sorbent (40.92−42.96 mg/g) was higher than that (32.15−34.13 mg/g) for the dry one. Physicochemical properties show an increase in sorbent acidity, exchange capacity and surface functionality after the reaction with acidified Se(IV); this indicates the oxidation process occurring on thesurface of biosorbent.

13.5 REGENERATION OF BIOSORBENTS

One of the fundamental requirements with any adsorbents including commercial adsorbents and biosorbents is their abilities to be regenerated and reused over a number of adsorption/desorption cycles. Natural polymers or biopolymers are biodegradable. This may be a serious disadvantage for long-term application in anions adsorption. Adsorbent recycling is necessary for cost-efficient use of these biopolymers for environmental applications.

The regeneration properties of some biosorbents are list in Table 13.7. Basically, biomaterial-based resins including anion exchange resins and chelate resins show relatively higher stability for reuse. Our groups prepared some agricultural by-product based resins for phosphate, nitrate and Cr(VI) removal (Xu et al. 2010b, 2011d, f). The resins with adsorbed ions can be effectively regenerated by both HCl and NaCl solutions through an ion exchange mechanism. Anirudhan et al. (2012) study the regeneration of phosphate loaded polyethylenimine-crosslinked cellulose resin by Na_2CO_3 (0.1 mol/L). The spent resin still retains 90.2% of uptake capacity after six regeneration cycles. Desorption of Cr(VI) from polyacrykamide-grafted sawdust by NaCl (0.5 mol/L) and NaOH (0.2 mol/L) was discussed by Raji and Anirudhan (1998). Regeneration efficient using NaClwas about 92.4% after three cycles, which was a bit lower than that (97.3%) of NaOH. Aryal et al. (2010) used 0.09 mol/L HCl to desorb the As(III) and As(V) ions from Fe(III)-treated *Staphylococcusxylosus*. The As(III) and As(V)

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Table 13.7. Desorption properties of some biosorbents for different anions

Biosorbents	*Anions*	*Eluents*	*Regeneration capacities*	*References*
Wheat straw based resin	Nitrate	HCl (0.1 mol/L)	87.4% after 4 cycles	Xu et al. (2010b)
		NaCl (0.1 mol/L)	86.6% after 4 cycles	
	Phosphate	HCl (0.1 mol/L)	90.5% after 4 cycles	
		NaCl (0.1 mol/L)	88.1% after 4 cycles	
Amine-crosslinked wheat straw	Phosphate	HCl (0.1 mol/L)	98.1%	Xu et al. (2011d)
Amine-crosslinked wheat straw	Cr(VI)	HCl (0.1 mol/L)	74.8%	
Diethylenetriamine-crosslinked cotton stalk	Phosphate	HCl or NaCl (0.1 mol/L)	92% after 3 cycles	Xu et al. (2011f)
Polyethylenimine-crosslinked cellulose	Phosphate	Na_2CO_3 (0.1 mol/L)	90% after 6 cycles	Anirudhan et al. (2012)
Protonated cross-linked chitosan	Perchlorate	NaOH	More than 90% after 15 cycles	Xie et al. (2010)
Amine-crosslinked coconut coir pith	As(V)	HCl (0.1 mol/L)	93.8% after 4 cycles	Anirudhan and Unnithan (2007)
Amide loaded-rubber wood	Cr(VI)	NaOH (0.2 mol/L)	99.2% after 1 cycle; 97.3% after 3 cycles	Raji and Anirudhan (1998)
		NaCl (0.5 mol/L)	98.2% after 1 cycle; 92.4% after 3 cycles	

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Fe(III)-treated *Staphylococcus xylosus*	As(III) and As(V)	HCl(0.09 mol/L)	100%	Aryal et al. (2010)
Zr(IV)-loaded orange waste gel	As(III) As(V)	NaOH (1 mol/L)	96% 95%	Biswas et al. (2008)
Zn (IV)-impregnated collagen fiber	Fluoride	NaOH	More than 97%	Liao et al. (2006)
Zn(IV)-loaded orange waste gel	Fluoride	NaOH (0.1 mol/L)	90% after 10 cycles	Paudyal et al. (2012)
La(III) incorporated chitosan beads	Fluoride	NH_4Cl (1 mol/L)	81.22%	Bansiwal et al. (2009)
Fe-modified husk activated carbon	Cr(VI)	NaOH (0.1–2.0 mol/L)	7.7–18.4%	Liu et al. (2010)
$ZnCl_2$-treated Casurina-equisetifolialeaves carbon	Cr(VI)	NaOH (1 mol/L) HCl (2 mol/L)	45% 60%	Ranganathan (2000)
$ZnCl_2$-treated coir pith carbon	Phosphate	HCl NaOH	30% (pH 2.0) 50% (pH 11.0)	Namasivayam and Sangeetha (2004)
Copper impregnated coconut husk carbon	As(III) As(III)	30% H_2O_2 Distilled water	88.6–94% 2.23%	Manju et al. (1998)

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ions can be 100% desorbed from the chelate resin in a short period of time. Desorption of As(V) and As(III) from Zr(IV)-loaded orange waste gel was conducted by Biswas et al. (2008) using 1 mol/L of NaOH. The elution was found to be very efficient since 95% and 96% of the adsorbed As(V) and As(III) was eluted using less than 15 ml of eluent. The adsorption of anions by these amine or metal-loaded biomaterialresins proceeds via electrostatic interaction, ion exchange, and ligand exchange. As a result, desorption occurs quickly through these reversible reactions.

In contrast to those of biomaterial-based resins, it seems that the adsorbed anions are difficult to be eluted from the biomaterials based activated carbons. Liu et al. (2010) regenerate the spent Fe-modified husk activated carbonafter adsorption of Cr (VI) using NaOH solutions (0.1—2.0 mol/L). They observed that the NaOH solutions can only elute 7.7–18.4% of the adsorbed Cr(VI). Ranganathan (2000) desorbed the Cr(VI) from $ZnCl_2$-treated Casurinaequisetifolia leaves carbon by 1 mol/L of NaOH and 2 mol/L of HCl. The regeneration efficiencieswere only 45% and 60%. A similar result was observed in the work of Namasivayam and Sangeetha (2004), in which NaOH and HCl can only elute 30–50% of phosphate from $ZnCl_2$-treated coir pith carbon. The adsorbed anions were attached to the porous structures of biomaterials activated carbons resulting in the decrease in desorption capacity. Of course, the high regeneration efficiency can be realized but it may need some different eluents. Manju et al. (1998) desorb the adsorbed As(III) from copper impregnated coconut husk carbon 30% H_2O_2 in 0.5 M HNO_3. H_2O_2 in dilute HNO_3 achieves 94.1%, 90.5 and 83.4% of As(III) recovery after 1, 2 and 3 cycles. The higher desorption of As(III) by H_2O_2 in dilute HNO_3 was due to the formation of neutral H_3AsO_3 molecules which were not adsorbed onto the positive surface of activated carbon.

However, there may be an inherent disadvantage of these biosorbentswith respect to the weight losses during eluting process, partially due to the destruction of cellulose when using acidic and alkaline eluents. Xu et al. (2011c) used eluents of HCl and NaOH solutions for desorption of phosphate from wheat straw based resins. Although both the acidic and alkaline eluents can efficiently desorb the phosphate from the resins, 1–3% of weight of the resin was lost after one elution cycle (90 mins). Similar loss in weight was also observed by Lodeiro et al. (2006), who reported a weight loss (27%) of protonated Sargassummuticum after the eleventh sorption-desorption cycles by using 0.1 mol/L of HNO_3 solution as the eluent. A long eluent time might cause the destruction of cellulose/hemicellulose structure in these biosorbents. On thecontrary, a short elution process could be ineffective, so it is important to balance this procedure appropriately.

13.6 CONCLUSIONS AND FUTURE PERSPECTIVES

In this chapter, we present the applications of biomass-based adsorbents for anionic pollutants removal. These renewable biomasses are used as starting

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materials for various biosorbents production. Two types of biosorbents, biomaterial-based resins and biomaterial based activated carbons are intensively used. Virgin biomaterials show few adsorption capacities for most anions except Cr(VI) ions. Cr(VI) removed by natural biomaterials is through a "redox reaction." Most biomaterial based resins are prepared by introducing some amine/quaternary ammonium groups or multi-valentmetal ions on these virgin biomaterials, forming the anion exchange/chelate resins. They have equal or even greater adsorption capacities for all anions as compared with those of commercial resins.

Uptake of anions by biomass-based carbons is relatively lower as compared with those of biomass-based resins. Currently, metal impregnated biosorbents are mainly used for fluoride, cyanide and arsenic uptake. The spent biosorbents can be regenerated by acid, alkali and sodium chloride treatments. However, weight losses of the resins are observed due to the destruction of cellulose at acidic and alkaline conditions.

In future research, it is worthwhile to investigate towards (a) modification of biomaterial-based adsorbents in pilot plants, (b) evaluation of economic feasibilityand (c) applications of these adsorbents in field conditions. Some biomaterial-based activated carbons have been commercially used, but they are mainly applied for removal of dyes or organic materials. Rare references related to pilot-scale produced or commercially used biomaterial-based resins were reported. As a result, attempts atpreparation of biomass-based resins in pilot scale should be made. Economic feasibility of the products should also be evaluated. Some reported work has discussed the costs of their bio-products, but most costs are evaluated in lab scales and treatment costs of the disposals produced during the preparing processes may be out of consideration in most cases. Additional, the costs of the biosorbents will also vary when/where the adsorbents were made, in/for developed countries, developing countries or underdeveloped countries. The particular biosorbents which show excellent uptake of anions in the laboratory under batch conditions may fail in field conditions. Some factors may affect these adsorption processes including (1) the selected biosorbents applied for anions removal, (2) the range of initial concentrations of anions, (3) pH in water, (4) the existed competing ions and their concentrations in water, and (5) proper operation and maintenance. Selection of a suitable biosorbent for an effectiveanion removal is important and is also a complicated task. It would be worthwhile if more biosorbentsare efficiently applied in different field conditions.

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CHAPTER 14

Agricultural By-Products for Phosphorous Removal and Recovery from Water and Wastewater: A Green Technology

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14.1 INTRODUCTION

Phosphorus (P) is a critical nutrient for the plant growth (Mezenner and Bensmaili 2009). In addition, as a component of DNA, RNA, ATP, phospholipids, P plays an important role in animal lives (Karachalios 2012). Furthermore, P is one of the principal materials for many industries, such as fertilizer, pesticide, steel production, etc. (Choi et al. 2012). The excessive amount of P in aquatic medium may originate from natural sources (e.g. precipitation, soil erosion, decomposition of organic matters) and/or artificial sources (e.g. mining, fertilizers, detergents, human and animal excreta). Karachalios (2012) claims that the agricultural runoffs contribute more than 50% to the freshwater eutrophication. The level of PO_4-P in municipal wastewater is in the range of 4–15 mg/L, while it may exceed 10 mg/L in industrial wastewater (Peleka and Deliyanni 2009). According to Biswas (2008), each person discharges 2–3 g P into domestic wastewater via feces and urine per day. The concentration of P in receiving water bodies greater than 0.02 mg/L may induce eutrophication (Ismail 2012; Mallampati and

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Valiyaveettil 2013). This phenomenon leads to the depletion of oxygen in aquatic medium, thus threatening the aquatic lives (Jyothi et al. 2012). To prevent aquatic medium from eutrophication, United States Environmental Protection Agency recommended that the PO_4^{3-} levels should not be higher than 0.05 mg/L if streams discharge into lakes or reservoirs (Benyoucef and Amrani 2011; Ismail 2012). To meet more stringent environmental regulations, the removal of P from water and wastewater is necessary (Kalmykova and Fedje 2013). Also, there was a warning that the global existing rock P reserves could be depleted in 50–100 years (Ogata et al. 2012; Eljamal et al. 2013). Due to increasing scarcity of natural P ores, the P recovery from water and wastewater has recently become a matter of urgent (Anirudhan et al. 2006; Zhang et al. 2012).

Understanding different forms of P in aqueous solutions enables an appropriate selection of treatment technologies (Neethling 2011). Though, in natural water bodies, P can exist in different forms (Figure 14.1), only orthophosphate can accelerate the algae growth, inducing the eutrophication (Bhojappa 2009). Depending on pH values of the aquatic medium, orthophosphate may exist in various species. In strongly alkaline conditions, PO_4^{3-} is the main form, whilst in weakly alkaline conditions, HPO_4^{2-} is dominant. In weekly acidic conditions, $H_2PO_4^-$ prevails, whereas H_3PO_4 is most common in strong acidic conditions (Karachalios 2012).

Until now, various technologies are available for controlling PO_4^{3-} pollution. These processes can be classified as chemical methods (precipitation, crystallization, anion exchanger, and adsorption), biological methods (assimilation, enhanced biological phosphorus removal, land treatment system, constructed wetlands), and physical methods (microfiltration, reverse osmosis, electrodialysis, and magnetic separation) (Hu et al. 2005; Zhang et al. 2007; Bhojappa 2009; Benyoucef and Amrani 2011). Of these methods, chemical precipitation and biological processes are most commonly used. However, each method represents its own demerits (Table 14.1). The chemical precipitation is often prone to high chemical expense, effluent neutralization requirement, inadequate efficiency for dilute P solutions, etc. (Kumar et al. 2010; Zhang et al. 2011; Mallampati and Valiyaveettil 2013). Similarly, the biological process associated with activated sludge systems

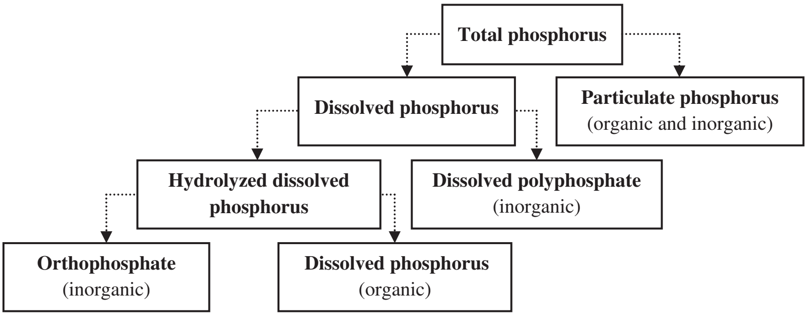

Figure 14.1. Different forms of phosphorus in aqueous solutions

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Table 14.1. Comparison of different technologies for phosphorous removal

Methods	*Effluent features*	*Advantages*	*Disadvantages*
Chemical precipitation	EPC: 0.005–0.04	• Easy to install • Flexible • High P removal efficiency • Less space	• Inappropriate for wastewater with low P concentrations • High cost for chemicals • Chemical sludge generation • Neutralization of effluent • Do not recycle P • Cannot meet strict regulations
Crystallization	EPC: 0.3–1.0	• Final product can be used as a fertilizer without further processing	• Chemicals and operation skills are necessary • Complex process • Increased salinity
Biological P removal	EPC: 0.1–0.3 RE < 30	• Avoiding chemical use • Potential P recovery	• More complex technology • Low removal efficiency (10–30%) • Biological sludge handling • External carbon source may be required • Sensitive to changes in temperature and P load (min. ~0.02 mgP/L is required) • Inefficient P recovery • Cannot meet strict regulations
Enhanced biological P removal	$0.02 \leq \text{EPC} < 0.1$, depending on duration RE: 100	• Can remove P to very low levels • Modest cost • Minimal sludge production	• More energy consumption • More space

(Continued)

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Table 14.1. Comparison of different technologies for phosphorous removal (Continued)

Methods	*Effluent features*	*Advantages*	*Disadvantages*
Constructed wetlands	EPC: 0.02; RE: 39–99, depending on plant type	• Low cost • Low technology	• Sediments
Magnetic separation	EPC: 0.1–0.5	• High P removal • Low power input	• Chemicals required • Technology is complex
Membrane technology	EPC: 0.04 (MBRs, Tertiary membrane filtration); 0.008 (RO); <0.005 (Electro dialysis)	—	• High capital & operation cost
Ion exchange		• Simple operation • Adaptability to various solution compositions and flow rates • High P removal • Struvite produced can be used in agriculture	• High capital & operation cost • Complex technology • Chemicals required • Low selectivity • Materials originated from nonrenewable resources
Adsorption	EPC: 0.005–0.01 RE > 80	• Simple operation • Cost-effectiveness • Recommended for low P concentration wastewater • Few chemicals involved • Without additional sludge • Potential P recovery • Multiple regeneration of adsorbents	• Experimental technology • High cost • Disposal problems after use

Note: EPC = Effluent phosphorous concentration (mgP/L); RE = Removal efficiency (%)

Sources: Biswas (2008), Everglades Hub (2013), Kumar et al. (2010), Li et al. (2009), Loganathan et al. (2014), Mallampati and Valiyaveettil (2013), Nguyen et al. (2012), Ning et al. (2008), Peleka and Deliyanni (2009), and Zhang et al. (2011)

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suffers from drawbacks, such as low removal efficiency (≤30%), complicated operation, high energy consumption and footprint (Ning et al. 2008; Peleka and Deliyanni 2009). On the other hand, adsorption is proven to be affordable, effective and best suited for low levels of PO_4^{3-} (Li et al. 2009; Zhang et al. 2011). Notably, this method is believed to have an advantage when used for P recovery, owing to the selective P adsorption capability (Loganathan et al. 2014). Previously, activated carbon or anion exchanger resins are commonly used for P decontamination. However, the problems associated with high cost, no renewability and disposal after use hinder their widespread application in developing countries (Karthikeyan et al. 2004). Hence, increasing attention has been paid to agricultural by-products (AWBs) in an attempt to search for a viable alternative option (Jyothi et al. 2012). It is desirable to develop AWBs that have low cost, high effectiveness, good selectivity, potential renewability, and high adaptability to various process parameters (Ning et al. 2008).

There is growing interest in the use of AWBs for P removal/recovery. There are many reasons accounting for this (Figure 14.2). Firstly, this practice can prevent surface water from eutrophication, owing to the production of cleaner effluents, reduction of P pollution caused by mining activities, and mitigation of P

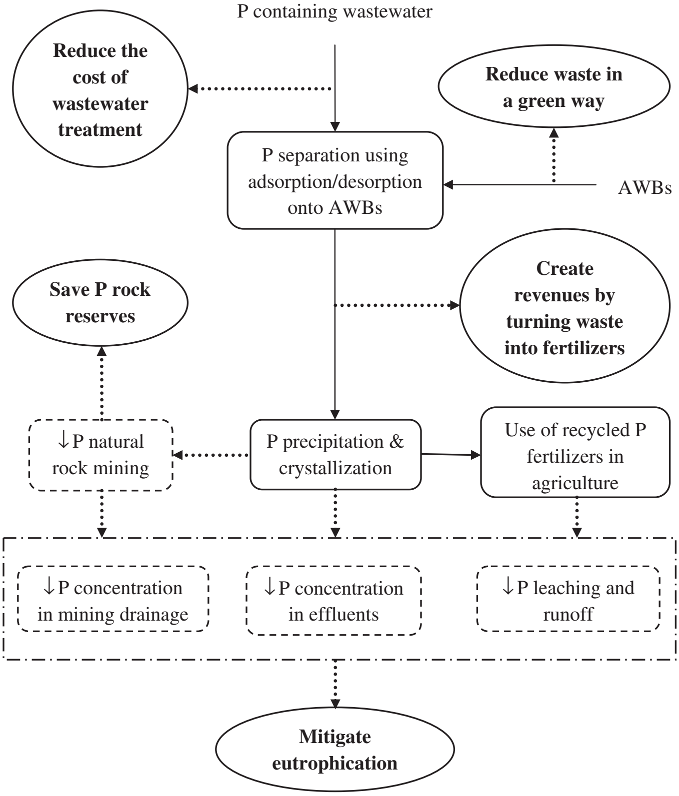

Figure 14.2. The benefits of using AWBs for P removal/recovery from wastewater

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leaching and runoff. Secondly, huge amounts of agricultural wastes generated worldwide represent an environmental burden. The recycling wastes to control PO_4^{3-} pollution provides a viable option to reduce wastes in a low cost and green way (Tshabalala et al. 2004; Ismail 2012; Eljamal et al. 2013). This also fits well with one of the 12 principles of Green Chemistry, i.e. "use of renewable resources" (Srivastava and Goyal 2010). In addition, the successful exploitation of P from wastewater will diminish the use of mineral P, and thus saving exhausting P rock reserves. Moreover, a large amount of anion exchanger resins created from abundant, cheap and renewable materials may help to fill a need for innovative, inexpensive and efficient method for PO_4^{3-} removal. Consequently, the cost of water treatment will be reduced (Liu et al. 2012). Eventually, by converting waste into fertilizers and useful materials for water treatment, this practice may create revenues (Huang et al. 2010; Peng et al. 2012). Apparently it may provide a sustainable, efficient and profit regenerating solution for P management (Kuzma 2011). For these reasons, this practice should be considered as a promising green technology.

This chapter focuses on the fundamental and applied aspects of the removal/recovery of PO_4^{3-} from water and wastewater using AWBs. Part I (Section 14.2) provides new insights into adsorption and desorption mechanisms. In addition, it refers to the effect of process parameters Part II (Section 14.3) evaluates the adsorption performance of AWBs in both natural and modified forms. Also, this section mentions the recovery process of PO_4^{3-} using AWBs in terms of drivers, technologies, and barriers. Part III (Sections 14.4 and 14.5) summarizes the recent developments and proposes the future work.

14.2 PROCESS FUNDAMENTALS

14.2.1 Mechanistic Aspects of Phosphorus Sorption Process

Insights in sorption mechanisms are necessary for optimizing the sorption process. Due to the complexity of these processes, various information (pH profile, desorption, kinetic, activation energy, etc.) and techniques (FTIR, XRD, TEM, etc.) have been used. The reported types of adsorption of PO_4^{3-} by AWBs include ion exchange, ligand exchange, surface precipitation, and diffusion.

14.2.1.1 Ion Exchange

This mechanism is considered as physical adsorption (electrostatic attraction). It is associated with very fast, weak and reversible adsorption, which occurs through the outer-sphere complex. This replaces any ion on the surface of an ion exchanger by a chemically equal number of another ion while preserving the electroneutrality of the ion exchanger (Loganathan et al. 2014). The ion exchange mechanism can be found in many studies removing P by AWBs, such as banana stem (Anirudhan et al. 2006); wood residues (Karachalios 2012); giant reed (Xu et al. 2011a); etc. A typical method to predict the type of adsorption is based on the activation energy (E) magnitude. While E values in the range of 8–16 kJ/mol represents the chemical adsorption, E values lower than 8 kJ/mol stand for physical adsorption.

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The E values for the sorption of P onto modified wheat residue, modified sawdust and calcined waste eggshell were found to be 3.39 3.088, 0.4 kJ/mol, respectively. This implies that physical adsorption might be dominant sorption mechanism in these cases (Xu et al. 2009; Benyoucef and Amrani 2011; Kose and Kivanc 2011). Based on the effect of pH, Anirudhan et al. (2006) concluded that in the pH range of 5.0–7.0, the removal of P by quaternized banana stem could mainly be attributed to ion exchange between Cl^- of quaternary mine group and $HPO_4^{2-}/H_2PO_4^-$ in the solution as follows:

$$\begin{aligned}&2BS - CH_2 - N^+H(CH_3)_2Cl^- + HPO_4^{2-}\\&\quad \rightarrow [BS - CH_2 - N^+H(CH_3)_2]_2HPO_4^{2-} + 2Cl^-\\&BS - CH_2 - N + H(CH_3)_2Cl^- + H_2PO_4^-\\&\quad \rightarrow BS - CH_2 - N + H(CH_3)_2H_2PO_4^- + Cl^-\end{aligned}$$

Similarly, Xu et al. (2011a) proposed that the ion exchange could be an important pathway for the remediating P by modified giant reed. The replacement of chloride ions in the amine groups of quaternized giant reed by phosphate ions in the solution could occur as follows:

$$\begin{aligned}&R' - N + (CH_2CH_3)_3 \ldots Cl^- + H_2PO_4^-\\&\quad \rightarrow R' - N + (CH_2CH_3)_3 \ldots H_2PO_4^- + Cl^-\end{aligned}$$

From FTIR results, De Lima et al. (2012) suggested that the modification of coconut shell fibers with ammonium quaternary salt led to the integration of $-NH_2$ groups into the material. Consequently, the removal of P by quaternized coconut shell fibers occurred mainly via electrostatic interactions between $-NH_2$ groups and PO_4^{3-} anions.

14.2.1.2 Ligand Exchange

This is considered as chemical sorption, which is characterized by fast, strong and less reversible adsorption with reduced zero point charges. It may happen through the inner sphere complex, when PO_4^{3-} anions create a covalent chemical bond with a metallic cation on the surface of AWBs, leading to the liberation of other anions, which formerly attached to the metallic cation (Loganathan et al. 2014). This mechanism was reported for the case of decontaminating P by natural and iron impregnated coir pith (Krishnan and Haridas 2008). The authors suggested that in the pH range of 2.0–3.5, the ligand exchange occurred between $H_2PO_4^-$ ions and surface OH^- groups to form inner-sphere complexation as follows:

$$CP - OH + H_2PO_4^- \xrightarrow[H^+]{H^+} CP - (H_2PO_4) + H_2O$$

$$CP - Fe(OH) + H_2PO_4^- \rightarrow CP - Fe(H_2PO_4) + H_2O$$

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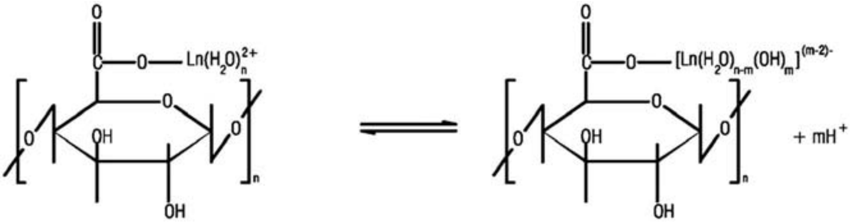
Likewise, based on the effect of pH, Biswas et al. (2007) concluded that the adsorption of P by metal loaded orange waste (SOW) gels was possibly due to ligand exchange mechanism between PO_4^{3-} ions and OH^- ions coordinated on the metal ions impregnated on the orange waste gels (Schemes 14.1 &14.2). The authors suggested that loaded metal ions could be readily converted into hydrated forms e.g. $[Ln(H_2O)_n]^{3+}$, $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$, and $[Zr_8(OH)_{20}(H_2O)_{24}]^{12+}$ species with the abundant amount of OH^- ions and H_2O molecules. The H_2O molecules were deprotonated by releasing H^+ ions to form OH^- ions, which could be replaced by PO_4^{3-} ions via the ligand exchange mechanism.

14.2.1.3 Surface Precipitation

When the concentration of components of the precipitate surpasses the solubility product of the precipitate, the precipitation of P with metallic ions may take place on the surface of AWBs. This mechanism is described as fast and hardly reversible adsorption. Using the X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) results, Shin et al. (2005) verified the contribution of surface precipitation to the PO_4^{3-} binding onto La(III) loaded bark fiber. Based on kinetic studies, Namasivayam et al. (2005) concluded that the removal of P by oyster shell powder (OSP) was probably through precipitation of P as calcium phosphate and then turned into hydroxyapatite on the surface of OSP.



Scheme 14.1. Formation of exchangeable hydroxyl ions during hydrolysis, where m = 1 or 2; Ln stands for La(III), Ce(III), Fe(III)

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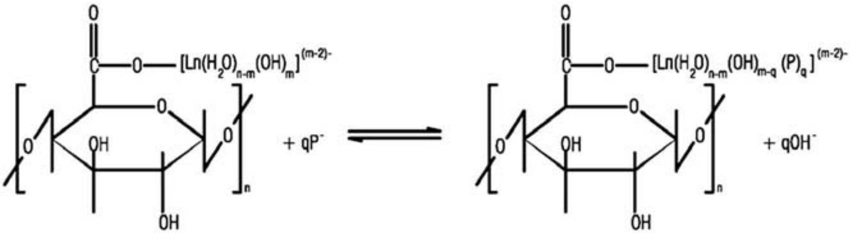

Scheme 14.2. Ligand exchange reaction, where q = 1 or 2 and P represents phosphate anion

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14.2.1.4 Intraparticle Diffusion

This process is known as physical sorption, which takes place inside pores and cavities of AWBs. It is characterized by irreversible and very slow adsorption, which may last for days to months (Loganathan et al. 2014). If intraparticle diffusion mechanism prevails, a plot between the PO_4^{3-} adsorption capacity and the square root of the contact time should be a straight line passing through the origin. The relationship attained in a study by Karachalios (2012) was non-linear. That clearly indicated that intra-particle diffusion could not play a major role in the sorption of PO_4^{3-} onto quarternized wood residues. Based on Transmission electron microscopy (TEM) results, Riahi et al. (2009) suggested that intra-particle diffusion led to the accumulation of PO_4^{3-} into internal cells of date palm fibers.

14.2.1.5 Co-existing Mechanisms

Due to the complex nature of the sorption process using AWBs, it is quite common that the process can be attributed to several mechanisms. Based on the effect of pH and desorption results, Anirudhan et al. (2006) and Namasivayan and Sangeetha (2004) concluded that ion exchange and chemisorption mechanisms could be important pathways for the removal of P by quaternized banana stem and $ZnCl_2$ activated carbon, respectively. Tshabalala et al. (2004) observed a reduction in PO_4^{3-} uptake with increasing ionic strength and presence of SO_4^{2-}, NO_3^- anions. For that reason, they suggested that ion exchange and Lewis acid-base interactions might be responsible for retention of PO_4^{3-} ions onto cationized milled wood residues. From P surface loading and spectroscopic analysis results, Shin et al. (2005) claimed that ion exchange and surface precipitation could contribute to the elimination of P by La(III) treated juniper bark fiber. Similary, physisorption and chemisorption mechanisms are found to co-exist in the studies conducted by Mezenner and Bensmaili (2009), Huang et al. (2010), and Benyoucef and Amrani (2011). In a more recent study, Karachalios (2012) explored that the adsorption process of PO_4^{3-} onto quaternized pine bark residues resulted from both boundary layer and intra-particle diffusion mechanisms.

14.2.2 Mechanistic Aspects of Phosphorus Desorption Process

Desorption plays an important role in enabling the reusability of AWBs and recovery of P. The P can be efficiently eluted from spent AWBs by distilled water, salts, acids, and bases (Table 14.2).

In an attempt to reduce the cost of chemicals used for desorption and mitigate adverse impacts on the environment, some researchers have used distilled water as an eluent. Namasivayan and Sangeetha (2004) investigated desorption of P from spent $ZnCl_2$ activated coir pith carbon using distilled water at various pH values (2–11). Desorption was shown to be favored at pH 2 (30%) and pH 11 (50%), while suppressed in pH range of 3–11 (<10%). The high desorbability at pH values 2&11 was explained by the dissociation constants of phosphate and the dominant phosphate species at different pH values. At pH 2, unionized H_3PO_4 species are dominant. These P species have low affinity toward the biosorbent, and thus

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Table 14.2. Comparison of PO_4^{3-} desorption capability of different elution solutions

Biosorbent	*Elution solution*	*Desorption efficiency (%)*	*Remark*	*References*
Modified banana stem	NaOH 0.1 M	First cycle 97.1 Fourth cycle 90.7	No weight loss	Anirudhan et al. (2006)
Zr(IV)-loaded SOW gel	NaCl HCl NaOH 0.2 M	NaCl 0 HCl < 40 NaOH 95	NaOH exhibited anextremely high desorption ability without any remarkable release of loaded Zr	Biswas (2008)
La(III)-loaded SOW gel	HCl 0.4 M	85	Lathanum was leaked	Biswas et al. (2007)
Modified coconut shell fibers	HCl	C1–50; C2–40; C3–40 RC1–35; RC2–7	Significant loss of P adsorption capacity and remarkable reduction in P removal efficiency	De Lima et al. (2012)
Granular date stones (GDS) Palm surface fibers (PSF)	KCl 0.01 M	GDS 10–11.2; PSF 12.1–13	Low desorbability	Ismail (2012)
Quarternized pine bark residues	NaCl 0.2 M	99.8	Minor loss (5.59%) in PO_4^{3-} sorption capacity after 5 uninter-rupted sorption—desorption cycles	Karachalios (2012)
Calcined waste eggshell	NaOH 0.5 M and NaCl 0.5 M	NaOH 37.6 NaCl 0.7	—	Kose and Kivanc (2011)
Apple peel	Distilled water at different pH values (2–12)	Acidic pH: minimum desorption pH 12: 90 (10 min.)	Zr was not detached at various pH values	Mallampati and Valiyaveettil (2013)

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$ZnCl_2$ activated coir pith carbon	Distilled water at different pH values (2–11)	pH 2: ~30; pH 11: 50; pH 3–11: <10	Low desorbability	Namasivayan and Sangeetha (2004)
Zr(IV) loaded saponified orange waste	NaOH 0.2 M	93	Zr was not leaked during elution process	Ohura et al. (2011)
Iron(III) loaded carboxylatedpolyacrylamide grafted sawdust	Different extractants were tested, including $NaNO_3$, NaCl, Na_2SO_4, HCl, HNO_3, NaCl-HCl, H_2SO_4, NH_4NO_3-HNO_3 and NaOH	NaOH 96.8 Na_2SO_4 73.6 NH_4NO_3-HNO_3 50.8 HCl 36.8 NaCl 34.5	Adsorption capacity reduced by 8.9% after 3 cycles, recovery of phosphate decreased from 98.2% in the 1st cycle to 92.8% in the 3rd cycle, 3% sorbent weight loss after treatment with NaOH 0.1M	Unnithan et al. (2002)
Giant reed	HCl 0.1 M NaCl 0.1 M NaOH 0.1 M	HCl 100 NaCl 100 NaOH 100	Weight loss (1–3%)	Xu et al. (2011a)
Wheat straw anion exchanger	NaCl 0.1 M HCl 0.1 M	NaCl 86.6–95.4 HCl 87.4–97.5	Marginal reductions in their initial adsorption capacities	Xu et al. (2010)
Cotton stalk (CS) and wheat stalk (WS)	NaCl 0.1 M HCl 0.1 M	HCl CS 93.1–98.4; WS 93.7–98.9 NaCl CS 92.3–97.1; WS 95.0–98.2	5% weight loss with HCl 0.1M	Xu et al. (2011b)
Wheat straw (WS)	HCl 1 M	Medium cost resin: 98–100	12–18% weight loss	Xu et al. (2011c)
Sugarcane bagasse	NaOH 0.05 M	95.6		Zhang et al. (2012)

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providing favorable conditions for P desorption. At pH 11, more OH^- ions are available in the solution, leading to a stronger competition with HPO_4^{2-} and PO_4^{3-} for binding sites. That was the reason why the efficient desorption was obtained at pH 11. Nevertheless, the maximum desorption efficiency was the relatively low (50%). This was probably due to the fact that PO_4^{3-} ions were removed by both ion exchange and chemisorptions mechanisms, whereas only PO_4^{3-} ions removed by ion exchanged was desorbed. On the other hand, Mallampati and Valiyaveettil (2013) observed a relatively high desorption capacity (90%) in very short time (10 min.), when distilled water pH 12 was employed in case of desorbing P from Zr(IV) loaded apple peels. The successful desorption of P at high pH value was explained by the replacement of PO_4^{3-} on apple peel surface by OH^- anions in the solution.

Another means of desorption of P from AWBs is using neutral salts, e.g. NaCl, KCl. In some studies, the use of these salts at different concentrations resulted in particularly high desorption efficiencies, e.g. 99.8% for NaCl 0.2 M from quaternized wood residues (Karachalios 2012); 95.4% for NaCl 0.1 M from wheat straw anion exchanger (WS-AE) (Xu et al. 2010); 100% for NaCl 0.1 M from modified giant reed (Xu et al. 2011a). Conversely, very poor desorption capacities could be found in other studies, e.g. 0.7% for NaCl 0.5 M from calcined waste eggshell (Kose and Kivanc 2011); 11.2% and 13% for KCl 0.01 M from granular date stones and palm surface fibers, respectively (Ismail 2012). Loganathan et al. (2014) suggested that neutral salts were efficient eluents for weak and reversible sorption, where ion exchange could be an important pathway for the removal of P (e.g. Xu et al. 2010, 2011a, b, c; Karachalios 2012). In contrast, for strong and less reversible sorption, which was controlled by such mechanisms as ligand exchange, surface precipitation, or chemisorptions, the efficacy of these salts was usually low (e.g. Kose and Kivanc 2011; Ismail 2012). The higher concentrations of neutral salts seem to favor desorption. A rise in the concentration of NaCl as an eluent from 0.001 to 0.1 M led to a significant improvement (48.7%) in P desorption efficiency of modified giant reed (Xu et al. 2011a). However, it should be emphasized that the use of neutral salts as desorbents at high concentrations may increase the salinity in arable lands once P desorbed by this method was recovered and applied as fertilizers (Loganathan et al. 2014). One advantage of desorbing by this method is a minor loss in the adsorption capacity and weight of AWBs after several cycles of operation. For example, the adsorption capacity of was found to decrease by 5.59% after 5 operation cycles for NaCl 0.2 M (Karachalios 2012); 9.58% after 4 operation cycles for NaCl 0.1 M (Xu et al. 2010). The slight weight loss (1–3%) was reported when NaCl 0.1 M was used for desorption of P from modified giant reed (Xu et al. 2011a). This property facilitates the reusability of AWBs.

In some cases, to improve desorption efficiency of P, distilled water and neutral salts have been replaced by acids or bases. Among these, NaOH and HCl are widely used. NaOH and HCl normally demonstrated remarkable desorption capacities. For example, the desorption efficiency was found to be 97.1% for NaOH 0.1M (Anirudhan et al. 2006); 85% for HCl 0.4 M and 95% for

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NaOH 0.2 M (Biswas 2008); 97.5% for HCl 0.1 M (Xu et al. 2010); 100% for HCl 0.1 M and NaOH 0.1 M (Xu et al. 2011a); 95.6% for NaOH 0.05 M (Zhang et al. 2012). High efficacy of acids or bases could be explained by the low affinity of dominant P species, such as H_3PO_4 (in acidic medium), HPO_4^{2-} and PO_4^{3-} (in alkaline medium), toward binding sites on AWBs surface. Another reason for that was the stronger competition in alkaline medium between OH^- ions and PO_4^{3-} for binding sites on AWBs. It is worth mentioning studies conducted by Ismail (2012) and Zhang (2012), where the adsorption was controlled by chemisoprtion mechanism. While KCl 0.01 M demonstrated very poor desorption capacities (11.2–13%), the satisfactory elution was observed for NaOH 0.05 M (95.6%). This provides strong evidence that, bases are superior to neutral salts in desorbing P in case of strong sorption. Both Xu et al. (2011a) and Zhang et al. (2012) found that, higher concentration of NaOH enabled desorption of P from spent AWBs. This was probably due to a stronger competition between OH^- ions and PO_4^{3-} for binding sites. Though HCl and NaOH were proven to be effective eluents, their application could result in some side effects. The loss in the adsorption capacity was shown to be 12% for NaOH 0.1 M (Anirudhan et al. 2006) or 10.53% for HCl 0.1 M (Xu et al. 2010). Particularly, the complete loss of the adsorption capacity of modified coconut shell fibers was recorded after the second cycle of reuse. This could be ascribed to the physical ruin of the biosorbent (De Lima et al. 2012). Xu et al. (2011c) revealed a weight loss of 12–18% as a result of using HCl 1 M as a desorbent. They attributed this to the corrosion of cellulose/hemicellulose structure. In addition, Biswas (2008) reported the release of La(III) during desorption when HCl 0.4 M was used as an eluent. In view of practical application, these effects are undesirable as they may reduce the stability and thus restricting reusability of AWBs. Hence, these factors need to be taken into consideration in exploring for appropriate desorbents. The appropriate desorbents should meet the following criteria: high desorption efficiency, satisfactory reusability of the biosorbent (e.g. negligible reduction in adsorption capacities after many cycles of reuse, marginal weight loss, etc.), and minimal detrimental impacts on the environment.

In some cases, desorption efficiency was found extremely poor e.g. 11.2–13% (Ismail 2012); 0.7–37.6% (Kose and Kivanc 2011); 11–13% (Riahi et al. 2009). It is recommended to use phosphorous bearing AWBs as fertilizers or soil conditioners in acid soils, due to their high contents of nutrients (P, Ca, Mg, etc.) (Loganathan et al. 2014). However, from the recovery of P point of view, with a desire to use recycled P to replace mineral P in many industries, appropriate AWBs should be easily regenerated and reused. This property needs to be taken into consideration when the selection of potential AWBs is made.

14.2.3 Factors Influencing Phosphorus Biosorption

14.2.3.1 Effect of pH

The pH value of the solution influences the dissociation, P species abundance, the chemical state of binding sites, and affinity of P species towards binding sites.

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The pH profiles are useful for elucidating sorption mechanisms, optimizing process, and selecting appropriate eluents. Thus, efforts have been directed toward identifying optimum pH values in various AWBs-PO_4^{3-} adsorption systems.

Generally, AWBs tend to effectively sequester PO_4^{3-} anions in a specific pH range, while extremely acidic or alkaline medium is found to suppress the process. Yue et al. (2010) found that pH range of 4–9 favored the adsorption of PO_4^{3-} onto modified giant reed (MGR), whereas pH < 4 or pH > 9 was found to be disadvantageous to the process. The authors explained this by dissociation constants of phosphate, dominant phosphate species in the solution, and affinity of phosphate ions towards binding sites. The dissociation constants of H_3PO_4, $H_2PO_4^-$ and HPO_4^{2-} are 2.12, 7.21 and 12.67, respectively (Biswas 2008). Consequently, the dominant P species can vary, depending on pH value of the aquatic medium.

As can be seen from Figure 14.3, in the pH range of 4-9, $H_2PO_4^-$ and HPO_4^{2-} species were dominant. Due to their strong affinity toward binding sites, the sorption of P was enhanced. In contrast, at pH < 4, the H_3PO_4 and HPO_4^{2-} species were most common. Their inferior affinities toward binding sites led to the poor removal of P. In the same way, at pH > 9, HPO_4^{2-} and PO_4^{3-} species were prevalent. The weak affinity of these species for active site combined with strong competition between OH^- ions and PO_4^{3-} ions for adsorption sites hampered the process. Similarly, the effective pH range was found to be 5–7 for modified banana stem (Anirudhan et al. 2006); 7–10 for metal loaded orange waste gel (Biswas 2008); 3.5–6.0 for quaternized pine bark residues (Karachalios 2012); 3–10 for $ZnCl_2$ activated coir pith carbon (Namasivayan and Sangeetha 2004); 3–11 for calcined waste eggshell and modified sugarcane bagasse (Xu et al. 2011a; Zhang et al. 2012); 4–9 for modified giant reed (Yue et al. 2010), etc. This trend more or less agrees with the findings reported by Riahi et al. (2009) and Ismail (2012). They both found that an increase in the pH value led to a decrease in the P uptake. The authors explained this phenomenon by stronger repulsion force in the alkaline medium. The optimum pH values were found to be low (e.g. 2, 3) by Krishnan and Haridas (2008), Jeon and Yeom (2009), and Mallampati and Valiyaveettil (2013).

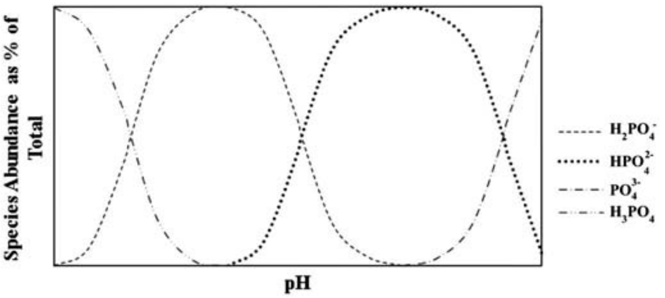

Figure 14.3. Orthophosphate species as a proportion of the total orthophosphate concentration

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On the other hand, high optimum pH values (e.g. 7.5, 10) were reported by Biswas (2008), Benyoucef and Amrani (2011), and Jyothi et al. (2012). The former was explained by the dominance of $H_2PO_4^-$ species and their affinity toward binding sites in acidic medium (Mallampati and Valiyaveettil 2013). In contrast, the latter was attributed to the possible existence of natural compounds and metal ions (e.g. Ca, Mg, Fe, Al, Cu, Zn) inside these AWBs, which had strong affinity toward HPO_4^{2-} in alkaline medium (Jyothi et al. 2012). It is worth pointing out that, in some studies, a wide pH range was found to have a marginal effect on the sorption of PO_4^{3-}, e.g. 4-10 for crab shells (Jeon and Yeom 2009); 5.0–10.5 for oyster shell powder (Namasivayam et al. 2005); 2–7.5 for scallop shells (Yeom and Jung 2009). Especially, De Lima et al. (2012) claimed that pH could hardly affect the sorption of PO_4^{3-} onto coconut fiber. It seems that many AWBs are highly effective in a wide pH range. This property represents an appreciable advantage of AWBs over conventional adsorbents for PO_4^{3-} removal.

14.2.3.2 Effect of Temperature

Normally, the adsorptive removal of PO_4^{3-} by AWBs is temperature sensitive. Some adsorption processes are endothermic, whilst others have exothermic nature. Mezenner and Bensmaili (2009) found that the retention of PO_4^{3-} by iron hydroxide eggshell was enhanced with a rise in the temperature from 20 to 45°C. From the positive ΔH° (81.84 kJ/mol), they concluded that the adsorption was endothermic. It was assumed that, higher temperature led to the better solubility of iron hydroxide eggshell compound, and thus producing more iron and calcium hydrolysis complexes. Consequently, the phosphate precipitation was enhanced. Similar observations were noticed by Boujelben et al. (2008), Yeom and Jung (2009), Kumar et al. (2010), Benyoucef and Amrani (2011), Chen et al. (2012), and Peng et al. (2012). Benyoucef and Amrani (2011) explained this phenomenon by the enlargement of pore sizes, whereas Kumar et al. (2010) ascribed this to the better dissolution of PO_4^{3-} ions and higher rate of intra-particle diffusion at higher temperature. On the contrary, Yue et al. (2010) explored that the P uptake by modified giant reed declined from 19.89 to 17.79 mg/g as the temperature increased from 20 to 60°C, indicating the exothermic nature of the adsorption process. From negative values of ΔG° and ΔH°, Karachalios (2012) concluded that the adsorption of PO_4^{3-} by quaternized pine bark residues was exothermic. These results were in harmony with those reported by Kose and Kivanc (2011) and Xu et al. (2009). They explained that higher temperature resulted in stronger leakage of PO_4^{3-} ions from AWBs surface into the solution (Xu et al. 2009). Particularly, the change in the temperature from 15 to 45°C could hardly affect the sorption of PO_4^{3-} onto crab shell (Jeon and Yeom 2009).

14.2.3.3 Effect of Initial Phosphorus Concentration

Typically, the uptake capacity of PO_4^{3-} increased, whilst the PO_4^{3-} removal efficiency decreased with a rise in the initial concentration of PO_4^{3-} ions. On the one hand, Mezenner and Bensmaili (2009) claimed that the extent of

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PO_4^{3-} removal by iron hydroxide eggshell waste decreased from 95 to 64% with increasing initial concentration of phosphate from 2.8 to 110 mg/L. Similar tendency has been reported for sugarcane bagasse by Zhang et al. (2012). The authors explained this by higher ratio of PO_4^{3-} moles to the active binding sites at higher PO_4^{3-} initial concentrations. For a specific dose of AWBs, the amount of binding sites is unchanged. Therefore, an increase in initial concentration of PO_4^{3-} led to the decrease in its percentage removal accordingly. On the other hand, Riahi et al. (2009) reported that the PO_4^{3-} adsorption capacity of date palm fibers increased from 1.45 to 5.85 mg/g as the initial phosphate concentration increased from 10 to 110 mg/L. These results were in consistent with those reported by Anirudhan et al. (2006), Mezenner and Bensmaili (2009), Xu et al. (2009), Kumar et al. (2010), Yue et al. (2010), and Zhang et al. (2012). Both Kumar et al. (2010) and Yue et al. (2010) attributed this to the stronger driving force to convey PO_4^{3-} ions from solution to the surface of AWBs at higher PO_4^{3-} initial concentrations. Mezenner and Bensmaili (2009) and Riahi et al. (2009) ascribed this to increasing interaction between binding sties and PO_4^{3-} ions, which resulted from the increase of PO_4^{3-} ions provided by higher PO_4^{3-} initial concentrations.

14.2.3.4 Effect of AWBs Dosage

The general trend is that PO_4^{3-} removal efficiency increases with a rise in the AWBs dose to a certain level then remains constant or reduces slightly with further increase in the AWBs dose. The better PO_4^{3-} removal efficiency at higher AWBs dose was explained by more binding sites for PO_4^{3-}adsorption and larger surface area available at higher dose of AWBs (Xu et al. 2009; Kose and Kivanc 2011; Zhang et al. 2012). The reduction in the PO_4^{3-} removal efficiency when the AWBs dose exceeded the optimum dose could be attributed to the resistance to mass transfer, particle aggregates and repulsive forces between binding sites at higher dose (Mezenner and Bensmaili 2009; Riahi et al. 2009; Ismail 2012). On the contrary, an increase in the dose of AWBs results in a reduction in P uptake capability. Karachalios (2012) found that the PO_4^{3-} uptake by modified pine bark residues decreased from 55 to 25 mg/g as the dose increased from 0.5 to 5 g/L. These results are in harmony with those reported by Yue et al. (2010) and Zhang et al. (2012). This could be ascribed to the lower PO_4^{3-} concentration gradient between solution and sorbent surface (Zhang et al. 2012). Conversely, Riahi et al. (2009) explored that the PO_4^{3-} uptake increased from 3.75 to 4.69 mg/g as date palm fiber dose increased from 2 to 6 g/L. However, further increase in biosorbent dose suppressed the sorption process. This can be explained by poor interaction between PO_4^{3-} ions and the biosorbent as a result of the roll up of fibers at excessive doses. In view of practical application, for the same removal efficiency, the lower the AWBs dose, the better the efficacy of AWBs is. For the referring purpose, PO_4^{3-} removal efficiency and the corresponding dose of AWBs in various adsorption systems were introduced as follows: 79.8% for 1 g/L of MSBG (Zhang et al. 2012); 92.5% for 2 g/L of modified wheat residue (Xu et al. 2009); 85–87% for 5 g/L of date palm wastes (Ismail 2012); 99.6% for 10 g/L of calcined waste eggshell (Kose and Kivanc 2011); and 98% for 16 g/L of modified giant reed (Yue et al. 2010).

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14.2.3.5 Effect of Interfering Anions

Examining the effect of co-existing ions on the adsorption of PO_4^{3-} by AWBs is necessary to enhance the practical application of these biosorbents. Namasivayan and Sangeetha (2004) reported that Cl^-, NO_3^-, MoO_4^{2-}, VO_3^- scarcely affected the PO_4^{3-} removal by $ZnCl_2$ activated coir pith carbon. Equally, Biswas et al. (2007) revealed that the adsorption of PO_4^{3-} onto La(III) loaded SOW gel was not substantially influenced by the addition of Cl^-, CO_3^{2-}, SO_4^{2-}. In a later study, Biswas (2008) revealed that Cl^- (0.56 mM), CO_3^{2-} (0.33 mM), SO_4^{2-}(0.42 mM) could hardly affect the sorption of PO_4^{3-} (0.20 mM). Kose and Kivanc (2011) claimed that the addition of SO_4^{2-}, NO_3^- and NH_4^+ with the concentrations ranging from 10 to 50 mg/L had minor influences on the retention of PO_4^{3-} by calcined waste eggshell. Jyothi et al. (2012) discovered that such foreign anions as Cl^-, SO_4^{2-}, NO_3^-, F^- and CO_3^{2-} with the same concentration had minimum interference on the sorption of PO_4^{3-} by thermally activated barks/stems and their ashes of *Ficus religiosa, Cassia auriculata, Punica granatum* and *Calotropis gigantean*. The adsorption of PO_4^{3-} by AWBs was not affected by the presence of co-anions, implying the potential for employing these AWBs to the real wastewater. On the other hand, Namasivayan and Sangeetha (2004) explored that the presence of ClO_4^-, SeO_3^{2-} and SO_4^{2-} with the same concentrations as PO_4^{3-} hampered the removal of PO_4^{3-} ions. Likewise, Karachalios (2012) claimed that SO_4^{2-} was superior to NO_3^- in competing with PO_4^{3-} for binding sites. The higher Cl^- concentrations resulted in the lower PO_4^{3-} uptake. It is interesting to note that presence of divalent cations (i.g. Ca^{2+}, Mg^{2+}, Cu^{2+}, Zn^{2+}, Fe^{2+} and Ni^{2+}) with the concentration 10 times greater than that of PO_4^{3-}, boosted the PO_4^{3-} extraction by thermally activated barks/ stems and their ashes of *Ficus religiosa,Cassia auriculata, Punica granatum* and *Calotropis gigantean* (Jyothi et al. 2012). The positive effect of divalent cations on the adsorption process suggests a way further to improve the PO_4^{3-} adsorption capacity of these biosorbents.

14.2.3.6 Effect of Contact Time

The contact time is an indicator of the speed of the adsorption process. Therefore, it is a critical factor in evaluating the efficacy of AWBs (Eljamal et al. 2013). In many cases, the adsorption was found to be rapid, reaching the equilibrium in approximately 1 h. The equilibrium time was found to be 20 min. for quaternized wood residues (Karachalios 2012); 25 min. for modified giant reed (Yue et al. 2010); 40 min. for modified sawdust (Benyoucef and Amrani 2011); and 60 min. for natural date palm wastes (Ismail 2012) and sugarcane bagasse (Zhang et al. 2011). In contrast, the longer contact time was necessary for the equilibrium to be reached by other AWBs. It was shown to be 15 h for La(III), Ce(III) and Zr(IV) loaded SOW gels (Biswas 2008); 12 h for iron impregnated coir pith (Krishnan and Haridas 2008); and 6 h for Zr(IV) loaded apple peels (Mallampati and Valiyaveettil 2013). The short contact time means that AWBs do not have to be kept in reactors for a long time, and thus the space can be saved. This can be

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considered as an advantageous property of potential AWBs, from a practical application point of view.

14.2.3.7 Effect of Particle Sizes of AWBs

Chen et al. (2012) found that PO_4^{3-} uptake capacity increased with a decrease in oyster shell diameter from 590 to 180 μm. Similarly, Yeom and Jung (2009) revealed that 100 mg PO_4^{3-}/L could be removed entirely by 1 g of scallop shells of 0.045 mm diameter in 3 h, whereas it was scarcely eliminated by that of 3 mm in 80 h. In the same way, Jeon and Yeom (2009) found that crab shells particles 1 mm in diameter showed a removal percentage 85%, whereas particles 3.35 mm could remove only 50%. These proved that smaller size of AWBs had an advantage when used for the adsorption of P. However, for prevention of a clogging problem in a packed-bed reactor, the optimum particles sizes need to be identified.

14.3 APPLICATIONS

14.3.1 Phosphorus Adsorption Performance by Unmodified AWBs

Unmodified AWBs have received far less attention for being used as adsorbents for the removal of PO_4^{3-} than their modified counterparts. Up to date, only a few reports exist on the use of raw AWBs for eliminating PO_4^{3-} e.g. Krishnan and Haridas (2008), Jeon and Yeom (2009), Riahi et al. (2009), Yeom and Jung (2009), Xu et al. (2011a), Ismail (2012), and Zhang et al. (2012). Table 14.3 introduces some natural AWBs and their reported adsorption capacities for PO_4^{3-}. For comparison purpose, the levels of PO_4^{3-} retention by typical conventional adsorbents are shown in Table 14.4.

Among existing raw AWBs, crab shell displayed the highest PO_4^{3-} adsorption capacity (108.9 mg/g) (Jeon and Yeom 2009). This value is higher than those obtained with the majority of the commercial adsorbents (3.36–60 mg/g). This was assumed that not only calcium carbonate but also proteins and cellulose-like backbone of the crab shells played significant roles in the PO_4^{3-} retention. The extremely good adsorption capacity places crab shell among the best AWBs currently available for PO_4^{3-} removal, in term of the adsorption capacity. In contrast, other unmodified AWBs displayed the adsorption capacity in the range of 1.10–26.66 mg/g. These values are significantly lower when compared with many well-known commercial adsorbents (31.74–131.77 mg/g). Obviously, with very few exceptions, the removal of PO_4^{3-} by unmodified AWBs was not efficient enough for practical implications. This can be explained by the fact that as the lignocellulosic materials, unmodified AWBs contain a large amount of negatively charged functional groups (–OH, –COOH) on their surface. Consequently, raw AWBs are supposed to be less effective in decontaminating anionic contaminants than cationic ones (Mallampati and Valiyaveettil 2013). Because of the lack of efficacy, the widespread use of unmodified AWBs for decontaminating PO_4^{3-} from wastewater is still limited.

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Table 14.3. Phosphate adsorption capacity and processing parameters of diverse phosphate - AWBs adsorption systems

Biosorbent	*Ads. cap. (mg PO_4^{3-}/g AWBs)*	*pH*	*Tem. (°K)*	*Initial P con. (mg/L)*	*Bios. dose (g/L)*	*Cont. time (min.)*	*Shaking speed (rpm)*	*References*
Natural AWBs								
Giant reed	0.836 column	5–10 (opt)	—	—	—	—	—	Xu et al. (2011a)
Sugarcane bagasse	1.10	4–11 (opt)	293	50 PO_4^{3-}	1	180	120	Zhang et al. (2012)
Coir pith	4.35	3		50 PO_4^{3-}	2	960		Krishnan and Haridas (2008)
Date palm fibers	13.33	6.8	291 ± 2	50PO_4^{3-}	6	120	200	Riahi et al. (2009)
Scallop shells	23.00	—	—	—	—	—	—	Yeom and Jung (2009)
Palm surface fibers	26.05	7–7.5	298	5, 10, 25, 50 P	5	120	200	Ismail (2012)
Granular date stones	26.66	7–7.5	298	5, 10, 25, 50 P	5	120	200	Ismail (2012)
Crab shells	108.9	2.0 (opt)	—	—	—	—	250	Jeon and Yeom (2009)
Modified AWBs								
Coir pith	5.10	3–10	308	10–40 PO_4^{3-}	6	—	200	Namasivayan and Sangeetha (2004)
Juniper fibre	7.08	—	298	10 P	2–20	1440	150	Han et al. (2005)
Coir pith	7.74	6 (opt)	308	40 P	4	180	150	Kumar et al. (2010)
Bark	12.65	—	298 ± 1	0.1 ÷ 500 P	2.5	1440	7	Tshabalala et al. (2004)
Eggshell	14.49	—	293–318	2.8–110 PO_4^{3-}	2.5–20	—	—	Mezenner and Bensmaili (2009)

(Continued)

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Table 14.3. Phosphate adsorption capacity and processing parameters of diverse phosphate - AWBs adsorption systems (Continued)

Biosorbent	*Ads. cap. (mg PO_4^{3-}/g AWBs)*	*pH*	*Tem. (°K)*	*Initial P con. (mg/L)*	*Bios. dose (g/L)*	*Cont. time (min.)*	*Shaking speed (rpm)*	*References*
Biomass char	15.11	—	298 ± 0.5	30 PO_4^{3-}	1	300	100	Peng et al. (2012)
Wood particles (modified by 2 methods)	2.05 & 17.38	—	298	100 PO_4^{3-}	4	1440	150	Eberhardt and Min (2008)
Soybean hulls	19.84	7	298	620 P	10	1440	300	Marshall and Wartelle (2004)
Apple peel	20.35	2 (opt)	303	5–200 PO_4^{3-}	10	360	200	Mallampati and Valiyaveettil (2013)
Modified AWBs								
Sugarcane bagasse	21.30	4–11	293	50 PO_4^{3-}	1	180	120	Zhang et al. (2012)
Coir pith	22.05	3		50 PO_4^{3-}	2	960		Krishnan and Haridas (2008)
Eggshell	23.02	2–10	298	100 PO_4^{3-}	2 (opt)	60	140	Kose and Kivanc (2011)
Wood	26.03	—	298 ± 1	0.1–200 P	1.67	1200	7	Karthikeyan et al. (2004)
Juniper bark fibre	33.35	6 (opt)	298	1–450 P	1	720		Shin et al. (2005)
La(III) loaded orange waste gel	42.72	7.5 (opt)	303	20P	1.7	1440	140	Biswas et al. (2007)

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Ce(III) loaded orange waste gel	42.72	7.5 (opt)	303	20P	1.7	1440	140	Biswas et al. (2007)
Fe(III) loaded orange waste gel	42.72	3.0 (opt)	303	20P	1.7	1440	140	Biswas et al. (2007)
Bark	44.65	—	298–1	0.1-200 P	1.67	1200	7	Karthikeyan et al. (2004)
Wheat residue	45.70	—	—	50–500 PO_4^{3-}	—	—	—	Xu et al. (2010)
Giant reed	54.67 column	5–10 (opt)	—	—	—	—	—	Xu et al. (2011a)
Giant reed	60.95	4–9 (opt)	293	10–200 P	1	60	200	Yue et al. (2010)
Corn stover	62.70	7	298		10	1440	300	Wartelle and Marshall (2006)
Skin split waste (loaded with 2 types of metals)	21.65 & 72.00	7	303	47.5–285 PO_4^{3-}	1	1440	—	Huang et al. (2009)
Banana stem	72.46	2–10	303	10–300 PO_4^{3-}	2		200	Anirudhan et al. (2006)
Sawdust of Aleppo pine	116.25	7.5 (opt)	298	300 PO_4^{3-}	2	40	120	Benyoucef and Amrani (2011)
Pine bark residues	205.63	3.5–6 (opt)	293	200 P	1.25 (opt)	1440	200	Karachalios (2012)

Note: Ads. cap. = Adsorption capacity; Tem. = Temperature; Con. = concentration; Bios. = Biosorbent; Cont. = Contact

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Table 14.4. Maximum adsorption capacity of various conventional adsorbents

Adsorbent	q_{max} ($mg\ PO_4^{3-}/g$)	*References*
Natural adsorbents		
Zeolite	0.92	Jiang et al. (2013)
Pb-Zn tailings	1.07	Wang et al. (2013)
Pyrrhotite	1.15	Li et al. (2013)
Granular boehmite	8.40	Ogata et al. (2012)
Fe-Mn binary oxide	22.99	Zhang et al. (2009)
Composite metal oxides synthesized from Mn ore tailings	26.30	Liu et al. (2012)
Pumice	36.40	Karimaian et al. (2013)
Hydrous zirconium oxide	61.00–66.00 (298–338 K)	Rodrigues et al. (2012)
Fe-Zr binary oxide	76.31 (pH 8.5)	Ren et al. (2012)
Tantalum hydroxide	78.50–97.00 (298–338 K)	Yu et al. (2012)
AMD (Acid mine drainage sludge)	98.00	Bhojappa (2009)
Fe-Zr binary oxide	102.35 (pH 5.5)	Ren et al. (2012)
Goethite	144.00	Peleka and Deliyanni (2009)
Titanium	151.02	Choi et al. (2011)
Modified adsorbents		
Naturally iron oxide coated sand	0.88	Boujelben et al. (2008)
Synthetic iron oxide coated	1.50	Boujelben et al. (2008)
Iron oxide coated crushed brick	1.80	Boujelben et al. (2008)
Sponge iron	3.37	Jiang et al. (2013)
Vesuvianite doped with La(III)	4.05	Li et al. (2009)
Activated carbon fiber loaded with La(III) oxide	5.85	Zhang et al. (2011)
Zeolite modified with La/Al	7.44	Meng et al. (2013)
Activated carbon fibre doped with La(III)	6.34–7.92 (NaCl 0.001 to 0.1 M)	Liu et al. (2011)
Activated carbon doped with Fe(III)	8.13	Wang et al. (2012)
Activated alumina	9.90	Li et al. (2009)

Table 14.4. Maximum adsorption capacity of various conventional adsorbents (Continued)

Adsorbent	*q_{max} (mg PO_4^{3-}/g)*	*References*
Montmorillonite pillared with Al/ La–Al	10.31/13.02	Tian et al. (2009)
Bentonite modified with Al/Fe/Fe-Al	12.7/11.20/10.50	Yan et al. (2010)
Activated carbon doped with Fe(II)	14.12	Wang et al. (2012)
Zeolite modified with lanthanide	24.60	Ning et al. (2008)
Silica sulphate	46.32	Jutidamrongphan et al. (2012)
Pumice modified with $MgCl_2$	54.27	Karimaian et al. (2013)
Hydrotalcite coated with sulphate	68.09	Choi et al. (2012)
Fe(III)-AM-PGMACell	70.11	Anirudhan and Senan (2011)
Activated alumina coated with sulphate	152.21	Choi et al. (2012)
Zeolite coated with sulphate	341.66	Choi et al. (2012)
Commerical adsorbents		
Zr-MCM 41	3.36	Jutidamrongphan et al. (2012)
Whatman QA-52	14.26	Marshall and Wartelle (2004)
Zirconium ferrite	27.73	Jutidamrongphan et al. (2012)
Duolite A-7	31.74	Anirudhan et al. (2006)
Amberlite IRA-400	32.24	Marshall and Wartelle (2004)
Aluminium oxide	34.57	Peleka and Deliyanni (2009)
Zirconium ferrite	39.84	Biswas (2008)
Dowex	40.23	Anirudhan and Senan (2011)
Hydrotalcite	60.00	Peleka and Deliyanni (2009)
Zirconium loaded MUROMAC	131.77	Biswas (2008)

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14.3.2 Phosphorus Adsorption Performance by Modified AWBs

Most of unmodified AWBs are inefficient in decontamination of P from water and wastewater. The reason is supposed to be the lack of anion binding sites on the AWBs surface. Thus, to improve the affinity of AWBs towards P, AWBs need to be cationized (Nguyen et al. 2012; Mallampati and Valiyaveettil 2013). This could be done via metal loading, hybridizing with inorganic chemicals, and grafting with ammonium type chemicals (Han et al. 2005).

Among these methods, metal loading appears to be preferred, because of its simplicity and effectiveness. It was found that metal oxides (e.g. Fe, Al, Mn, etc.) in some low-cost materials played important roles in their PO_4^{3-} retention capability (Penn et al. 2007; Liu et al. 2012). These may suggest a solution for the enhancement of P uptake in AWBs, which is metal impregnation. It was assumed that metals can be deposited on the surface of AWBs via chemical interactions e.g. substitution for Ca(II) or binding onto active sites (Han et al. 2005). It is expected that metal treated AWBs with high positive charges can sequester effectively PO_4^{3-} anions (Cheng et al. 2013). The common metals used for cationization of AWBs include Zn(II), Fe(II, III), La(III), Ce(III), Zr(IV). These metals can be used alone or in combination (Eljamal et al. 2013). Each metal has its own merits and demerits when used as modifiers of AWBs. While La(III) has a high affinity toward PO_4^{3-} anions and non toxicity, it suffers from drawbacks associated with the limited reusability (Zhang et al. 2011). Zr(IV) possesses favorable characteristics, such as high affinity and selectivity, large surface area, and chemical stability. Nevertheless, high cost is a critical factor, limiting its commercial application in PO_4^{3-} removal (Mallampati and Valiyaveettil 2013). Similarly, though the properties of cheapness, easy acquiring and non-hazardousness enable the use of Fe(II, III) for this purpose, their week point is less sorption efficiency. Based on this, it seems to be a good idea to use loading metals collectively to make use of their advantages while mitigating their drawbacks (Ren et al. 2012). Some researchers have treated raw AWBs directly with metal solutions, e.g. Han et al. (2005), Krishnan and Haridas (2008), Huang et al. (2009), Kose and Kivanc (2011), and Mallampati and Valiyaveettil (2013). Krishnan and Haridas (2008) found that, the maximum PO_4^{3-} adsorption capacity of Fe impregnated coir pith (CP-Fe-I) was improved 5-6 times as compared to natural coir pith (CP), owing to iron impregnation. The adsorption capacity of AWBs directly loaded with metals was in the range of 7.08–23.02 mg/g (Table 14.5). These values were found to be in the same order of magnitude as those achieved for modified conventional adsorbents (0.88–14.12 mg/g), but still far lower when compared with many commercial adsorbents (27.73–131.77 mg/g) (Table 14.4). To further improve the P uptake capacity of modified AWBs, efforts have been directed toward strengthening the anchor of metals on the surface of AWBs via reactions with carboxylation or bases. Eberhardt and Min (2008) explored that the PO_4^{3-} adsorption capacity by wood particles modified by carboxymethylation and Fe(II) was 8.47 times higher than that of wood particles pretreated with Fe(II) alone. Similar observation was noticed by Carvalho et al. (2011). They reported that due to carboxymethylation, the adsorption capacity of Fe(II) by sugarcane bagasse fibers was boosted 371.25%.

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This was supposed to be responsible for a rise in the PO_4^{3-} removal efficiency, from 94 to 97%. In their 2007 and 2008 studies, Biswas (2008) used $Ca(OH)_2$ and NaOH to enhance the incorporation of La(III), Ce(III), Fe(III) and Zr(IV) into orange waste. The modified orange waste gels displayed satisfactory sorption behaviors. The PO_4^{3-} uptake capacity reached as high as 42.72 mg/g for gels loaded with La(III), Ce(III) and Fe(III) and 174.68 mg/g for gels loaded with Zr(IV). The former can be in competition with some modified adsorbents while the latter is superior to all commercial adsorbents given in Table 14.4. The effectiveness of metal loaded AWBs is found to rely on the type and concentration of metal solutions as well as method of metal loading onto the AWBs surface. Wang et al. (2012) reported that AC/N-Fe(II) exhibited better adsorption capacity for PO_4^{3-} than AC/N-Fe(III). The authors ascribed this to higher intra-particle diffusion and binding energy of AC/N-Fe(II) in comparison with AC/N-Fe(III). Shin et al. (2005) found that the level of PO_4^{3-} capture by La(III) loaded juniper bark fiber was improved from 20.05 to 33.35 mg/g as the concentration of $La(NO_3)_3.6H_2O$ increased from 0.01 M to 0.1 M. Nada and Hassan (2006) revealed that etherification was more efficient than oxidation and esterification in deposition of all four investigated heavy metals (i.e., Cu, Fe, Ni, Cr) onto carboxymethyl cellulose.

Another way to cationize AWBs is quarternization. This can be done via reactions between hydroxyl (OH^-) groups in AWBs with amines ($-NH_2$) groups in quaternary ammonium compounds (Nada and Hassan 2006; Karachalios 2012; Karachalios 2012). This process includes two steps, namely cross-linking and quarternization (Marshall and Wartelle 2004). Quartenization improves the PO_4^{3-} adsorption capacity of raw AWBs, possibly owing to better anion exchange capacity (Wang et al. 2010), larger surface area and higher number of amine groups (Xu et al. 2010). Various quarternization reagents have been tested for this purpose, e.g. dimethylamine (Anirudhan et al. 2006); urea (Benyoucef and Amrani 2011; Karachalios 2012); 2-hidroxypropyltrimethyl ammonium chloride (De Lima et al. 2012); polyallylamine hydrochloride (Karthikeyan et al. 2004); trimethylammoniumchloride (Marshall and Wartelle 2004; Wartelle and Marshall 2006); ethylenediamine and triethylamine (Wang et al. 2010; Yue et al. 2010; Xu et al. 2011a), etc. In most cases, quarternized AWBs exhibited the enhanced adsorption capacities for PO_4^{3-} as compared to raw AWBs. Zhang et al. (2012) revealed that the PO_4^{3-} uptake capacity of quarternized sugarcane bagasse (MSBG) and raw sugarcane bagasse (SBG) was 21.30 and 1.1 mg/g, respectively. They explained this by the difference in the zeta potential between MSBG (32 mV) and SBG (−22 mV) after quarternization. Due to electrostatic interactions, the former favored the retention of PO_4^{3-}, while the latter hinder the adsorption process. Similarly, Xu et al. (2009) found that modified wheat residue showed greatly higher PO_4^{3-} removal efficiency (92.5%) than raw wheat residue (4.8%). In a more recent study, Xu et al. (2011a) reported that amine grafted giant reed showed an extremely high PO_4^{3-} adsorption capacity (54.67 mg/g) as compared with raw giant reed (0.863 mg/g). It is interesting to note that quaternization of banana stem not only improved PO_4^{3-} removal efficiency by 25.8%, but also reduced COD

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by 83.40% as compared to raw materials (Anirudhan et al. 2006). Compared to some well-known commercial adsorbents (3.36–131.77 mg/g), comparable and higher adsorption capacities could be obtained with quaternized AWBs (45.7–205.63 mg/g) (Tables 14.4, 14.5). The extremely good adsorption capacity for PO_4^{3-} makes quaternized AWBs attractive for practical application. In view of searching potential AWBs for quaternization, Wartelle and Marshall (2006) recommended to use AWBs with low lignin-to-cellulose ratios, because of their strong affinity toward quarternizing reagents. These results highlight the potential of improvement of PO_4^{3-} uptake capacity of AWBs using quaternization.

In addition to metal loading and quaternization, thermal activation is shown to be efficient in boosting the P removal. Huang et al. (2010) found that preheating oyster shell in the temperature range of significantly 100–400°C improved its adsorption capacity for PO_4^{3-} ions. While untreated oyster shells could hardly remove PO_4^{3-} from 80 mL wastewater with PO_4^{3-} concentration of 20 g/L, the removal efficiency of preheated oyster shells reached up to 100% after 3 or 4 days. This is attributed to the increase in the pore size and surface area. The temperature range of 500–700°C resulted in the decrease in the P removal efficiency, owing to the collapse of pore structure while lack of $CaCO_3$ decomposition. The P removal percent increased again as temperature increased from 750 to 900°C. This can be explained by the dominant presence of CaO, which plays an important role in the adsorption of PO_4^{3-}. Peng et al. (2012) found that better PO_4^{3-} uptake was achieved for pine sawdust char (BC) produced at the higher pyrolysis temperature. The maximum adsorption capacity of BC is comparable to Whatman QA–52 and higher–when compared with Zr-MCM 41.

14.3.3 Phosphorus Recovery

14.3.3.1 Drivers for Phosphorus Recovery

The P recovery is becoming a matter of interest in recent years. There are several drives for this. Firstly, the P recovery can contribute to conserving the global P rock reserves, which will be depleted within 150 years (Tyagi and Lo 2013; Loganathan et al. 2014). As the recycled P can replace the mineral P used in agriculture and phosphate industry, the P recovery is expected to diminish the amount of P rock mined annually, which is estimated at 160 million tons (Cornel and Schaum 2009; Kuzma 2011; Kalmykova and Fedje 2013). Secondly, the P recovery can protect the water environment from eutrophication by reducing P concentration in effluents. The increasing use of recycled P products as slow release fertilizers in the agriculture reduces the risk of P leaching and loss, and thus indirectly mitigating the eutrophication (Garcia-Belinchon et al. 2013). Moreover, the P recovery can create revenues by converting waste into commercial products. It is estimated that the P recovery from sewage sludge can produce a profit of about US$ 2.1 per capita and year (Tyagi and Lo 2013). Finally, this process may prevent struvite scale, which is a threat to most of the engineered systems (Kuzma 2011).

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Table 14.5. A summary on modification methods for developing better AWBs

Biosorbent	*Modifying reagents*	*Maximum adsorption capacity ($mg\ PO_4^{3-}/g$)*	*References*
Metal impregnation			
Wood particles	Fe(II) salt	2.05	Eberhardt and Min (2008)
Coir pith carbon	Zn(II) salt	5.10	Namasivayan and Sangeetha (2004)
Juniper fiber	Acid mine drainage (AMD)	7.08	Han et al. (2005)
Wood particles	Carboxymethylation + $FeCl_2$	17.38	Eberhardt and Min (2008)
Juniper bark fiber	$La(NO_3)_3.6H_2O$ 0.01M	20.05	Shin et al. (2005)
Apple peel	$ZrO_2Cl.8H_2O$	20.35	Mallampati and Valiyaveettil (2013)
Skin split waste	Al(III) salt	21.65	Huang et al. (2009)
Coir pith	$Fe(NO_3)_3.9H_2O$	22.05	Krishnan and Haridas (2008)
Eggshell	Calcination	23.02	Kose and Kivanc (2011)
Juniper bark fiber	$La(NO_3)_3.6H_2O$ 0.1M	33.35	Shin et al. (2005)
Orange waste	$Ca(OH)_2 + La(III)/Ce(III)/Fe(III)$ salts	42.72 for 3 types of gels	Biswas et al. (2007)
Sugarcane baggage fibers	Carboxymethylation	67.50	Carvalho et al. (2011)
Skin split waste	Fe(III) salt	72.00	Huang et al. (2009)
Sugarcane baggage fibers	Carboxymethylation + $FeCl_2$	152.00	Carvalho et al. (2011)
Orange waste gel	$Ca(OH)_2$ + NaOH + Zr(IV) salt	174.68	Biswas (2008)

(Continued)

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Table 14.5. A summary on modification methods for developing better AWBs (Continued)

Biosorbent	*Modifying reagents*	*Maximum adsorption capacity (mg PO_4^{3-}/g)*	*References*
Quarternization			
Milled pine bark	Poly-allylamine hydrochloride (PAA HCl) + Epichlorohydrin	12.65	Tshabalala et al. (2004)
Wheat residue (Low/medium/ high cost resins)	Epichlohydrin + N,N-Dimethylformamide + Ethylenediamine + Triethylamine	16.50/32.05/52.40	Xu et al. (2011c)
Soybean hulls	N-(3-chloro-2-hydroxypropyl) + Trimethylammonium chloride	19.84	Marshall and Wartelle (2004)
Sugarcane bagasse	Epichlorohydrin + N,N-Dimethylformamide + Dimethylamine + Pyridine	21.30	Zhang et al. (2012)
Milled woods/bark	Poly-allylamine hydrochloride (PAA HCl) + Epichlorohydrin	26.03/44.65	Karthikeyan et al. (2004)
Yellow pine (wood/bark)	Poly-allylamine hydrochloride (PAA-HCl) or 3 chloro -2- hydroxypropyltrimethylammonium chloride	22.83/36.65	Karthikeyan et al. (2002)
Wheat straw	Epichlorohydrin + Triethylamine + Pyridine	45.70	Xu et al. (2010)
Cotton stalk/ wheat stalk	Epichlorohydrin + N,N-Dimethylformamide + Diethylenetriamine + Trimethylamine	51.54/60.61	Xu et al. (2011b)
Giant reed	Epichlohydrin + N,N-Dimethylformamide + Ethylenediamine + Triethylamine	54.67	Xu et al. (2011a)

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Giant reed	Epichlohydrin + N,N-Dimethylformamide + Ethylenediamine + Triethylamine	60.95	Yue et al. (2010)
Corn stover	N-(3-chloro-2-hydroxypropyl) + Trimethylammonium chloride	62.70	Wartelle and Marshall (2006)
Banana stem	Epichlorohydrin + N,N-Dimethylformamide + Dimethylamine + Pyridine	72.46	Anirudhan et al. (2006)
Sawdust of Aleppo pine	Surface activation, acid prehydrolysis, urea treatment	116.25	Benyoucef and Amrani (2011)
Green coconut shell fibers	Ammonium quaternary salt (2-hidroxypropyltrimethyl ammonium chloride)	200.00	De Lima et al. (2012)
Wood residues	Choline chloride derivative + Urea + Imidazole	205.63	Karachalios (2012)
Thermal activation			
Pine sawdust char	Fast pyrolysis	15.11	Peng et al. (2012)

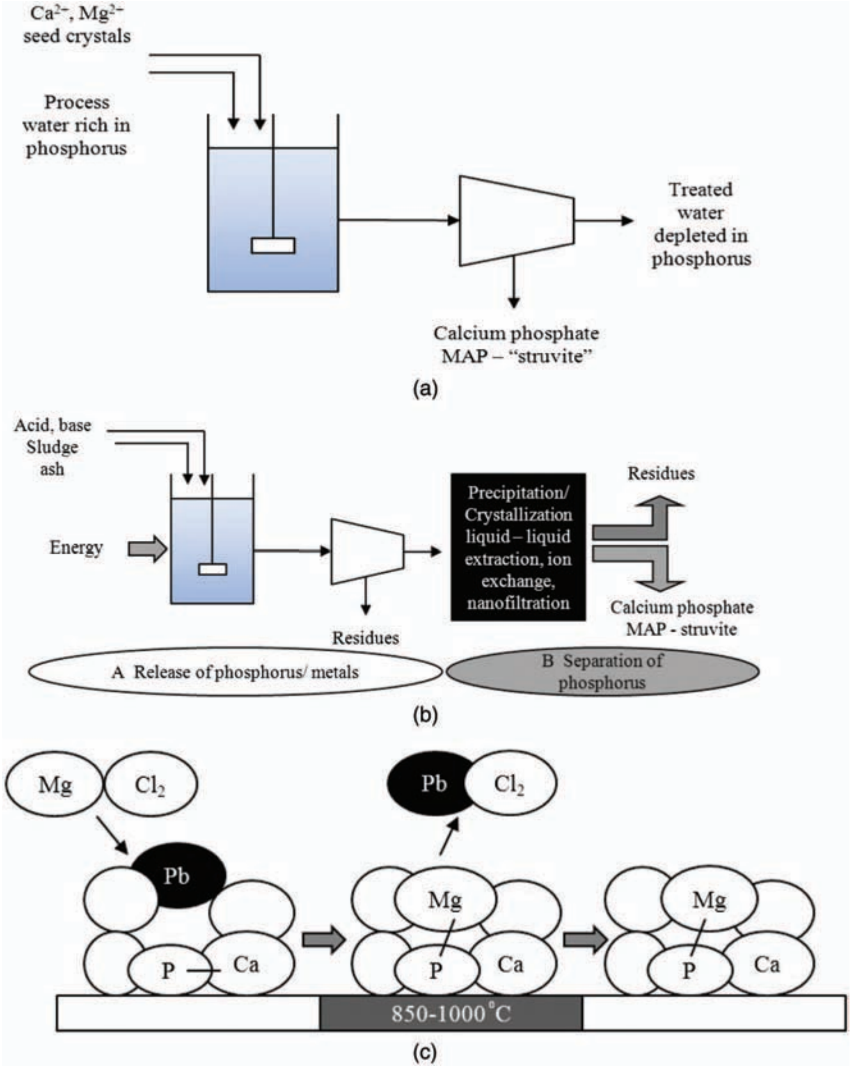

Figure 14.4. Phosphorus recovery technologies: (a) the principle of precipitation/ crystallization technologies; (b) the principle of wet-chemical technology; (c) the principle of thermo-chemical technology

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14.3.3.2 Phosphorus Recovery Technologies

Till date, various technologies are available for P recovery. Depending on the WWTPs products (water, sludge or ash) utilized for P recovery, the P recovery technology can be precipitation/crystallization, wet-chemical or thermo-chemical, respectively (Figure 14.4). Due to very low P concentration (≤5 mg/L), effluents

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of WWTPs cannot be a good source, as high volume needs to be treated. On the contrary, the higher P concentration (20–100 mg/L) in the sludge liquor reduces the volume to be treated, and thus this product is widely used (Schick et al. 2009). As P in the sludge and ash is biologically/chemically bonded to other substances, it needs to be extracted by acids or bases before being separated by means of precipitation, ion exchange, nanofiltration, etc. This is the principle of wet-chemical technology. By using chlorine compounds (e.g. KCl, $MgCl_2$) and high temperature (>1000°C), thermo-chemical technology is expected to remove heavy metals in the form of vaporized heavy metals chlorides, and thus enabling P separation. The P recovery potential may vary, depending on the utilized WWTPs products. While the recovery rate from the water phase is limited to 55%, the values from sewage sludge and ash can reach 90% (Cornel and Schaum 2009; Nieminen 2010). Among influential factors, pH and molar ratios of Mg^{2+}, NH_4^+, and PO_4^{3-} are found to play the critical roles in the P recovery process (Liu et al. 2012). The most common products of this process are magnesium ammonium phosphate (MAP, struvite) and calcium phosphate (Cornel and Schaum 2009).

14.3.3.3 Phosphorus Recovery by Means of Adsorption

P recovery is defined as the utilization of any process for precipitating or crystallizing P from wastewater, sewage sludge, and ash into a pure product for recycling purposes (Green et al. 2004). Although P recovery as struvite or calcium phosphate is widely known, only a few reports exist on the use of adsorption for this purpose. Ebie et al. (2008) investigated the P recovery in decentralized advanced Johkasou by means of adsorption onto Zr(IV). The spent adsorbent was immersed in the NaOH 7% solution to elute P. Because of the two-step desorption process, the desorption efficiency was enhanced from 80 to 95%. The maximum recovery efficiency (95.6%) was achieved by crystallization using low-temperature concentrator in vacuo. The recovered P product ($Na_{3.25}(OH)_{0.25}PO_{4.}12H_2O$) had the purity of >95% with the permissible levels of hazardous elements (e.g. As, Hg, Pb, Cd, and Ni). The tests on germination rate and fertilizer response showed that recovered P was as good as Na_2HPO_4, a chemical fertilizer. As the elution solution after crystallization was recycled as a desorbent, the chemical costs and the disposal problems could be mitigated. Similarly, Midorikawa et al. (2008) utilized a high-speed adsorbent for P recovery from municipal wastewater secondary effluent. Due to the particularly high removal percentage (99.5%) and desorption efficiency (97%) of this adsorbent, P was successfully separated. $Ca(OH)_2$ was added to precipitate eluted P as calcium phosphate. With 16% P and very low levels of toxic substances, the recovered product could be used as a replacement for P ore and fertilizer. The works on P recovery via a combination of biosorption onto AWBs and precipitation/crystallization are rare. Most of the studies are limited to desorption of P and reusability of AWBs. It was found that some AWBs possessed very high desorption efficiencies with good reusability, e.g. modified banana stem (Anirudhan et al. 2006); Zr(IV) loaded orange waste gel (Biswas 2008); Zr(IV) loaded apple peels (Mallampati and Valiyaveettil 2013); modified sugarcane

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bagasse (Zhang et al. 2012), etc. Unfortunately, these AWBs have not been used in combination with precipitation/crystallization for P recovery.

Biswas (2008) claimed that P could be efficiently extracted from incinerated sewage sludge ash (ISSA) using 0.05 M H_2SO_4 or 0.1M HCl. Due to the selective adsorption onto Zr(IV) loaded orange waste gel, the extracted P was separated from other contaminants, e.g. Ca, Fe, Al, etc. The adsorbed P could be easily eluted using NaOH 0.2M. That paves the way to the recovery of P from ISSA. Kose and Kivanc (2011) proposed a procedure whereby the P eluted from calcined waste eggshell by NaOH 0.5 M could be recovered as calcium phosphate by the addition of solid CaO. Desorption and recovery efficiencies of P were 37.6% and 37.72%, respectively. It is inferred from the obtained results that, adsorption may hold a promise for P recovery from wastewater, but it has not been fully exploited. Based on published results, a diagram of P removal/recovery from wastewater by means of adsorption onto AWBs is proposed (Figure 14.5).

14.3.3.4 Barriers for Phosphorus Recovery

Until now, P recovery is still an un-established process. The reason for this remains in the quality of recycled P fertilizers (Sartorius et al. 2012). The excessive

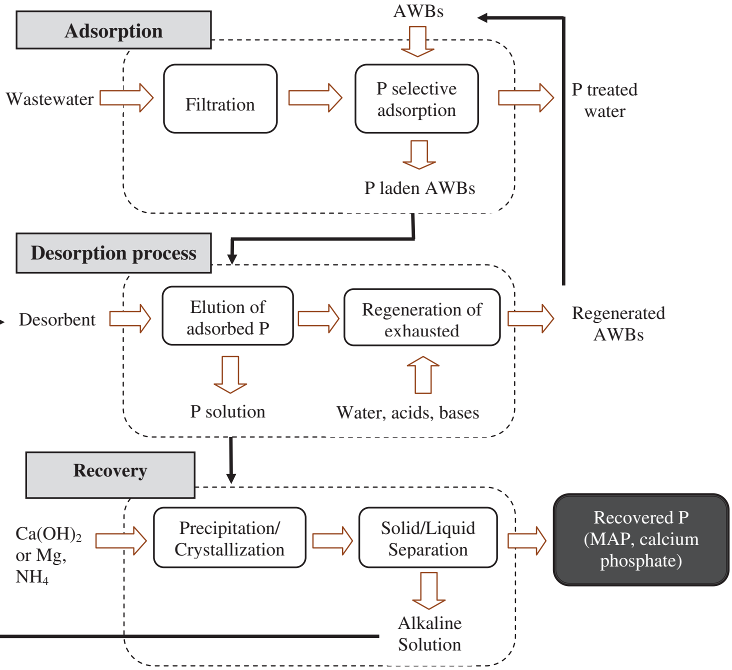

Figure 14.5. Diagram of P removal/recovery from water and wastewater via adsorption onto AWBs

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level of heavy metals in P fertilizers recovered from municipal solid waste incineration fly ash prevents them from being used in arable lands (Kalmykova and Fedje 2013). In addition, recycled P seems to be more expensive than mineral P (Cornel and Schaum 2009). The cost for P recovered from sludge liquor by ion exchange was 8.2 €/kg while that for mined P was only 0.652 €/kg (Bottini and Rizzo 2012). These findings are in harmony with those reported by Tyagi and Lo (2013), who claimed that recovered P was 22 times more costly than mined P. Molinos-Senante et al. (2011) suggested that the P recovery would not be a financially viable option, unless the environmental benefits were considered. These constraints are expected to be addressed in the next 20 years in developed countries (Sartorius et al. 2012).

14.3.4 Selection of Potential AWBs for P Removal and Recovery

The selection of proper AWBs for PO_4^{3-} removal/recovery plays an important role as it may affect the whole process. However, up to date, little work has been done on building the guideline for this. Consequently, while one AWB can be successfully tested in the lab, unexpected results can be obtained from its practical application. Thus, this section briefly discusses key criteria for screening potential AWBs in PO_4^{3-} removal/recovery.

It is well recognized that the main advantage of biosorbents as compared to other methods is their "cost-effectiveness" (Srivastava and Goyal 2010; Everglades Hub 2013). Hence, this should be considered as a fundamental principle in selecting potential adsorbing materials. As mentioned above, the removal and recovery of PO_4^{3-} from wastewater using AWBs includes two steps: the separation of PO_4^{3-} followed by the precipitation/crystallization of PO_4^{3-}. While the first step can be done via selective adsorption with AWBs, the second step can be accomplished by using $Ca(OH)_2$, $CaCl_2$, etc. For that reason, ideal AWBs should have high affinity toward PO_4^{3-} anions to ensure their efficient removal. As raw AWBs are often prone to less adsorption efficiency, modification methods are required to improve PO_4^{3-} uptake capacity of raw AWBs. In addition, high selectivity is needed for separation of PO_4^{3-} anions from other pollutants. Moreover, easy desorption property may be necessary as it paves the way to P recovery. It should be noted that, these properties are necessary but not adequate for successful removal/recovery of PO_4^{3-}. Penn et al. (2007) suggested that while the cost and availability should be considered, in view of large scale application, the particle size or hydraulic properties may be significant if AWBs are used in the column mode. Similarly, Srivastava and Goyal (2010) highlighted reusability property as an efficient way to make the process cost-saving. Accordingly, ideal AWBs should have no physical damage, minor diminished P uptake, marginal weight loss, trivial loaded metal leakage, etc. after many cycles of adsorption and desorption. In the same way, Loganathan et al. (2014) suggested that suitable adsorbents for P removal/recovery should have a high sorption capacity, good hydrological conductivity and easy regeneration and proper reuse. Besides these things, from our own experience, we highly recommend that appropriate AWBs

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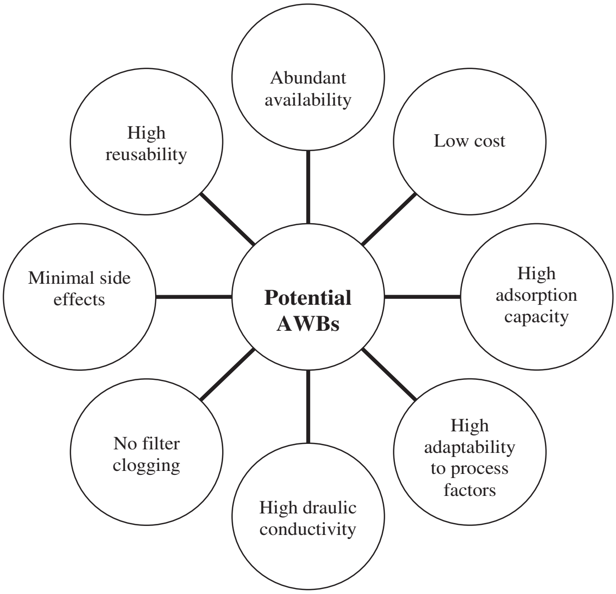

Figure 14.6. Selection criteria of potential AWBs used for P removal/recovery

should not cause any significant detrimental effects on the quality of aqueous solutions (e.g. color, turbidity, DO, COD, BOD, heavy metals, etc.).

Regarding the availability characteristic of AWBs, we suggest using wastes or by-products from food processing industries (e.g. orange peel, sugarcane bagasse, soybean milk residues, etc.) for developing potential AWBs, due to their stable quality and supply source. Keeping the above views in mind, appropriate AWBs for P removal/recovery should own the following properties (Figure 14.6):

- Abundant availability;
- Low cost;
- High affinity toward PO_4^{3-};
- High adaptability toward process parameters;
- High reusability;
- High hydraulic conductivity;
- No filter clogging; and
- Minimal side effects to the water environment.

14.4 RECENT ADVANCES

The adsorptive removal and recovery of PO^{3-} from water and wastewater using AWBs is a relatively new process. In the initial stage of its development, the results

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obtained mainly focus on basic knowledge. Understanding the operation principles is expected to enable the application of AWBs in the future. The recent developments drawn from studies on removal and recovery of PO^{3-} from water and wastewater using AWBs include:

- Confirming that raw AWBs are frequently inefficient in P removal and thus satisfactory decontamination of P requires appropriate modifications. The common methods are found to be metal loading and quaternization of AWBs. Side effects of modifying AWBs are also identified;
- Some potential AWBs have been found, mainly based on the maximum adsorption capacity;
- The mechanisms of the adsorption/desorption processes have been initially elucidated. This provides useful information for process optimization and selection of appropriate desorption solutions;
- The effects of process parameters have been investigated in an attempt to comprehend and optimize the process. For example, understanding the effect of pH can help to explain the desorption mechanism and choose the appropriate desorption solutions, whereas identification of the effect of particle sizes, contact time, interfering anions, etc. on the adsorption of P onto AWBs is necessary for their practical application; and
- The recovery of P based on the combination of adsorption onto AWBs and precipitation/ crystallization is initially investigated in the labs.

14.5 CONCLUSION AND FUTURE WORK

Due to increasing concerns relevant to water quality deterioration and depletion of global P rock reserves, the P removal/recovery has recently become a matter of interest. Even though various technologies are presently available, adsorption seems to have advantages when used for P recovery. Due to selective adsorption property of AWBs, P can be separated from other contaminants and thus enabling P recovery in the next stage. Though AWBs in both natural and modified forms can be used for P removal, the low P uptake capacity of raw AWBs hinders their widespread application. In contrast, satisfactory adsorption behaviors can be obtained with AWBs modified by metal loading, $-NH_2$ groups grafting, and thermal activation. However, this should be applied with caution, due to possible side effects. While several mechanisms are reported for the sorption of PO_4^{3-} onto AWBs (e.g. ion exchange, ligand exchange, chemisorption, surface precipitation, and diffusion), it is found that desorption of PO_4^{3-} from spent AWBs can be largely attributed to anion-exchange mechanism. Of influential factors, pH appears to play the most important role. In many cases, AWBs demonstrated the ability to remove PO_4^{3-} efficiently in a short time (<1 h), in the presence of interfering anions, over a wide pH range (4–9). These properties provide favorable conditions for their practical applications. The adsorbed P could be desorbed by distilled

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water, salts, acids, bases. Distilled water and neutral salts are proven to be effective as long as ion exchange mechanism dominates. Conversely, when other mechanisms can be important pathways, acids or bases should be used alternatively. The P recovery process is in its initial stage of development. It can be done via a combination of P separation using AWBs and P precipitation/crystallization using $Ca(OH)_2/CaCl_2$. Off these, the first step can be successfully accomplished through adsorption onto AWBs.

Although significant efforts had been contributed to make progress in the removal and recovery of PO_4^{3-} by AWBs, there are still many points for future research as follows:

1. Further improve modification methods that currently exist in the directions of cost saving, effectiveness, and environmental friendliness. This can be done via examining various quaternizing reagents and combined loading metals;
2. Keep searching for novel potential AWBs in view of practical application, which should have favorable physical properties, less harmful effects, low cost, abundant availability in addition to high affinity and selectivity towards PO_4^{3-} anions;
3. Developing a systematic and comprehensive method with essential tools to better understand mechanisms of adsorption and desorption;
4. Examining potential AWBs in the column mode on the real wastewater to promote large-scale application of these biosorbents; and
5. Employing potential AWBs in the PO_4^{3-} recovery process at the pilot and full scales. Further work in this matter includes process optimization, product quality improvement, simultaneous recovery of other resources, cost-benefit analysis, field trials, etc.

As a final remark, the adsorptive removal and recovery of PO_4^{3-} from water and wastewater using AWBs can provide a sustainable, efficient, beneficial solution for P management. Thus, it should be considered as a promising green technology. However, the above challenges need to be addressed before ready-to-use recycled P products can be achieved.

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CHAPTER 15

Removal of Trace Organic Contaminants by Integrated Membrane Processes for Water Reuse Applications

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15.1 INTRODUCTION

The occurrence of trace organic contaminants (TrOC) in the environment has received significant attention in recent years from the scientific community and the public health and ecological conservation authorities (Hai et al. 2014; Luo et al. 2014). TrOCs consist of a diverse and expanding array of natural as well as anthropogenic substances, which are commonly detected in waters at trace concentrations ranging from a few ng/L to several μg/L. They include industrial chemicals, chemicals used in households, chemicals excreted by people and animals, and chemicals formed in wastewater and drinking-water treatment processes. Some key classes of TrOCs include pharmaceuticals and personal care products (PPCPs), endocrine disrupting compounds (EDCs), pesticides, industrial chemicals, steroid hormones and phytoestrogens (Bhandari et al. 2009). TrOCs are biologically active and can, therefore, impose acute and chronic toxicity on aquatic organisms, accumulate in the ecosystem and cause loss of biodiversity as well as a range of possible adverse effects on human health. To address existing and impending water shortages, many communities around the world are working to increase water conservation and reuse. The 'low

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concentration' and diversity of TrOCs not only complicate their detection and analysis but also create challenges to their efficient removal from water and wastewater for water reuse. In this Chapter, advanced technologies for the removal of emerging TrOCs from wastewater for reuse purposes are systematically reviewed and discussed. In particular, integrated membrane processes for TrOC removal are delineated.

15.2 TRACE ORGANIC CONTAMINANTS (TROCS) IN AQUATIC ENVIRONMENTS AND THEIR CONCERNS

Conventional wastewater treatment plants (WWTPs) have been only designed for the removal of basic contaminants such as bulk organic matter and nutrients (i.e. phosphorus and nitrogen), and not specifically for TrOCs. Accordingly, a major pathway for these TrOCs entering the aquatic environment is the secondary treated effluent discharged from WWTPs. Table 15.1 depicts examples of widespread occurrence of some common TrOCs in surface water in different countries.

The potential effects of TrOCs on aquatic organisms and humans have been well documented (Schwaiger et al. 2004; Carlsson et al. 2006; Bhandari et al. 2009; Bolong et al. 2009). These compounds can disrupt the endocrine system by mimicking, blocking and also hampering functions of hormones, thereby affecting health of human and animal species (Bolong et al. 2009). Schqaiger et al. (2004) studied the possible effects in rainbow trout due to prolonged exposure to diclofenac. They reported histopathological changes in the kidney and liver when the fishes were exposed to 5 μg/L of diclofenac for 28 days. EDCs cause a wide range of adverse effects on aquatic organisms e.g., feminisation of male fishes (Jobling et al. 1998), demasculinisation of alligators (Guillette et al. 2000), growth inhibition, immobilisation, mutagenicity, increased mortality and changes in population density (Colborn et al. 1994; Alzieu 2000). For example, bisphenol A has been shown to have estrogenic effects in rats (Ishido et al. 2011). Bisphenol A mimics estradiol and causes direct damage to the DNA of cultured human breast cells (Iso et al. 2006). Some steroid hormones such as estrone, 17β-estradiol and 17α-ethinylestradiol have a high specific biological estrogenic activity even at extremely low concentrations (Bolong et al. 2009) and may cause feminisation in male fish. Table 15.2 presents a few recent reports on the effects of TrOCs on aquatic organisms and humans.

In the environment, TrOCs may be present as a mixture of various compounds and their transformation products. Mixtures of TrOCs may impose a more complicated effect when compared to that of a single compound (Fent et al. 2006; Backhaus et al. 2008; Kümmerer 2009). For example, eco-toxicity tests with antibiotics showed that the combined toxicity of antibiotics can lead to either synergistic, antagonistic or additive effects (Christensen et al. 2006). However, in general, knowledge about the toxicity of TrOC mixtures is still limited.

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Table 15.1. Occurrence of some common TrOCs in surface waters in different countries

	Concentration (ng/L)								
Compound	*Canada*[a,1]	*China*[2]	*France*[3]	*Germany*[4,5]	*Greece*[6]	*Korea*[7]	*Spain*[a,8]	*UK*[9]	*US*[10]
Ibuprofen	0.98 (79)	ND–1417	ND–8	—	1–67	<15–414	—	0.3–100	ND–77
Naproxen	1 (87)	ND–328	ND–6.4	—	3–322	—	—	0.3–149	—
Ketoprofen	—	—	ND–22.0	—	0.4–39.5	—	—	0.5–14	—
Diclofenac	—	—	ND–35.0	—	0.8–1043	—	—	0.5–261	—
Mefenamic acid	—	—	—	—	—	<30 – 326	—	0.3–169	—
Carbamazepine	3 (749)	—	ND–31.6	102–1194	—	<4–595	—	0.5–684	ND–9.6
Gemfibrozil	—	—	—	—	—	—	—	-	—
Atenolol	—	—	ND–34.0	—	—	<100–690	—	1–560	—
Sulfamethoxazole	0.2 (284)	—	ND–5.1	—	—	—	—	0.5–4	ND–38
Trimethoprim	—	—	—	—	—	—	—	7–122	ND–9.1
Triclosan	0.4 (25)	35–1023	—	124–220	3–39	ND	—	5–95	ND–9.8
Galaxolide	—	—	—	35–1814	—	—	—	—	—
Tonalide	—	—	—	5–273	—	—	—	—	—
Estrone	—	ND–65	—	—	—	3.6–69.1	—	—	—
Estradiol	—	ND–2	—	—	—	1.1–10.1	—	—	—
Ethinylestradiol	—	ND–1	—	—	—	ND–1.9	—	—	—
Estriol	—	ND–1	—	—	—	—	—	—	—
Caffeine	—	—	—	—	—	—	—	—	ND–225
Nonylphenol	—	36–33231	—	—	558–2704	115–336	—	—	—
Bisphenol A	2.1 (87)	6–881	—	192–215	55–162	7.5–334	—	6–68	—

(Continued)

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Table 15.1. Occurrence of some common TrOCs in surface waters in different countries (Continued)

	Concentration (ng/L)								
Compound	*Canada*[a,1]	*China*[2]	*France*[3]	*Germany*[4,5]	*Greece*[6]	*Korea*[7]	*Spain*[a,8]	*UK*[9]	*US*[10]
TCEP	—	—	—	<3–184	—	—	—	—	—
TCPP	—	—	—	<4–379	—	—	—	—	—
Atrazine	—	—	—	—	—	—	11 (39)	—	—
Diazinon	—	—	—	—	—	—	10(216)	—	—
Diuron	—	—	—	—	—	—	72(408)	—	—

[a] Median concentration with maximum concentration in the brackets; [b] Data were derived from [1](Kleywegt et al. 2011); [2](Peng et al. 2008); [3](Vulliet et al. 2011); [4](Regnery and Püttmann 2010); [5](Reinstorf et al. 2008); [6](Stasinakis et al. 2012); [7](Kim et al. 2009); [8](Köck et al. 2010); [9](Kasprzyk-Hordern et al. 2009); and [10](Wang et al. 2011)

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Table 15.2. Recent reports on the adverse effects of TrOCs

Compounds	*Concentration (μg/L)*	*Type of risk*	*References*
Diclofenac	0.5–50	Affect tissues of gills and kidney of freshwater fish brown trout	Hoeger et al. (2005)
Ibuprofen, diclofenac, 17β-estradiol and 17β-estradiol-17 acetate	0.01	Chronic toxic effect such as inhibited polyp regeneration and reduced reproduction in hydra	Carlsson et al. (2006)
17α-ethinylestradiol (EE2)	0.005–0.05	Modulation of brain and inter-renal steroid genic acute in juvenile salmon	Lyssimachou and Arukwe (2007)
Triclosan	0.3–30	Disrupts gene expression in *Rana catesbeiana*	Veldhoen et al. (2006)
Estriol	0.1–30	Disruption of vitellogenisis in shrimp	Holbech et al. (2006)
Nonylphenol	100	Multi-generational reproductive process disruptions on *Daphnia magna*	Brennan et al. (2006)
Carbamazepine	20*	Cause ataxia, movement disorders, anticholinergic toxidrome in human	Soderstrom et al. (2006)

*mg/kg body weight

15.3 WATER REUSE: IMPORTANCE AND QUALITY CONTROL ISSUES

The lack of clean water is a global problem. In the Earth's hydrologic cycle, freshwater supplies are fixed and constant while water demand is rising (Howell 2004; Tadkaew et al. 2007; Hai and Yamamoto 2011). Furthermore, due to environmental pollution, the quality of the planet's water gradually deteriorates, presenting challenges for the major users. Increasing demand for water, and drought and water scarcity are now critical issues facing many urban and rural

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communities worldwide (Howell 2004; Tadkaew et al. 2007; Jimenez and Asano 2008; Hai and Yamamoto 2011). In order to keep this essential resource available and suitable for use, effective water treatment has become an area of global concern. Water recycling is a pragmatic approach to mitigate or solve the problems of water supply. There is a growing interest in using non-traditional water resources by means of water reclamation and water recycling for long-term sustainability. However, the presence of TrOCs in treated sewage challenges water reclamation. Given the potential adverse impact of TrOCs on human health and the ecosystem and their ubiquitous occurrence in municipal sewage, their removal during wastewater treatment has become a vital issue in recent years. Intensive treatments are required to eliminate the risks to human health and aquatic ecological wellbeing when secondary treated effluent is used as water source in water reclamation.

15.4 SPECIFIC TREATMENT TECHNOLOGIES FOR TROC REMOVAL

TrOCs may possess a range of chemical properties, which render them more persistent to conventional biological treatment. Thus, there is an urgent need to enhance the treatment capacity of existing technologies and to develop new treatment processes to ensure adequate removal of TrOCs during wastewater treatment. In this section, we review the removal of TrOCs by existing and advanced treatment processes in details.

15.4.1 Activated Carbon Adsorption

TrOCs can be effectively removed by activated carbon. However, in some cases, highly variable removal efficiencies have been reported (e.g., Ghosh et al. 1999; Fuerhacker et al. 2001; Matsui 2002; Yoon et al. 2003). Indeed, TrOC removal by activated carbon can be significantly affected by the physicochemical properties of the compounds and operational conditions. Snyder et al. (2007) conducted a comprehensive study of the removal of a range of PPCPs and EDCs by powdered activated carbon (PAC) adsorption and reported variable removal of the PPCPs investigated in their study (from 17% for ibuprofen to up to 95% for pyrene at 5 mg/L). These results are consistent with a study by Bolong et al. (2009) who reported 40 to 60% removal of several PPCPs including ibuprofen, meprobamate and sulfamethoxazole by activated carbon adsorption. Snyder et al. (2007) indicated that 5 mg/L of PAC could remove more than 90% of EDCs after a contact time of 4 h. On the other hand, Fuerhacker et al. (2001) obtained 49–81% removal of 17β-estradiol by granular activated carbon (GAC) within 1–3 hours of contact time. Esplugas et al. (2007) reported that a 60 to 99% removal of 17β-estradiol and 17α-ethinylestradiol, respectively, could be achieved by using activated carbon. Pesticides such as atrazine could be removed effectively (by 90%) using PAC at 2 hours of contact time (Knappe et al. 1997; Ghosh and Philip 2005). High removal of disinfection by-products (for example 90% for

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trihalomethanes) was achieved using an activated carbon dose of 500 mg/L (Kristiana et al. 2011). In a pilot-scale study in the USA, a 50% reduction of trihalomethanes formation was reported using a dose of 100 mg/L of PAC (Kristiana et al. 2011).

The removal rate of TrOCs by activated carbon depends on their physiochemical proprieties such as charge and hydrophobicity. The removal efficiency of positively charged compounds using activated carbon is usually higher than those for negatively charged compounds (Verliefde et al. 2007; De Ridder et al. 2011). The adsorption of charged contaminants can be strongly affected by the solution pH and the presence of natural organic matter in the water matrix (Newcombe et al. 1997; Biniak et al. 1999). Additionally, hydrophobicity can play an important role in the removal efficiency of such TrOCs by activated carbon. Snyder et al. (2007) reported that the breakthrough of hydrophilic compounds can occur faster than hydrophobic compounds. Nguyen et al. (2012) reported that hydrophilic and recalcitrant compounds such as fenoprop, ketoprofen, naproxen, diclofenac, and carbamazepine were not effectively removed by MBR treatment; however, they were removed by 98% during post-treatment by GAC. Nguyen et al. (2012) attributed the high removal to mechanisms other than hydrophobic interactions (such as ion exchange, hydrogen bonding and surface complexation) which can also play a role in the sorption of hydrophilic compounds onto GAC (Nguyen et al. 2012). Similarly, compounds with higher hydrophobicity such as nonylphenol ($\log D = 6.19$) may not always show higher removal efficiency by activated carbon compared with less hydrophobic chemicals such as carbamazepine ($\log D = 2.67$) (Akkanen et al. 2004; De Ridder et al. 2011; Nguyen et al. 2012).

The presence of background organic matter in water can affect the adsorption rate of TrOCs by activated carbon. Up to 8–12 mg/L of background organic matter can be found even in clean ground waters, which may reduce the adsorption of organic contaminants on activated carbon surface (Stenzel and Merz 1989). Jarvie et al. (2005) stated that low molecular weight background organic matter might occupy a portion of smaller pores (>1 nm) in GAC. Matsui et al. (2002) reported the removal of only 50% of synthetic organic chemicals in the presence of background natural organic matter (NOM). The removal efficiency of atrazine by activated carbon was shown to be strongly affected by the presence of NOM and the adsorption decreased by 65% due to competition with background organic matter (Martín-Gullón and Font 2001). In addition, because of the high competition between background organic matter and TrOCs for adsorption sites in activated carbon, a significant decrease in the adsorption capacity for these contaminants can occur in the presence of background organic matter (Knappe et al. 1998; Quinlivan et al. 2005). For example, the adsorption of pesticides such as simazine and atrazine are strongly influenced by the presence of background organic matter (Jarvie et al. 2005). Interestingly, when GAC was fed with permeate of an NF system, which has a low concentration of organic matter, a high removal efficiency of up to 97% was observed for pharmaceuticals (Verliefde et al. 2007).

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NOM can cause partial or complete pore blockage near the pore entrance in activated carbon particle (Quinlivan et al. 2005), which can influence the adsorption and desorption of TrOCs (Quinlivan et al. 2005; To et al. 2008). Pre-loading of background organic matter on activated carbon can reduce the sorption kinetics of different TrOCs (such as erythromycin, diclofenac, bisphenol A and dichlorophenoxyacetic acid) (Corwin and Summers 2011). For example, a 50% reduction in the removal of pharmaceuticals by GAC was observed due to pre-loading of highly hydrophobic NOM on GAC (De Ridder et al. 2011).

15.4.2 High Pressure Membrane Filtration

High-pressure membrane filtration, including nanofiltration (NF) and reverse osmosis (RO), has been widely used to remove a wide variety of organic pollutants (e.g., Nghiem and Schäfer 2002; Agenson et al. 2003; Xu et al. 2006; Hofman et al. 2007; Vogel et al. 2010). In a full-scale study, Verliefde (2008) reported a high rejection (>95%) of most investigated TrOCs by the Triseps (X20 and ACM5) and Hydranautics (ESPA1 and ESPA4) RO membranes. In another study, an NF270 membrane achieved a high rate of rejection for charged pharmaceuticals, i.e., 99% for sulfamethoxazole and 96% for ibuprofen, where removal of both TrOCs was enhanced by charge repulsion (Nghiem 2005). Several pesticides could be effectively rejected (>99%) by NF/RO membranes (Williams 2003). However, the rejection of some uncharged and small molecular weight organic contaminants by NF/RO membrane can be incomplete (Agus and Sedlak 2010). For instance, using four newly manufactured NF and RO membranes, atrazine rejection was increased from 10.9 to 14.9%, and 68.4 to 97.5% by using sulfonated polyethersulfone and poly(vinyl alcohol)/polyamide membranes, respectively, whereas compared to atrazine, the rejection of diazinon increased from 44.6 to 44.8% with sulfonated polyethersulfone membranes and 95.1 to 99.5% by poly (vinyl alcohol)/polyamide membranes (Kiso et al. 2000).

The low rejection of some small molecular weight and uncharged TrOCs by NF/RO membranes, as mentioned above, has been widely reported in the literature (Kimura et al. 2003; Bellona et al. 2004; Nghiem et al. 2004; Xu et al. 2005; Agus and Sedlak 2010; Steinle-Darling et al. 2010). For example, at extended stages of filtration there was poor rejection of chloroform and bromoform by RO (e.g., TFC-HR and XLE) and NF membranes (e.g., NF-90 and TFC-SR2) (Xu et al. 2005). Chloroform and bromoform are both neutral and have a molecular weight of 119.4 and 252.7 g/mol, respectively. The charge of the TrOCs and that on the membrane can play a significant role in the rejection of TrOCs. For example, rejection of a charged compound by NF/RO membranes is usually higher than for a neutral compound with the same molecular weight or size (Xu et al. 2005). Since most pharmaceuticals are negatively charged particularly at natural pH, a considerable number of these compounds may be completely rejected by charge repulsion between the compound and membrane charges (Nghiem 2005). Xu et al. (2005) reported that highly negative surface charge membranes such as the loose

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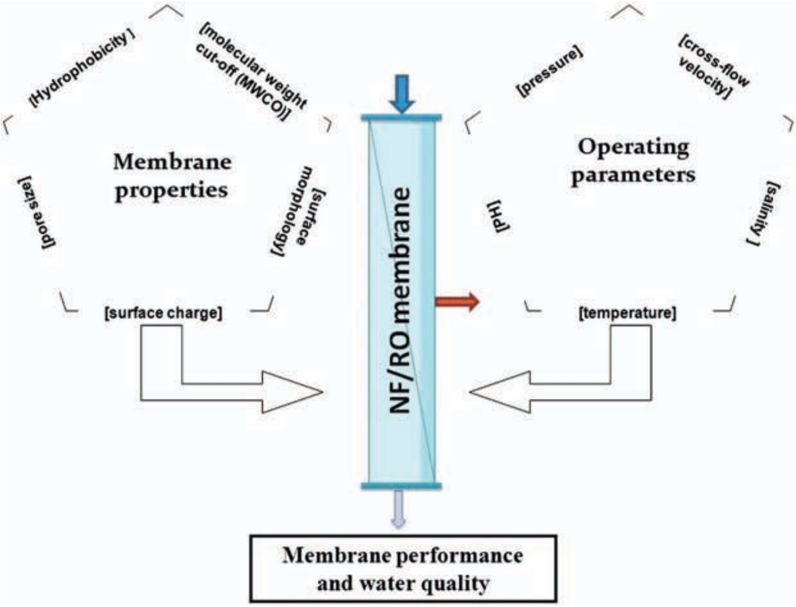

Figure 15.1. Major parameters affecting the performance and production of most of membranes

NF200 membrane, with a molecular weight cut-off (MWCO) of 300 g/mol, could reject more than 89% of low molecular weight negatively charged compounds such as ibuprofen. A high rejection of other pharmaceuticals such as dichloroacetic acid (91%) and trichloroacetic acid (94%) was also achieved using the ESNA (NF) and RO-XLE (RO) membranes (Kimura et al. 2003).

The properties and operational parameters of the membrane play an important role in the rejection of TrOCs by NF/RO membranes (Figure 15.1). These parameters may need to be adjusted to achieve a high rejection of TrOCs and a better overall system performance. Membrane properties such as MWCO, the degree of desalting, roughness, hydrophobicity, and surface charge can influence the rejection of trace organics. A higher rejection of TrOCs with a higher molecular weight than the membrane MWCO is achieved via sieving (Cornelissen et al. 2005; Verliefde 2008). For example, Kimura et al. (2003) reported a 99% rejection of bisphenol A using a low pressure RO membrane (RO-XLE), while only 50% was rejected using a loose NF-270 membrane which has a much larger MWCO (Nghiem et al. 2004).

Membranes with a high degree of desalting are expected to effectively reject most TrOCs such as pesticides, which showed the highest rejection with these membranes (Bellona et al. 2004). A UTC60 aromatic polyamide membrane (an NF membrane) which has a low NaCl rejection (55%), demonstrated a poor rejection of several trace organics such as 47% for bisphenol A and 5% for chloroform (Agenson et al. 2003). Moreover, higher membrane roughness has

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been highly correlated with a lower rejection of large organic contaminants (Bellona et al. 2004).

The hydrophobicity and charge of an active layer of the membrane can also affect the rejection of various TrOCs (Xu et al. 2005). The surface hydrophobicity of a membrane can be determined by measuring the contact angle. The rejection of some organics could be improved by increasing the hydrophobicity of the membrane because it reduces the affinity between the neutral organic solute and the surface of the membrane (Ben-David et al. 2010). Furthermore, the amount of charge in the surface of the membrane affects the degree of electrostatic repulsion and rejection of negatively charged solutes that are subjected to dynamic property changes during the membrane process (Xu et al. 2005). For example, Bellona and Drewes (2005) studied the rejection of negatively charged organic acids (2-naphthalenesulfonic acid and 1,4-dinaphthalenesulfonic acid) by negatively charged NF membranes (e.g., NF-90 and NF-200). According to their findings, the rejection was larger than expected based on steric exclusion, and was mainly driven by the surface charge of the membrane and correlated with the degree of ionization of these compounds (Bellona and Drewes 2005).

Operational parameters such as feed solution pH, salinity, temperature, pressure, and cross-flow velocity can influence the rejection of TrOCs by NF/RO membranes. The feed solution pH can govern the speciation of ionisable TrOCs (and to a lesser extent, the membrane surface charge) and thus their rejection. For instance, Bellona et al. (2004) claimed that when using NF/RO at pH values between 3 and 9, more than 90% of trace organics such as estrone can be rejected. Sulfamethoxazole and ibuprofen are also highly soluble at high pH (in the alkaline region) where the compounds are negatively charged, but when the solution pH decreases, their solubility decreases sharply (Nghiem and Hawkes 2007). Nghiem and Hawkes (2007) reported an almost complete rejection of sulfamethoxazole using the NF-270 membrane at a pH above 8.

Feed solution salinity can cause the effective radius of a charged pore of the membranes to increase as the ionic strength of the feed solution increases because this leads to a decrease in the rejection of monovalent and divalent ions (Bolong et al. 2009). The removal ratio depends on the concentration of salt because the presence of ions can affect the degree of hydration of the membrane. For example, high removal efficiencies (>90%) were achieved by an RO membrane for some antibiotics such as tetracycline, when the salinity increased (Wei-Ying et al. 2009).

Temperature is another parameter that can affect the water flux and rejection of TrOCs (Steinle-Darling et al. 2010). Increasing the feed temperature can lead to a change in the structure and morphology of the polymer matrix, causing an increase in the mean pore radius and MWCO (Sharma et al. 2003). An increase in the solubility of some TrOCs can occur due to the increase in the temperature of the surrounding solution (Wei et al. 2011).

Operating pressure and cross-flow velocity are important factors which can affect the volume and quality of a product. An increase in the operating pressure can reduce the shielding of negative charges on the surface of a membrane, which makes repulsion more effective and enhances the rejection of negatively charged

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contaminants by NF/RO membranes (Binyam et al. 2009). Also, the permeate flux increases with cross-flow velocity over a range of operating conditions because increasing the cross-flow velocity increases the flux and rejection of TrOCs due to a reduction in concentration polarization (Steinle-Darling and Reinhard 2008; Binyam et al. 2009).

The hydrophobicity of both contaminant and membrane can affect the rejection of TrOCs by NF/RO membranes. Contaminants such as steroid hormones with a high hydrophobicity ($\mathrm{Log}\, D > 3.2$), can adsorb onto the surface of the membrane due to hydrophobic–hydrophobic interactions (Ng and Elimelech 2004; Verliefde et al. 2008b). Nghiem et al. (2004) reported that the rejection of natural hormones by the NF270 and NF90 membranes was lower than that expected based on steric hindrance. They explained this phenomenon by the adsorption of these hydrophobic compounds onto the surface of the membrane followed by diffusion through its polymeric matrix (Steinle-Darling et al. 2010).

Rejection of TrOCs by NF/RO membranes can also be affected by other factors such as natural organic matter, ionic strength, and membrane fouling. In the presence of effluent organic matter, rejection as high as 95% of ionic organics pharmaceutical and pesticides by tight NF and RO membranes was possibly caused by a decrease in the membrane's negative charge (Xu et al. 2005). Bellona et al. (2004) attributed an increased rejection of pesticides such as atrazine to adsorption by organic matter present in feed water, which in turn increased the size of the molecule and its electro-static interaction with the membrane. Ng and Elimelech (2004) reported that colloidal fouling can cause a rapid decrease in the rejection of the natural hormones progesterone and estradiol by NF/RO membranes. They verified that NF/RO membrane fouling by colloidal materials had a small effect on the rejection of large molecular weight compounds. High ionic strength feed water could shield the charge on the surface of the membrane that could lead to a decrease in the rejection of negatively charged organics (Bellona et al. 2004).

15.4.3 Advanced Oxidation Processes

Advanced oxidation processes (AOPs) have been used to remove organic pollutants from reclaimed effluent and groundwater (Azbar et al. 2004). Numerous studies in the literature have demonstrated the effectiveness as well as limitation of AOPs for the removal of TrOCs from wastewater (Esplugas et al. 2002; Contreras et al. 2003; Ternes et al. 2003; Andreozzi et al. 2004; Klavarioti et al. 2009). For example, oxidation using ozone can achieve from 92% to complete removal of many pharmaceutical and pesticides such as ofloxacin, sulfamethoxazole, propranolol, carbamazepine, clofibric acid, diclofenac, atrazine and diuron (Ternes et al. 2003; Andreozzi et al. 2004; Maldonado et al. 2006). Although quite a few other pharmaceutical and personal care products (ibuprofen, naproxen, caffeine, iodinated X-ray contrast medium, and tonalide) could not be oxidized using the same process (Ternes et al. 2003), UV treatment alone could lead to 75, 13, and 7% removal of diclofenac, iopromide, and sulfamethoxazole, respectively (Huber et al. 2003). Complete removal of several pharmaceuticals such as ofloxacin,

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sulfamethoxazole, propranolol, carbamazepine, clofibric acid and diclofenac was achieved using the combination of hydrogen peroxide and UV radiation (H_2O_2/UV) (Andreozzi et al. 2004), although only 30–40% of ibuprofen, diphenhydramine, phenazone, and phenytoin could be removed using H_2O_2/UV (Yuan et al. 2009).

The Fenton process has also been used to treat TrOCs from wastewater, particularly from that from hospitals and pharmaceutical manufacturers (Klavarioti et al. 2009). For example, using the Fenton Process at 5.1 mg/L of Fe^{+2} with a concentration of 10 mg/L H_2O_2 can achieve 75% removal of pesticides such as atrazine and 94% removal of some phenyl urea herbicides from ground water (Esplugas et al. 2007). Additionally, electrochemical oxidation using a TiO_2 anode has been shown to oxidise 80% of pharmaceutical compounds present (ofloxacin, sulfamethoxazole, propranolol, carbamazepine, clofibric acid and diclofenac) (Andreozzi et al. 2004; Klavarioti et al. 2009). In addition, the use of electrochemical oxidation and ferrate (iron(VI) and iron(V)) processes to remove endocrine disrupting chemicals demonstrated high elimination such as 95% for estrone, 17β-estradiol and bisphenol A (Jiang et al. 2005). Approximately 50% of trihalomethane disinfection byproducts can be removed from wastewater using UV-radiation with 400 mg/L TiO_2 (Gerrity et al. 2009).

15.4.4 Enzymatic Degradation

The enzymatic treatment process can be categorised between traditional chemical and biological processes. This involves chemical reactions based on the action of biological catalyst. The use of enzymes obtained from various plant and microbial sources for wastewater treatment have been actively studied in recent years. Enzymatic treatment processes have various advantages over conventional biological and chemical processes such as high specificity, application to xenobiotic recalcitrant compounds, high reaction rate, and reduction in sludge volume (Kudanga et al. 2010; Hai et al. 2013; Yang et al. 2013; Modin et al. 2014). Recent reports indicate great potential of using fungal peroxidases and laccase. This section reviews the application of laccase, lignin peroxidase (LiP) and manganese peroxidase (MnP) on TrOC removal. LiP and MnP are closely related enzymes and are often produced simultaneously by white-rot fungi, thus, these two enzymes will be discussed in one group in this review.

Laccases (Benzenediol: oxygen oxidoreductase; EC 1.10.3.2) are ligninolytic enzymes that are secreted by white-rot fungi during the degradation of lignin (the hard cover protecting wood). They are multi-copper atom containing enzymes that can also catalyse the oxidation of a wide range of phenolic substrates using oxygen as an electron acceptor (Riva 2006). The oxidation of a substrate typically involves formation of a free (cation) radical after the transfer a single electron to laccase. The oxidative efficiency of laccases depends on the redox potential differences between the reducing substrate and type 1 Cu in laccase., Laccases generally show lower redox potential (0.5–0.8 V) (Xu 1997; Kumar et al. 2003) compared to other oxidoreductases such as peroxidases, and, therefore, can attack only the phenolic moieties in the lignin polymer (20% of lignin polymer).

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LiP or ligninase (diarylpropane peroxidase; EC 1.11.1.14) is an extracellular monomeric glycoprotein with a heme group in its active centre. LiP is capable of catalysing depolymerisation of the aromatic polymer lignin and a variety of non-phenolic lignin model compounds in the presence of H_2O_2. MnP (EC 1.11.1.13) is also a glycosylated heme protein secreted by ligninolytic fungi into their environment. MnP preferentially oxidizes manganese (II) ions (Mn^{2+}), always present in wood and soils, into highly reactive Mn^{3+}, which is stabilized by fungal chelators such as oxalic acid. Chelated Mn^{3+} in turn acts as low-molecular weight, diffusible redox-mediator that attacks phenolic lignin structures. MnP is capable of oxidizing and depolymerizing natural and synthetic lignins as well as entire lignocelluloses (milled straw or wood, pulp) in cell-free systems (*in vitro*).

TrOC degradation by crude extracellular extract of white-rot fungi culture or a further purified solution has been reported in recent studies. The efficiency of enzymatic TrOC removal varies widely depending on the physicochemical properties of the target molecules. In general, the presence of electron withdrawing groups (EWG) (e.g., amide (-$CONR_2$), carboxylic (-COOH), halogen (-X), and nitro (-NO_2)) in TrOC structure generates an electron deficiency and thus renders the compounds less susceptible to oxidative catabolism, while electron donating groups (EDG) (e.g., hydroxyl (-OH) and amine (-NH_2)) are prone to oxidative attack (Tadkaew et al. 2011; Lloret et al. 2013). Table 15.3 presents widely studied and representative TrOCs in four categories based on the relationship of their chemical structures (EDG and/or EWG) and their removal by enzyme. For example, complete enzymatic removal of phenolic compounds (e.g., 17-α-ethinylestradiol, 17-β-estradiol, 17-β-estradiol-17-acetate, estrone, and estriol, bisphenol A, 4-tert-butyphenol) has been reported in the previous studies (Cabana et al. 2007; Cajthaml et al. 2009). On the other hand, treatment by laccase from *T. versicolor* was previously reported to inefficiently degrade clofibric acid, which contains chloride groups (Tran et al. 2010). Poor removal of metronidazole, propoxur, and carbamazepine was attributed to the presence of strong EWG (i.e. nitro, carbamate and amide, respectively) in their structures (Nguyen et al. 2013c, 2014b).

As noted earlier, only the compounds with phenolic moieties are amenable to degradation by laccase, while both LiP and MnP are capable of catalysing the degradation of lignin and a variety of non-phenolic lignin model compounds in the presence of H_2O_2. It is, therefore, interesting to note the comparative TrOC removal performance of these enzymes. Some phenolic compounds, namely, bisphenol A (Wang et al. 2012) and 17β-estradiol (Mao et al. 2010; Wang et al. 2012) which are amenable to laccase treatment, were not highly removed by LiP. MnP could degrade similar substrates like laccase, for examples, phenolic compounds such as bisphenol A (Hirano et al. 2000; Tsutsumi et al. 2001) and steroids hormones (such as 17β-estradiol, 17α-ethinylestradiol, genistein and estrone) (Suzuki et al. 2003; Tamagawa et al. 2005). MnP furthermore achieved higher degradation of methoxychlor (69%) than laccase or LiP (23–28%) (Hirai et al. 2004). Although comparison between data from different studies may not be

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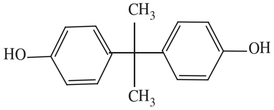
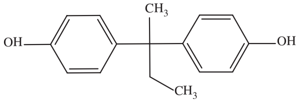
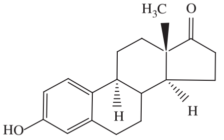
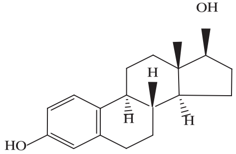
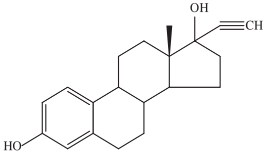
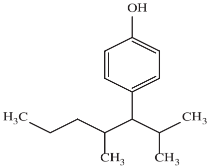
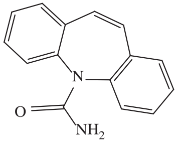
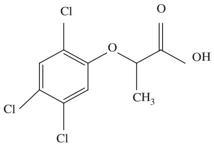
Table 15.3. Representative examples of TrOCs categorised according to the presence of electron donating or electron withdrawing groups and their enzymatic removal

Category	*Compounds*	*Chemical structure*	*Removal (%)*	*Compounds*	*Chemical structure*	*Removal (%)*
Compounds with EDG and showing mainly high removal	Bisphenol A		100^{a,b}	Bisphenol B		100^{a,b}
	Estrone		90–100^{c,d}	17-β-Estradiol		90–100^{c,d}
	17-α-Ethinyl-estradiol		100^{c,e}	Nonylphenol		70–97^{f}
Compounds with EWG and showing mainly low removal	Carbamazepine		5–37.5^{g,h}	Fenoprop		10^{h}

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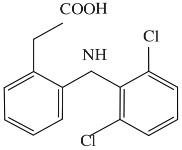
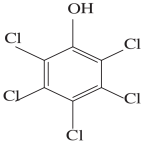
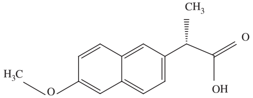
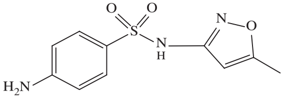
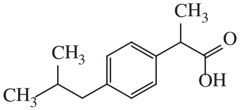
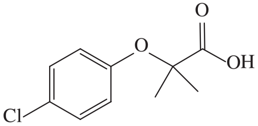
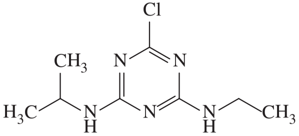
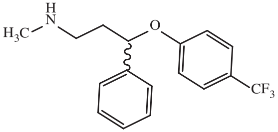
Compounds with EDG and EWG and showing mainly high removal	Diclofenac		80–100[g,i]	Pentachlorophenol		15-60[j,k]
	Naproxen		80-100[g,i,l]	Sulfamethoxazole		80-100[i,l]
	Ibuprofen		70-100[m]			
Compounds with EDG and EWG and showing mainly low removal	Clofibric acid		<10[h]	Atrazine		<10[h]
	Fluoxetine		<10[i,l]			

Major references: [a]Cabana et al. (2007); [b]Cajthaml et al. (2009); [c]Soares et al. (2005); [d]Auriol et al. (2008); [e]Lloret et al. (2010); [f]Saito et al. (2004); [g]Tran et al. (2010); [h]Nguyen et al. (2013c); [i]Eibes et al. (2011); [j]Jeon et al. (2008); [k]Ullah et al. (2000); [l]Rodarte-Morales et al. (2011); [m]Marco-Urrea et al. (2009)

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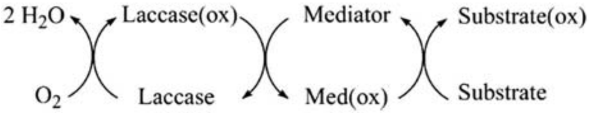

Figure 15.2. Schematic diagram illustrating the working principle of laccase-mediator systems
Source: d'Acunzo and Galli (2003); reproduced with permission from Elsevier

always valid due to the differences in experimental conditions, the above examples indicate the necessity of further systematic studies on this topic.

TrOC removal may depend on enzymatic activity. A study by Auriol et al. (2007) showed that 20 U/mL of initial laccase activity was required to completely remove estrogens from a synthetic wastewater within an hour. In the case of 17α-ethinylestradiol, however, an activity of 15 U/mL was sufficient. Kim and Nicell (2006a) reported 71% to complete triclosan (20 μM) degradation as the laccase activity was increased from 0.3 to 3 U/mL. The degree of bisphenol A degradation was also found to depend on laccase activity in a study by Fukuda et al. (2001). Zhang et al. (2008) reported improved degradation of chlorophenols at higher laccase activities, but recommended a laccase dose of 20 to 60 mg/L from the point of view of degradation quantity per unit laccase activity.

The presence of small-molecular weight redox-mediators can expand the catalytic activity of laccase. Mediators act as "electron shuttle," between laccase and the target substrate. With mediator addition, the enzymatic reaction becomes a two-steps process: i) the redox mediator first reacts with enzyme and generates strong oxidizing radicals and ii) the radicals oxidize the substrate (Burton 2003; d'Acunzo and Galli 2003; Lloret et al. 2010). Figure 15.2 presents the cyclic oxidation of substrate in laccase-mediator systems. Table 15.4 summaries of the properties of some mediators.

The mechanisms by which a redox-mediator plays a role in the reactions catalyzed by laccase have been characterized. Two main mechanisms are reported in the literature: i) a radical hydrogen atom transfer route for aminoxyl (=N-OH) and phenoxyl (C_6H_5-OH) type mediators, and ii) electron transfer route for structurally different mediators such as 2,2'-azino-bis(3-ethylbenzthiazoline-6-sulphonic acid) (ABTS). The first group includes compounds such as 1-hydroxybenzotriazole (HBT), N-hydroxyphthalimide (HPI), violuric acid (VA) and some natural phenolic compounds (i.e., syringaldehyde (SA), acetosyringone (ASG)). The oxidation of this type of mediator by laccase generates a highly reactive aminoxyl (=N-O*) or phenoxyl radical ($C_6H_5O^*$), owing to the enzymatic removal of an electron followed by release of a proton (d'Acunzo and Galli 2003). The oxidation of second type of mediator by laccase generates the cationic radical ($ABTS^{*+}$) which is slowly oxidized to the di-cation ($ABTS^{2+}$) (Cañas and Camarero 2010).

TrOC removal enhancement due to addition of mediators has been demonstrated in several studies. For example, Hata et al. (2010) reported that radicals generated in the laccase – HBT system could eliminate carbamazepine, while

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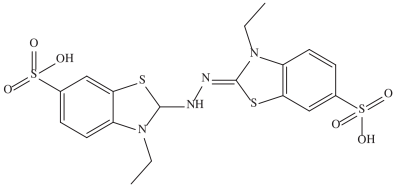
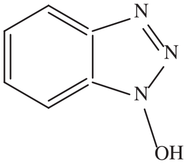
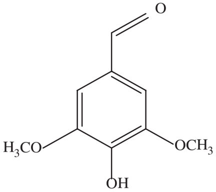
Table 15.4. Properties of selected redox-mediators

Compound (Molecular weight (g/mol))	*Chemical structure*	*Examples of substrates tested*	*References*
2,2′-azinobis-(3-ethylbenzothiazoline-6 -sulfonate (ABTS) ($C_{18}H_{24}N_6O_6S_4$) (548.67)		Textile dyes, TrOC (e.g., bisphenol A, nonylphenol)	Cabana et al. (2007); Weng et al. (2012)
1-hydroxibenzotriazole (HBT) ($C_6H_5N_3O$) (135.12)		Textile, dye or printing industries, phenols, non-phenolic lignin, steroid hormones	Hata et al. (2010); Suda et al. (2012)
Syringaldehyde (SA) ($C_9H_{10}O_4$) (182.17)		Synthetic dyes,TrOC (e.g., bisphenol A, triclosan)	Kim and Nicell (2006a); Torres-Duarte et al. (2009)

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laccase only could not. In another study by Lloret et al. (2010), naproxen was not significantly oxidised in the absence of any mediator. However, when HBT was present in the reaction medium a removal of 60% was achieved. Similarly, an enhancement of diclofenac removal (30% improvement) was achieved by the laccase-HBT system. The degree of enhancement depended predominantly on the type of mediator, TrOC structure and mediator concentration (Yang et al. 2013). For example, the removal of triclosan by laccase increased upon addition of ABTS, HBT and SA, but worsened by the addition of vanillin, *p*-coumaric acid and guaiacol (Murugesan et al. 2010). Another study showed that HBT promoted the degradation of naproxen (nearly 100% removal), but had little effect on ketoprofen (40% removal) (Tran et al. 2010). Mizuno et al. (2009) observed gradual increase in iso-butylparaben and n-butylparaben removal due to addition of HBT to laccase (from *T. versicolor*) over a concentration range of 0.2 to 2 mM, beyond which no further improvement was noticed. By contrast, Lloret et al. (2010) observed diclofenac removal to range from 40 to 80% for SA concentrations ranging from 0.1 to 0.5 mM, while a complete removal was achieved at 1 mM.

Contrary to the improvement of TrOC removal, mediator addition often leads to laccase inactivation. The free radicals generated from laccase-mediator systems can inactivate laccase by oxidizing the aromatic amino acid residues on the enzyme surface (Khlifi-Slama et al. 2012). The degree of laccase inactivation depends on the source of laccase, the type of mediator and mediator concentrations (Kurniawati and Nicell 2007). For example, Khlifi-Slama et al. (2012) observed a gradual increase in the extent of inactivation of laccase from *T. trogii* after addition of HBT at concentrations from 0.1 to 10 mM. On the other hand, Kurniawati and Nicell (2007) observed only a slight inactivation (<5%) of laccase from *T. versicolor* when a range of different mediators were used at concentrations up to 0.5 mM. In the presence of 0.05 mM SA, laccase was completely deactivated within 30 min. However, with a mediator concentration of 0.025 mM, a similar deactivation profile was observed as without the mediator (Mendoza et al. 2011). Therefore, an ideal mediator must be a good substrate for laccase, must generate stable radicals with strong oxidizing power but must not inhibit or deactivate the enzymatic activity.

Immobilisation of an enzyme may result in its increased stability against thermal and chemical reactions (Peralta-Zamora et al. 2003; Dodor et al. 2004; Nicolucci et al. 2011). The methods for enzyme immobilisation include chemical and physical methods. Chemical methods mainly include: (i) enzyme attachment to the matrix by covalent bonds and (ii) enzyme cross-linking by multifunctional reagents. Physical methods involve entrapment of enzyme molecules within a porous hollow fiber, in spun fibers within an insoluble gel matrix and/or enzyme entrapment within a reverse micelle (Durán et al. 2002). Unlike with the improvement of enzyme stability, the removal of TrOC by immobilised enzyme varies and depends on immobilisation techniques and types of carriers and enzymes. In some cases, lower removal efficiency was observed. For example, in previous studies utilising free laccase, bisphenol A (Fukuda et al. 2001; Cabana

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et al. 2007), nonylphenol (Okazaki et al. 2002) and triclosan (Kurniawati and Nicell 2007) were generally removed with high efficiency; however, when laccase was immobilised in order to increase stability and allow repeated use, in some cases, lower TrOC removal efficiency was observed (Cabana et al. 2007; Taboada-Puig et al. 2011; Songulashvili et al. 2012).

The pH of the reaction environment can have effect on both enzyme and substrate properties. Therefore, it may affect the performance of enzyme on the removal of pollutant. For example, Zhang and Geiben (2010) reported complete degradation of diclofenac by LiP over a pH range of 3.0–4.5. However, diclofenac degradation significantly decreased from 100% at pH 4.5 to 10% at pH 6.0. The decrease in degradation of diclofenac was in accordance with the inactivation of LiP at higher pH. The optimal temperature for enzymatic activity may differ greatly from one strain to another (Yang et al. 2013). However, 25–30 °C and 37–40 °C are usually reported as the optimum temperature for laccase and peroxidases, respectively. A few studies have observed the effect of salinity on the fungal growth and the TrOC removal efficiency by the whole cell fungal preparations. Kim and Nicell (2006b) investigated the effect of different sulphate and chloride salts and concluded that the chloride compounds (NaCl, NH_4Cl, $CaCl_2$ and $MgCl_2$) substantially inhibited bisphenol A conversion. The effect of metal ions has also been the subject matter of a few recent studies. For example, the presence of ions including SO_3^{2-}, S^{2-}, CN^-, Cl^-, Fe^{3+} and Cu^{2+} resulted in reduced treatment efficiency of triclosan by purified laccase from *T. versicolor* (Kim and Nicell 2006a).

15.4.5 Membrane Bioreactors

Membrane bioreactor (MBR) is a combination of a membrane filtration process with a suspended growth bioreactor. MBRs can be arranged in two configurations (e.g., internal/submerged and external/side stream) (Figure 15.3). Microorganisms in the bioreactor can transform organic molecules from large to small (more easily biodegradable substances) by oxidation reactions in aerobic processes

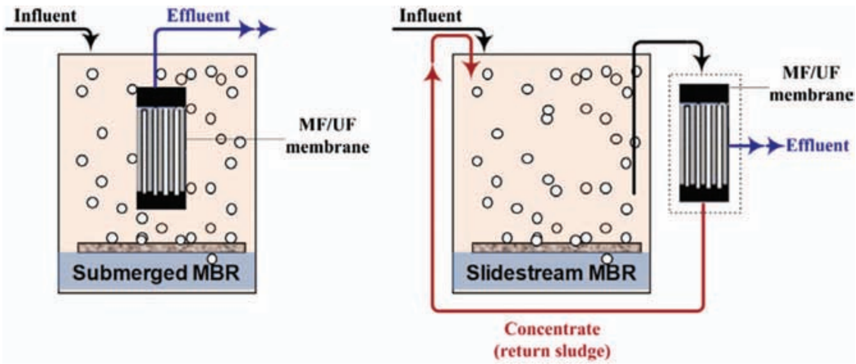

Figure 15.3. Membrane bioreactor (MBR) configurations

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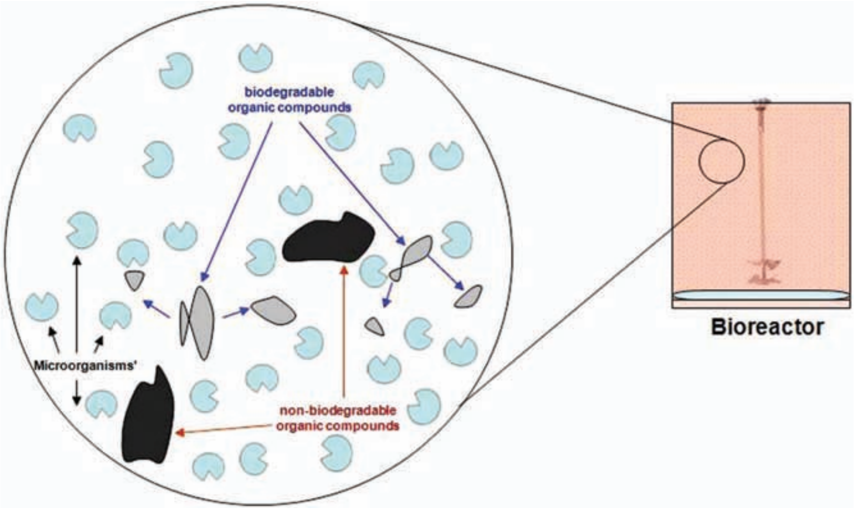

Figure 15.4. Biodegradation concept of some organics in MBR

(Ermawati et al. 2007) (Figure 15.4). Physical separation (using microfiltration or ultrafiltration membranes) of biomass and suspended solids is an additional technique provided by MBR. Biological degradation of wastewater contaminants with membrane filtration is integrated into MBR technology, which leads to the effective removal of organic and inorganic contaminants and biomass from municipal and/or industrial wastewater. Because of the combination used, an MBR system can potentially achieve consistent performance when treating high strength and fluctuating strength wastewater (Chang et al. 2008). Consequently, MBRs can supply high quality effluent suitable for discharge or reuse (Comerton et al. 2005; Atkinson 2006).

An MBR system can produce steady effluent quality and require a small plant footprint compared to a conventional activated sludge (CAS) process because this system combines aeration and filtration, in addition to clarification in a solitary process step (Figure 15.5) (Jiang et al. 2005; Radjenović et al. 2008; Schneider 2009). The quality and reliability of MBR effluent can produce dischargeable and reusable effluent with no further treatment (Urgun-Demirtas et al. 2005). Van Bentem et al. (2010) verified that MBR produces better quality effluent compared to CAS, or CAS with sand filtration. Their results demonstrated that CAS effluent contained higher SS (as compared to virtually none in MBR effluent), biochemical oxygen demand (BOD) and chemical oxygen demand (COD). Moreover, in a laboratory-scale study, Radjenović et al. (2009) showed that 56% of 40-hydroxydiclofenac (the major primary diclofenac metabolite) was removed using an MBR, as opposed to only 26% using the CAS treatment. The same researchers reported approximately 40% removal by MBR of mefenamic acid, indomethacin, and gemfibrozil, which were not removed by CAS. Furthermore, better removal compared to CAS treatment of some endocrine disruptor chemicals such as

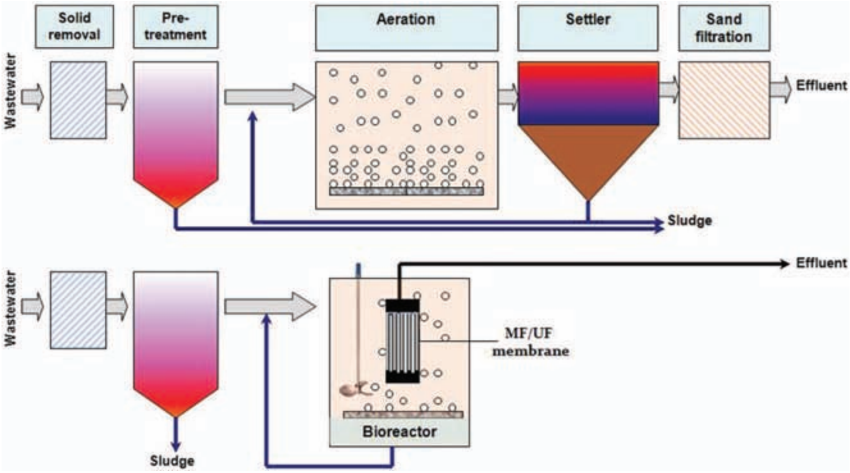

Figure 15.5. Membrane bioreactor versus conventional activated sludge

nonylphenol (NP) and nonylphenol ethoxylates (NPEOs) can be achieved by using MBR (Petrovic et al. 2003; González et al. 2006).

As noted earlier, the MBR system has a notably smaller physical footprint than CAS which results in a saving on space and the overall cost of the treatment plant (Figure 15.5). MBR systems can be operated at a higher mixed liquor suspended solid (MLSS) content than CAS, which in turn leads to the intensification of the treatment process and a smaller physical footprint (De Wever et al. 2007; Holakoo et al. 2007). Moreover, due to the absence of secondary clarifiers in MBR, significant economic savings in both footprint and overall cost can be achieved (Xing et al. 2001).

MBR produces less sludge than CAS because the food to microorganism (F/M ratio) is lower, which in turn leads to a better removal of organic and nutrient than the CAS (De Wever et al. 2007; Alaboud and Magram 2008). For example, under similar conditions of solids retention time (SRT) and organic loading rate, the MBR produced 20–30% less sludge than the CAS system (Wei et al. 2003).

MBR is more controllable than CAS because phase separation (sludge settling) has been removed from the process and replaced by microfiltration and ultrafiltration (MF/UF) (Rosenberger and Kraume 2002). This improvement reduces any operator oversight required to keep the system running efficiently. Furthermore, to achieve reusable quality water, the CAS would often be followed by a tertiary filtration system, which adds additional mechanical equipment, and the subsequent operating, maintenance and capital costs (Xing et al. 2001). By comparison, MBR technology does not require tertiary filtration or polymer additions which are essential in CAS, to meet reuse standards for suspended solids and turbidity (Xiang et al. 2003; Fan et al. 2006). This reduction in the number of unit processes improves the reliability of the MBR system and also reduces the operation and maintenance of this system.

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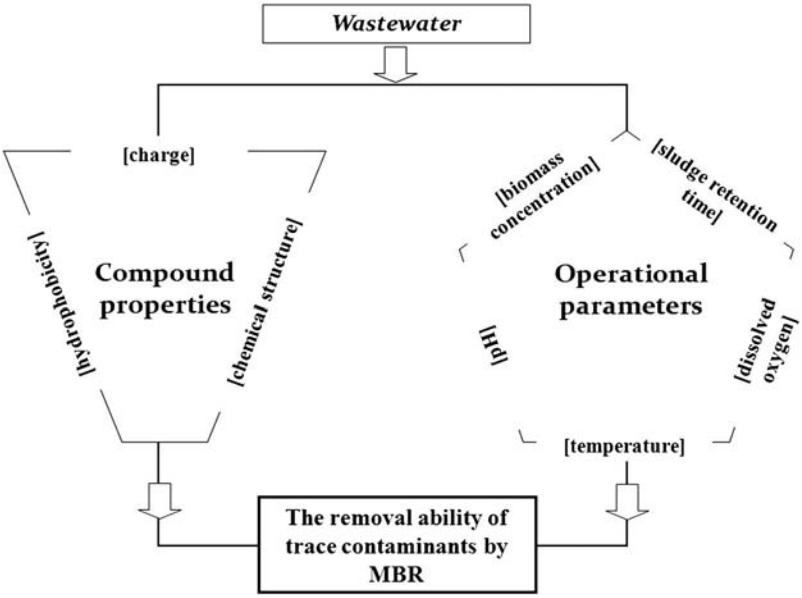

Figure 15.6. Factors affecting the removal of TrOCs in the MBR process

The combination of activated sludge and membrane filtration has made MBR an acceptable and popular technology for treating many types of wastewaters, particularly those that contain TrOCs (Petrovic et al. 2003; González et al. 2006; Snyder et al. 2007; Bérubé et al. 2010; Tadkaew et al. 2011). The efficient removal of TrOCs during MBR treatment depends on the physicochemical properties of the compounds and the operational parameters of the wastewater treatment plant (Figure 15.6). As can be seen from Table 15.5, there is considerable variation in the removal of TrOCs by MBR, ranging from almost zero (e.g., carbamazepine) to almost complete removal (e.g., ibuprofen and bezafibrate) (Nghiem et al. 2009; Tadkaew et al. 2011).

Physiochemical properties such as hydrophobicity, chemical structure, and compound polarity are important factors affecting the removal of TrOCs in MBR systems. An understanding of these factors can help develop the removal techniques of TrOCs by MBR and would result in a better selection of subsequent complementary treatment processes.

Hydrophobicity is a major factor affecting the sorption of TrOCs in water. Of the many TrOCs that can occur in wastewater, some are highly hydrophobic and can be readily removed by MBR treatment via bio-sorption. For example, around 80% of nonylphenol was eliminated in a pilot scale MBR process treating landfill leachate (Cirja et al. 2008). This high elimination rate can be attributed to the high hydrophobic nature of nonylphenol (log $D = 6.19$ at pH 8) (Unep 2002). In a laboratory-scale study, the removal of hydrophobic compounds (Log $D > 3.2$) such as amitriptyline 17β-estradiol, androsterone, and simvastatin by MBR was

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Table 15.5. Summary of reported TrOC removal efficiency by MBR

Contaminant	*Application*	*MBR scale*	*Removal (%)*
Pharmaceutical and personal care products (PPCP)			
Paracetamol	Analgesics	lab & pilot	>90 – 99.6[a,b,c,d,e]
Ofloxacin	Antibiotic	lab	94
Roxithromycin	Antibiotic	pilot	34–> 99[f,g,h]
Sulfamethoxazole	Antibiotic	lab & pilot	52–80.8[c,d,e]
Carbamazepine	Anticonvulsant	lab & pilot	1.4–> 20[g,i,j,k]
Fluoxetine	Antidepressant	pilot	98[e]
Paroxetine	Antidepressant	lab	89.7[c]
Hydrochlorothiazide	Diuretics	lab	66.3[c]
Diazepam	Tranquillizers	pilot	26[h]
Glibenclamide	Antidiabetic	lab & pilot	47.3–95.6[c,e]
Diethyltoluamide (DEET)	Insect repellent	pilot	–5.6, 0[l]
Bezafibrate	Lipid regulator & statin	pilot	76–> 97[c,g]
Clofibric acid	Lipid regulator & statin	lab & pilot	32.5–89.6[c,e,j]
Gemfibrozil	Lipid regulator & statin	pilot	40[e]
Pravastatin	Nacotic analgesic	lab & pilot	83.1–90.8[c,e]
Diclofenac	Anti-inflammatory	lab & pilot	0–65.8[e,h]
Ibuprofen	Anti-inflammatory	lab & pilot	97–> 99, 98[f,j,l]
Indomethacin	Anti-inflammatory	lab & pilot	39.7–46.6[c,e]
Mefenamic acid	Anti-inflammatory	lab & pilot	35.5–74.8[c,e]
Ketoprofen	Anti-inflammatory	lab & pilot	43.9–91.9[c,e]
Naproxen	Anti-inflammatory	lab & pilot	36–99.3[c,l]
Propyphenazone	Anti-inflammatory	lab & pilot	60–64.6[c,e]
Celestolide	fragrance ingredient	pilot	46–56[h]
Tonalide	fragrance ingredient	pilot	46–92[f,h,m]
Triclosan	Antiseptic	pilot	66, 73[l]
Pesticides			
Atrazine	herbicide	lab & pilot	5–40[j,n,o]
Linuron	herbicide	lab	22[o]
Endocrine Disrupting Chemicals (EDCs)			
Estrone (E1)	Hormone	pilot	>90[p]
Estriol (E3)	hormone	pilot	>99.8[i]
17β-estradiol	hormone	pilot	>90[p]
17α-ethinylestradiol (EE2)	hormone	lab	<1[q]
Total natural hormones	hormone	Pilot	95–99[f]
Bisphenol A (BPA)	plasticizer	lab & pilot	68.9–99[f,g,r]
Nonylphenol (NP)	Surfactant metabolite	pilot	80–90[s,t]
Total Nonylphenols	Surfactant metabolite	pilot	69–80[f]

(Continued)

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Table 15.5. Summary of reported TrOC removal efficiency by MBR (Continued)

Contaminant	Application	MBR scale	Removal (%)
Disinfection byproducts (DBPs)			
Trihalomethane ormation potential (THMFP)	DBP	lab	59–85[u]

Sources: [a]Joss et al. (2006); [b]Kim et al. (2007b); [c]Radjenović et al. (2007); [d]Radjenović et al. (2008); [e]Radjenović et al. (2009); [f]Kreuzinger et al. (2004); [g]Clara et al. (2005b); [h]Reif et al. (2008); [i]Clara et al. (2005a); [j]Bernhard et al. (2006); [k]Tadkaew et al. (2011); [l]Kim et al. (2007b); [m]Joss et al. (2005); [n]Bouju et al. (2008); [o]Alturki et al. (2010); [p]Joss et al. (2006); [q]Cirja et al. (2007); [r]Hu et al. (2007); [s]Wintgens et al. (2002); [t]Cirja et al. (2008); [u]Li and Chu (2003)

mostly greater than 85% at pH 8 (Tadkaew et al. 2011), however, in the same study less than 20% removal of hydrophilic and moderately hydrophobic compounds (Log $D < 3.2$) such as carbamazepine was observed.

The chemical structure of the TrOCs can affect their removal by MBR. Compounds with simple chemical structures (e.g., the absence of a branched alkyl chain) will be easy to degrade during treatment, whereas compounds with complex structures or having toxic groups (e.g., halogens and nitro group) have a higher resistance to biodegradation processes and degrade incompletely (Cirja et al. 2008). For example, pharmaceuticals are often complex molecules (e.g., ketoprofen and naproxen) with structures that are more resistant to degradation because the compound is made up of two aromatic rings (Cirja et al. 2008). Tadkaew et al. (2011) investigated the relationship between specific structural features of 40 TrOCs and their efficient removal by MBR under stable operating conditions. In their study high removal efficiencies (>85%) were achieved for most compounds containing EDG such as hydroxyl and primary amine groups, whereas only low removal efficiency (<20%) was obtained for compounds possessing strong EWG. In addition, even molecules with simple structure (e.g., not containing multiple rings) but containing chloride groups are difficult to remove by MBR. Cirja et al. (2008) stated there is a decrease in the degradation rate of aromatic compounds when the number of nitro and chlorine groups increases.

The polarity of TrOCs is a major aspect in the removal mechanism, where highly polar compounds can be eliminated by biodegradation even though the sorption process is limited (De Wever et al. 2007). Wintgens et al. (2002) examined the removal of some polar compounds such as nonylphenol and bisphenol A using wastewater from a dumpsite leacheate plant. The result showed that more than 90% of nonylphenol and bisphenol A were eliminated through the MBR process. Nghiem et al. (2009) expected a low removal of polar or negatively charged compounds by MBR due to the absence of their adsorptive ability. Conversely, positively charged pharmaceutical compounds (e.g., amitriptyline, clozapine, verapamil, risperidone and hydroxyzine) had the highest sorption

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potential onto wastewater sludge solids compared to neutral and negatively charged compounds (Stevens-Garmon et al. 2011).

Different factors influencing the removal of TrOCs in MBR have been the subject matter of recent studies. The operating conditions can strongly affect the overall performance of MBR, especially when removing TrOCs. Factors that have already been investigated include the sludge retention time (SRT), biomass concentration and morphology, pH, temperature, and dissolved oxygen (DO) (Cirja et al. 2008; Tadkaew et al. 2010; Tadkaew 2011).

High SRT is desirable to allow enough time for slow growing bacteria and the establishment of a more diverse biocoenosis to enable the degradation of a large number of TrOCs. Microbial enzymes for TrOCs in activated sludge require some time to adapt and then influence the pollutant's transformation or decomposition (Kim et al. 2007a; Cirja et al. 2008; Feki et al. 2009). A number of TrOCs such as ibuprofen, paracetamol, 17β-estradiol, and estrone are expected to be biologically transformed by more than 90% at high SRT (Joss et al. 2006). This long SRT enables a significant amount of biodegradable TrOCs to be degraded, even at higher volumetric loading rates (Urgun-Demirtas et al. 2005). In contrast, the removal of pharmaceutical wastes decreases at a low SRT (<8 days) (Cirja et al. 2008). For biodegradation of some pharmaceuticals, an SRT of 5–15 days is required, and for a given SRT, MBR offers a better elimination and an enhanced degradation than CAS (Golet et al. 2003; Lindberg et al. 2007).

The biomass feature is an important factor for TrOC removal in MBR. This is particularly true as there is a probability of adaptation and genetic mutation for MBR microorganisms to increase the adsorption and/or biodegradation of TrOCs (Cirja et al. 2008). Enhanced biosorption of TrOCs in MBR may occur when the concentration of the mixed liquor suspended solid (MLSS) is high and the sludge retention time is long, and this may lead to further removal via biodegradation (Hai et al. 2011). Weiss and Reemtsma (2008) reported that MBR intensifies the biological treatment of wastewater, which can improve the degradation of TrOCs (Weiss and Reemtsma 2008). High MLSS concentration such as 20 g/L in MBR could produce a high removal of nonylphenol ethoxylates (NPEOs) and other ionic and non-ionic surfactants, albeit not complete (Göbel et al. 2007). In addition, the surface and structure of biological flocs in activated sludge can be significantly influenced by the operating conditions (Radjenović et al. 2008). Radjenović et al. (2008) stated that a better removal of readily biodegradable TrOC in an MBR could be due to the sludge having a smaller size floc, which enhances mass transfer by diffusion and results in a high elimination of these contaminants.

The removal of TrOCs in MBR sludge can be influenced easily by the operational pH, which can affect the solubility of TrOCs present in wastewater and the physiology of bacterial culture (Nghiem and Hawkes 2007). For this reason, the pH can be a critical parameter influencing the removal rate of TrOCs during MBR treatment. For example, there was a high removal (up to 90%) for some pharmaceuticals at a pH lower than 6, while only around 70% were removed

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by the MBR when the pH dropped below 5 (Cirja et al. 2008), showing a high sensitivity to pH. Likewise, Tadkaew et al. (2010) reported high removal of ionisable TrOC (sulfamethoxazole, ibuprofen, ketoprofen and diclofenac) by MBR at a pH of 5 as compared to neutral pH (Tadkaew et al. 2010). The authors attributed this to the possible speciation of these compounds, and that they can exist predominantly in their hydrophobic form at acidic pH, leading to enhanced adsorption to the activated sludge.

Higher removal rates of some TrOCs in MBR can be achieved in warmer temperatures (25–30 °C) as opposed to winter temperatures (He et al. 2005; Zuehlke et al. 2006; Cirja et al. 2008; Tadkaew 2011), because higher biodegradation and hence contaminant removal are expected when the temperature in MBR is increased (Kurian et al. 2006). Cirja et al. (2008) reported that improved removal of certain TrOCs can be achieved in the summer compared to winter. On the other hand, Tadkaew et al. (2011) reported an insignificant impact of temperature on the removal of pharmaceuticals (e.g., sulfamethoxazole and ibuprofen) and endocrine disrupting compounds (e.g., bisphenol A, estrone and 17β-estradiol) except for carbamazepine. An increase in the temperature of the sludge (20 to 30 °C) significantly increased the removal rate of carbamazepine from 17.5 to 43% (Tadkaew 2011).

In MBR, the high MLSS concentration requires aeration to supply oxygen for microorganisms and prevent membrane fouling (Jiang et al. 2005; Cirja et al. 2008). Tadkaew (2011) investigated the removal efficiencies of some TrOCs such as naproxen, diclofenac, and carbamazepine in a laboratory-scale MBR. No improvement in the removal of these compounds after increasing the concentrations of DO was reported. By contrast the removal of ibuprofen was significantly enhanced (94%) at a DO concentration of 2 mg/L, but it then dropped to 58% when the concentration of DO was increased to 5 mg/L in the same MBR.

15.5 INTEGRATED MEMBRANE PROCESSES FOR REMOVAL OF TROCS

Activated sludge based processes (e.g., MBR) are the most pragmatic approach for wastewater treatment. However, as discussed in this chapter, conventional biological treatment alone may not be effective for all TrOCs existed in municipal and industrial wastewater. The low removal efficiency of biologically persistent and hydrophilic TrOC necessitates the integration of MBR with other membrane and physicochemical processes to ensure adequate removal of TrOCs. Because MBR can produce effluent with much lower bulk organic content when compared to CAS, significant synergy can be realised when it is integrated with other advanced treatment processes. In this section, we review the current literature on integration of MBRs with NF/RO, forward osmosis and activated carbon adsorption, and enzymatic membrane reactors (EMRs).

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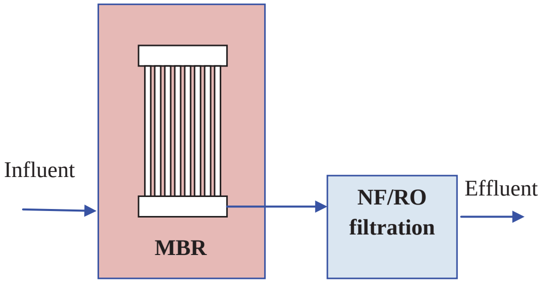

Figure 15.7. Schematic diagram of the combined MBR-NF/RO process

15.5.1 MBR-NF/RO

The combination of MBR and NF/RO membrane filtration (Figure 15.7) has been reported to yield stable and high treatment in terms of several basic water quality parameters (such as TOC, NO_3^-, and NH_4^+) along with the added advantage of stable permeate flux of NF/RO membranes over extended operating periods (Comerton et al. 2005; Qin et al. 2006; Tam et al. 2007; Dialynas and Diamadopoulos 2009; Jacob et al. 2010). A few recent studies have also demonstrated the advantages of combining MBR and NF/RO treatment with respect to the removal of TrOC (Alturki et al. 2010; Dolar et al. 2012). Alturki et al. (2010) reported effective removal of hydrophobic and biodegradable TrOCs by an MBR. The hydrophilic TrOCs, which passed through the MBR, were effectively removed by the following NF/RO membranes. The combination of MBR and a low pressure RO membrane resulted in removal to below the analytical detection limit of all 40 TrOC investigated in that study. Alturki et al. (2010) also reported negligible membrane fouling of the NF and RO membranes when fed with MBR permeate. Dolar et al. (2012) conducted a pilot study to investigate the complementarities of MBR treatment and the RO process. All 20 TrOC investigated in their study were removed by 99% or more by the pilot MBR-RO system. In addition to post treatment of MBR effluent, recent developments report integration of NF (Zaviska et al. 2013) or forward osmosis (Alturki et al. 2012) membranes with bioreactors, as described in Section 15.5.2.

15.5.2 Osmotic Membrane Bioreactor

An osmotic membrane bioreactor (OMBR) is the combination of FO in conjunction with an MBR (Kekre et al. 2008; Verliefde et al. 2008a). The OMBR process has the potential to become a sustainable alternative to conventional membrane processes (Lay et al. 2010). Verliefde et al. (2008a) attributed the superior water quality after OMBR to the existence of a barrier against the organic contaminants and natural organic matter (NOM) by the FO membrane, in addition to the intrinsic high removal efficiency of MBR. They stated that an RO system after OMBR can be operated with higher fluxes because all the bivalent ions can be removed by the OMBR. Furthermore, the FO membranes used in the OMBR are

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less susceptible to fouling by activated sludge solutions than the UF/MF membranes used in conventional membrane bioreactors (Verliefde et al. 2008a; Achilli et al. 2009), and therefore, OMBRs may realize a more compact system than conventional MBRs. However, increase of salt concentration in the bioreactor can change the microbial community due to salinity selection (Lay et al. 2010).

The OMBR process is still in its early stages of development so there are limited studies on how efficiently it can remove contaminants, apart from which the fouling and cleaning behaviour of OMBR remains largely unknown. Lay et al. (2010) elucidated the importance of the combination of high rejection membrane separation with a biological treatment to conduct high retention membrane bioreactors (HRMBR). They claimed that this type of process can produce high quality product water with high removal of smaller size organic contaminants, although HRMBRs did face an accumulation of salt in the bioreactor, which may have a negative impact on the operation conditions. The build-up of salt can only be alleviated by biomass wasting (Lay et al. 2010). Verliefde et al. (2008a) investigated the water flux behaviour and fouling propensity of a bench-scale study OMBR over a short time (7–8 h). Fresh activated sludge was used as feed for the process, while 0.5 M NaCl ($\pi = 24.3$ bars) was used as draw solutions on the other side. The results demonstrated a water flux rate of 5.8 L/m^{2}h for the FO mode (Verliefde et al. 2008a). Membrane fouling was not observed, but the duration of this study may not have been long enough for fouling to occur. A similar pilot OMBR has explored the effects of draw solution on membrane flux and air scouring on the tendency for fouling (Qin et al. 2010). In this study, domestic sewage was fed to the sludge, with NaCl/$MgSO_4$ as a draw solution in the other side. The values of the water flux were osmotic pressure dependent, as 3 and 7.2 L/m^{2}h at 5 and 22.6 bars, respectively. At an osmotic pressure of 5 and 22.6 bars, an insignificant decline in flux occurred between 190 h and 150 h respectively, and the decline happened at 22.6 bars when air scouring was provided after 150 h (Qin et al. 2010). Additionally, a submerged FO membrane module inside a bioreactor conducted by Achilli et al. (2009) to investigate the long-term water fluxes and membrane fouling at MLSS of 5.5 g/L. The results showed a lower water flux by only 18% in OMBR, which was mostly due to membrane fouling, when compared to experiments using double de-ionized water as a feed. During an OMBR experiment Achilli et al. (2009) used 50 g/L of NaCl as a draw solution which, with continuous reconcentration with an RO system, agonist 14 L of sludge fed by synthetic feed solution for 28 days. The average water flux during the OMBR experiment was approximately 9 L/m^{2}h with removal efficiencies of more than 99 and 98% for total organic carbon and ammonium-nitrogen ($NH4^+$-N), respectively (Achilli et al. 2009). Fouling of the FO membrane was not severe and could be controlled through weekly osmotic backwash to restore the water flux to approximately 90% of the initial rate.

A recent study conducted by Zhang (2011) used three different FO membrane modules to investigate the water and reverse salt fluxes in the OMBR process. The OMBR system was coupled with a two-pass NF system for the draw solute (Na_2SO_4) reconcentration and produced a final product. The results confirm that

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a hybrid OMBR-NF has the ability to achieve more than 99.6 and 95% of total organic carbon (TOC) removal after both NF passes, respectively. High-quality final permeate was also obtained with total dissolved solids (TDS) and a conductivity of less than 275 mg/L and 297 μs/cm, respectively (Zhang 2011).

15.5.3 MBR-Activated Carbon

Two different configurations of combining activated carbon adsorption with an MBR system may be perceived (Hai et al. 2014): i) addition of powdered activated carbon (PAC) directly into the reactor of the MBR (Yang et al. 2010; Li et al. 2011; Serrano et al. 2011; Nguyen et al. 2014c) and ii) post-treatment of the MBR permeate using either a granular activated carbon (GAC) column (Navaratna et al. 2012; Nguyen et al. 2012) or a continuously mixed reactor containing a slurry of PAC (Lipp et al. 2012). TrOC adsorbed onto PAC can be efficiently removed by the PAC-MBR system because of the complete retention of sludge by the membrane (Li et al. 2011). On the other hand, during GAC post-treatment, GAC can specifically target the residual TrOC in MBR permeate without significant competition or interference from the bulk organics (Nguyen et al. 2012, 2013a, b, c). Indeed, PAC addition into MBR (PAC-MBR) or GAC post-treatment (MBR-GAC) has been reported to significantly complement MBR treatment to obtain high overall removal of less hydrophobic and biologically resistant TrOC. However, periodic regeneration/replenishment of the activated carbon is necessary, because over an extended operating period, the breakthrough of TrOC is inevitable. According to Nguyen et al. (2013a), charged and hydrophilic TrOC are more likely to breakthrough first. A preliminary comparison between the PAC-MBR and MBR-GAC configurations by Nguyen et al. (2013a) also revealed that the former can perform better in terms of activated carbon usage.

15.5.4 Enzymatic Reactor

The application of enzymes in continuous systems such as wastewater treatment plants remains a challenge since the enzymes are easily washed out with treated effluent (Hai et al. 2012, 2013). The recovery of the enzyme and its reusability are key factors for feasibility of continuous operation of enzymatic reactors because the cost of the enzyme may limit their application (Lloret et al. 2012a). Enzyme immobilisation on a support is one of the approaches to tackle this major limitation of enzymatic reactors. Different supports, namely, polyacrylonitrile, polystyrene, SiO_2 (celite), chitosan and sol-gel has been used to immobilise laccase (Yang et al. 2013). For example, Cabana et al. (2009) immobilized laccase on SiO_2 that degraded nonylphenol, bisphenol A, and triclosan in a packed bed reactor. The use of membranes which have pore size smaller than the molecular weight of an enzyme is another approach to prevent enzyme washout from a continuous flow enzymatic reactor. This technique forms an enzymatic membrane reactor (EMR) which allows operation with continuous feeding and product withdrawal without loss of the enzyme. Depending on the case, enzyme molecules may be

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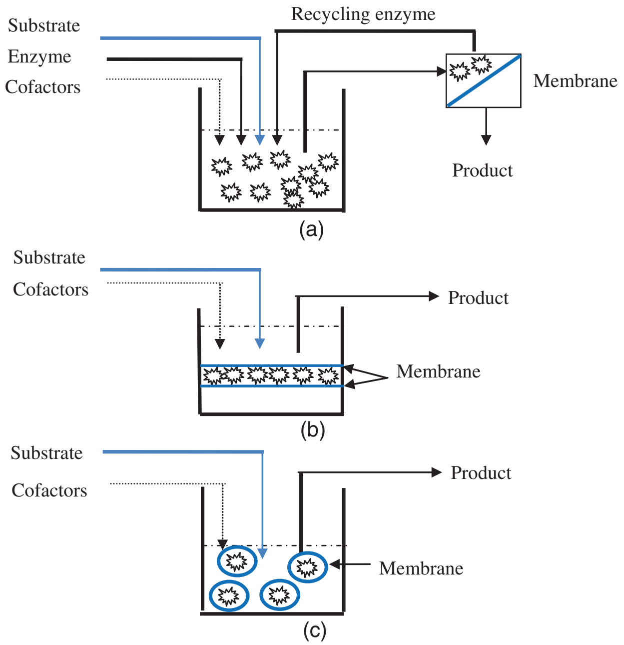

Figure 15.8. Schematic diagram of three different configurations of EMRs. (a) enzyme in suspension in a reactor coupled with membrane units, (b) enzyme immobilised within the membrane matrix itself and, (c) enzyme entrapped in gels or microcapsules

freely circulating on the retentate side or immobilised onto the membrane surface or inside its porous structure (Rios et al. 2004; Hai et al. 2013; Modin et al. 2014). The configurations of EMRs are presented in Figure 15.8.

Recent laboratory scale EMR studies have explored treatment of pollutants such as dyes using laccase (Chhabra et al. 2009; Mendoza et al. 2011) or MnP (Lopez et al. 2004). Mendoza et al. (2011) investigated the removal of azo dyes applying a laccase/mediator system in an EMR. They used a polysulfonate UF membrane (MWCO: 10 kDa) allowing a complete retention of enzyme within the reactor. Decolourisation yields of 52 to 95% depending on the dye type were reported (Mendoza et al. 2011). Chhabra et al. (2009) demonstrated over 95% decolourisation of acid violet by an EMR. Katuri et al. (2009) explored three different EMR configurations: direct contact EMR (i.e., laccase in suspension), laccase impregnated EMR (i.e., laccase enclosed in a dialysis bag housing a 12 kDa membrane, which prevented laccase diffusion into the buffer solution and allowed dye diffusion into the laccase solution for reaction) and immobilised EMR (laccase immobilised on poly-vinylidene fluoride (PVDF) and chitosan membranes) for the removal of acid azo dye. The decolourisation efficiency of each reactor configuration depends on enzyme stability and mass transfer limitations between

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enzyme and substrate. Among the different EMR configurations, immobilisation of laccase on PVDF and chitosan membranes showed better decolourisation efficiency of up to 8 and 21 batches, respectively. This was presumably due to a combination of improved enzyme stability and mass transfer.

There are only a few available studies on application of EMR for TrOC removal (Table 15.6). Lloret et al. (2012b) investigated the removal of two estrogens (i.e., estriol and 17β-estradiol) by a commercial laccase from *Myceliophthora thermophila* in an EMR equipped with UF membranes with a nominal pore size of 10 kDa. Removal efficiencies between 64 – 100% were obtained under an enzymatic activity of 500 U/L. The EMR allowed the reuse of the enzyme providing a substantial cost reduction. Nicolucci et al. (2011) immobilised laccase on polyacrylonitrile beads and submerged the beads in a fluidised bed reactor for the removal of bisphenols (i.e., bisphenol A, bisphenol B and bisphenol F). Complete removal (effluent concentration below detection limit) of all bisphenols was obtained from that study. In a more recent study, Nguyen et al. (2014a) used a commercial laccase in a direct contact EMR for the removal of diclofenac and bisphenol A. A stable removal of bisphenol A (>85%) and diclofenac (>65%) was achieved in that study.

Membranes of appropriate MWCO can retain enzymes within the reactor. However, enzyme denaturation due to various physical and chemical factors during continuous operation necessitates enzyme replenishment. In a study by Lopez et al. (2004), following a single addition of MnP at the beginning of operation, a sharp loss of enzymatic activity occurred (27%), while repeated pulses of MnP allowed maintenance of MnP activity between 100 and 200 U/L. Finally, enzymatic activity dropped to around 25% of the initial value at the end of the 13th run (approximately 30 h), which was presumably due to gradual degradation of the laccase structure over continuous UF filtration. Gradual loss of enzymatic activity during repeated application was responsible for the progressive increase in contact time required to achieve maximum dye decolourisation in a study by Katuri et al. (2009). Drop in enzymatic activity during EMR operation was also observed by Hata et al. (2010). The authors reported a rapid decrease in enzymatic activity during the first 4 h (a decrease from 10 to 3 nkat/mL) of operation. However, a strategy involving the addition of laccase and a mediator every 8 h enhanced the performance of carbamazepine removal. Lloret et al. (2012a), however, reported stable enzymatic activity over 10 h of operation of an EMR. Nguyen et al. (2014a) observed a complete denaturation of enzymatic activity after 72 h of operation of an EMR with a single addition of enzyme. The authors proposed a strategy to maintain enzymatic activity by addition of 200 μL of the commercial laccase solution per L of the reactor volume every 12 h (equivalent to a laccase dose of 23 mg/L.d). Apart from enzyme reinjection, different methods have been reported to minimize the loss of enzyme during operation of an EMR. For example, ethylenediaminetetraacetic acid and polyethylene glycol, which are believed to possess a protecting role for proteins, especially under oxidative stress, may be added to an EMR (Andersson et al. 2000; Mendoza et al. 2011).

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Table 15.6. Summary of recent studies on EMR for removal of TrOC and other resistant pollutants

Membrane material (MWCO, kDa)	*Enzyme (activity)*	*Compound (concentration, mg/L)*	*HRT (h)*	*Reactor volume (mL)*	*References*
UF polyethersulfone membrane (10)	Laccase (500 and 1000 U/L)	Estriol and 17β-estradiol (4)	1–4	250	Lloret et al. (2012b)
UF polyethersulfone membrane (10)	Laccase (500 U/L)	Estriol and 17β-estradiol (4)	2–4	250	Lloret et al. (2012a)
UF polyacrylonitrile membrane (6)	Laccase (70–100 μM/ min)	Diclofenac and bisphenol A (0.5)	8	1500	Nguyen et al. (2014a)
UF polyethersulfone membrane (10)	MnP (7000 U/L)	Orange II (100)	0.3, 0.75, 1 and 1.5	250	Lopez et al. (2004)
UF polyacrylonitrile (20)	Laccase (100 U/L)	Acid Violet 17 (76)	4, 6, 8, 10, and 16	250	Chhabra et al. (2009)
UF polyethersulfone (10)	Purified laccase (8750 U/L)	Acid azo (20)	3	70	Katuri et al. (2009)

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15.6 SUMMARY AND FUTURE OUTLOOK

Conventional treatment processes cannot achieve adequate removal of TrOCs from wastewater. Membrane technology is becoming increasingly important in wastewater treatment. For example, MBRs which use microfiltration (or loose ultrafiltration) membranes have appeared as an advanced alternative to CAS processes in terms of bulk organics removal. However, hydrophilic and resistant TrOCs are often inefficiently removed by MBRs. On the other hand, high retention membranes such as NF and RO membranes can achieve efficient retention of many TrOCs. However, severe membrane fouling restricts application of high retention membranes in direct filtration of wastewater. A number of studies have shown significant removal of TrOCs by other advanced processes such as activated carbon adsorption and advanced oxidation processes. Particularly enzymatic degradation has appeared as a 'green technology' over chemical degradation options. However, at the present stage of development, TrOC removal efficiency by these techniques depends on the dosage and applied contact time as well as the wastewater matrix. Hence, combined treatment processes need to be taken into consideration to ensure efficient treatment of the variety of TrOCs. This chapter demonstrates the potential benefits of combined systems having MBR at the core to treat the wide varieties of TrOCs from wastewater. However, in practice there are many factors affecting TrOC removal by these techniques. These factors include both structural and physicochemical characteristics of the TrOC as well as operational parameters of the processes, which require fine tuning. Further work is also required in areas such as improved understanding of the overall fate and degradation pathways of TrOCs undergoing various processes.

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CHAPTER 16

Application of Green and Physico-Chemical Technologies in Treating Water Polluted by Heavy Metals

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16.1 INTRODUCTION

Heavy metal can be defined as a set of elements that have high atomic weight, atomic number and specific gravity greater than 5. Generally, heavy metals comprise the basic metals, transition metals, metalloids, lanthanides and actinides. They are also known as toxic metals. Some of common heavy metals are listed in Table 16.1.

Heavy metals present in the environment go through different processes/stages and ultimately end up as waste. A generalised flow of heavy metal (life cycle) to waste is shown in Figure 16.1. Concentrations and distributions of different heavy metals may vary during different processes/stages. Approximately 20% of heavy metals may be removed during the waste treatment process and remain in residual sludge. Heavy metal removal efficiency can be up to 60%, depending on the metal solubility (European Commission 2001). Industrial effluent and residual domestic water are the main sources of heavy metal pollution in water streams. Unlike organic chemicals, heavy metals cannot be broken down into less harmful components. Industrial wastes generally contain common heavy metals such as arsenic, cadmium, copper, lead, zinc, chromium, nickel, manganese and mercury.

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Table 16.1. List of common heavy metals

Heavy metal	*Atomic weight*	*Atomic number*	*Occurrences*	*Forms*
Chromium	51.99	24	Found as chromite in chrome-iron ore ($FeCr_2O_4$)	Trivalent forms – $Cr(OH)^{2+}$, $Cr(OH)_2^+$ and $Cr(OH)_4^-$ Hexavalent forms- CrO_4^{2-} and $Cr_2O_7^{2-}$
Nickel	58.69	28	Pyrrotite and Garnierite	The most common aqueous species is Ni^{2+}
Copper	63.54	29	Chalcopyrite, Chalcocite, Cuprite, Malachite, Azurite and Bornite	Common aqueous species are Cu^{2+}, $Cu(OH)_2$, and $CuHCO_3^+$
Zinc	65.38	30	Sulphite sphalerite,	Common aqueous species $ZnOH^+$ and Zn^{2+}
Arsenic	74.92	33	Arsenopyrites, Realgar, Loellingite, Orpiment, Enargite and Arsenic Oxide	pH 3-7 $H_2AsO_4^-$ pH 7-11 $HAsO_4^{2-}$ pH < 3 H_3AsO_3
Selenium	78.96	34	Present as Selenate ion (SeO_4^{2-}), obtained as by-product of copper refining	Common aqueous species include Se^{2-}, HSe^-, and Se^0.
Molybdenum	95.95	42	Molybdenite and Wulfenite	Common aqueous species are $HMoO_4^-$ and MoO_4^{2-}
Cadmium	112.41	48	Occurs in sulphide minerals of the zinc ores such as sphalerite	Common aqueous species is Cd^{2+}
Mercury	200.59	80	Cinnibar	Common aqueous species are Hg^{2+}, $Hg(OH)_2^0$ and Hg^0
Lead	207.19	82	Galena, Anglesite and Cerussite	Common aqueous species are Pb^{2+} and hydroxide and carbonate complexes

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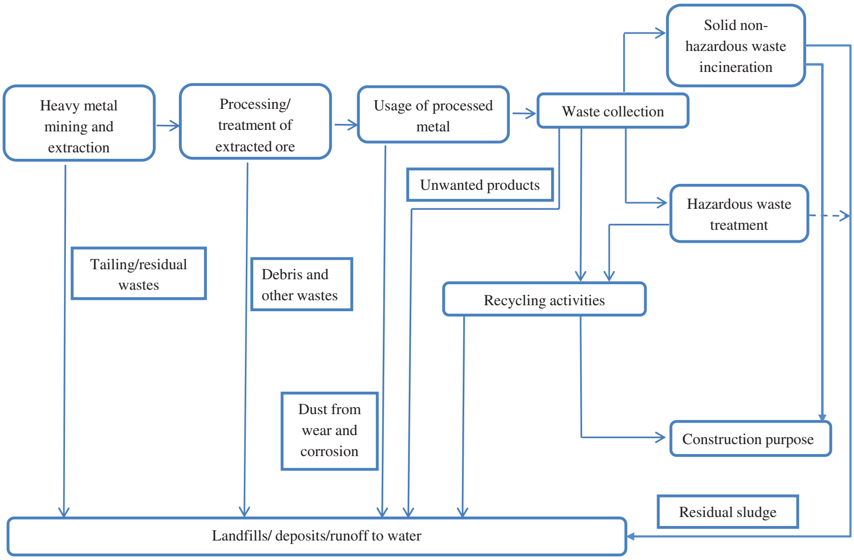

Figure 16.1. Generalised flow of heavy metals to waste

Bulk of the groundwater is contaminated by these heavy metals. This has created a widespread concern to the global community.

Various studies have been conducted on analysing the impact of the heavy metal contamination. Research reveals that heavy metal toxicity can result in renal impairment, skin blisters and pustules, anaemia, haemolysis, tissue edema, liver dysfunction, neuronal cell injury and various other consequences (European Commission 2002). Therefore, remediation of heavy metals present in water becomes imminent, and their removal becomes a necessity for water sustainability.

Numerous technologies have been employed in remediation of heavy metals in water. Electrocoagulation, ion exchange, chemical precipitation, membrane reactor, and nanotechnology, etc. are the most common technologies being employed in heavy metal remediation. Despite being widely used, these conventional techniques have disadvantages, such as (1) generation of large volumes of sludge, (2) additional waste disposal costs, (3) release of new toxic compounds of nano-size, and (4) operating costs of the membrane reactors. Generally, after the treatment of wastewater, the obtained sludge is disposed of to agricultural lands or landfills, and the treated water is discharged to the receiving water bodies. The quality of the waste sludge is determined by the toxic heavy metals present in them. Apart from landfills, solid waste incinerators are also extensively used in treatment of the residual wastes. With increasing population, the re-use of spent water from different sources is necessary to fulfil the demands of the future. The current landfill technique and discharge of the treated water to the sea is not a sustainable option for the long run.

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Remediation of heavy metals in wastewater by green technologies has been gaining considerable attention. One of the green technologies namely bioremediation has been widely accepted and employed. Bioremediation is a process by which the organic/inorganic pollutant is detoxified by the action of plants or microorganisms present in the environment. The main advantages of these green technologies are: (1) reduced costs as compared to conventional techniques; (2) non-invasive techniques which are less disruptive to the environment; (3) potential to treat more than one type of pollutant; (4) treatment of low concentration of pollutant, which is difficult with conventional techniques; (5) site specific application; and (6) faster remediation with manipulated environmental conditions.

A majority of the countries are looking to develop scientific solutions for more sustainable, innovative and effective use of water. With efficient green technologies, sustainable water management has gained further attention. A resourceful utilisation of water has become an order of the present era.

This chapter first identifies occurrences and usages of heavy metals along with current regulations and disposal methods of those heavy metals. Four heavy metals namely arsenic, chromium, lead and mercury have been considered in detail. A subsequent discussion on environmental and health impacts due to heavy metal pollution emphasizes the need to treat waters which are polluted by heavy metals. This leads into a review on current remediation strategies which are available for treatment. Treatment technologies such as chemical precipitation, ion exchange, adsorption, membrane filtration and coagulation/flocculation and their effectiveness in treating heavy metals are discussed in details. A question on the contribution of green technologies in treating heavy metals is answered next. The following eight green technologies have been evaluated for their performance in treating heavy metals: biosorption, biostimulation, bioaugmentation, bioleaching, biosurfactants, bioprecipitation, vermicomposting and phytoremediation. Finally the contribution of green technologies towards sustainable water management is assessed.

16.2 OCCURRENCES, USAGE, REGULATION AND DISPOSAL OF HEAVY METALS

Table 16.1 lists some common heavy metals (Clesceri et al. 1999). Predominantly the most toxic ones are arsenic, chromium, lead and mercury. In this section, we will focus on the occurrence, usage, regulation and disposal of these four heavy metals.

16.2.1 Arsenic

Arsenic (As) is the third element in Group 15 of the periodic table. It has the atomic number 33 with the atomic weight of 74.92 and its valence ranging from −3 to +5. The average concentration of Arsenic in the Earth's crust is 1.8 ppm,

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5.5 to 13 ppm in soils and less than 1×10^{-4} g/L in groundwater. Arsenic naturally occurs as pyrite in sulphide minerals. Arsenic is widely used in alloys with lead in storage batteries and ammunition. It is also used as a component in a wide range of products including wood preservative, drugs, dyes, paints, soaps and semiconductors.

The United States Environmental Protection Agency (USEPA) has set the Maximum Contaminant Level (MCL) of Arsenic in drinking water to be 1×10^{-5} g/L (U.S. EPA 2004). For the protection of aquatic life, the average concentration of arsenic should be lower than 7.2×10^{-5} g/L and maximum permissible concentration of 14×10^{-5} g/L. The United Nation Food and Agriculture Organization have recommended the concentration of arsenic for irrigation to be 1×10^{-4} g/L (Heikens 2006).

The disposal of Arsenic is carried out based on the concentration of contaminants in the waste. Generally the most widely used method for waste disposal is landfill. Treated wastes containing As are sometimes mixed with cow-dung in India and Bangladesh as the microorganisms present in them reduce the soluble arsenic species to gaseous arsine which is released into the atmosphere. Also residual As sludge is incorporated into the construction materials such as bricks, cement blocks and plinths. Over the last few decades, stabilisation/solidification, a pre-landfill technique is used to make the hazardous As wastes safe for disposal. The process involves mixing the waste into a cementitious binder system. This method encapsulates and incorporates the waste into the binder system, and produces a monolithic solid with improved structural integrity which has long-term stability and minimal leaching (Colin et al. 2010).

16.2.2 Chromium

Chromium (Cr) is the first element in group 6 of the periodic table. It has an atomic number 24, atomic weight 51.99 and has its valence ranging from 1 to 6. The average concentration of Cr in the Earth's crust is 122 ppm, 11 to 22 ppm in soils and $\sim 1 \times 10^{-4}$ g/L in groundwater. Chromium is chiefly present as chrome-iron ore ($FeO.Cr_2O_3$). Chromium is mainly used in alloys, electroplating, tanneries and pigments. Chromium is also used as catalyst for processing hydrocarbons.

The USEPA has set the Maximum Contaminant Level of total chromium in drinking water to be 1×10^{-4} g/L, which includes both chromium (III) and chromium (VI) (U.S. EPA 2004). The recommended concentration of chromium for irrigation is 1×10^{-4} g/L.

The concentrations of Cr in surface water depend on the degree of pollution in the water body. In Europe, 30–60% of the total Cr in the wastewater treatment plants came from the commercial source, and the domestic source contributed 20–40% (European Commission 2001). For example, in Melbourne about 46% Cr load to Eastern Treatment Plant was identified to come from the trade wastes (Tjandraatmadja et al. 2010). In year 2000, the European Union recorded usage of around 17,000 tonnes of chromium trioxide and 25,000 of dichromates. A study in Australia showed domestic sources (which include laundry, bathroom, kitchen

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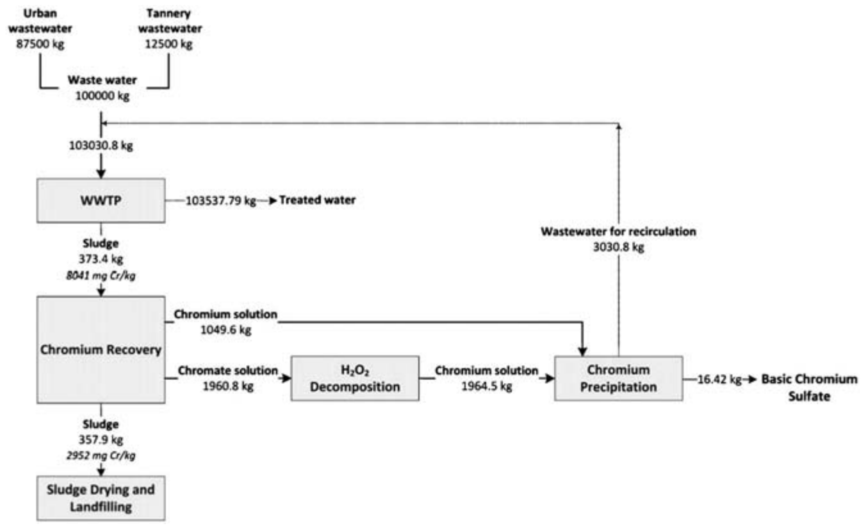

Figure 16.2. Schematic diagram of mass flow of Chromium in a wastewater treatment plant.

Source: Kilic et al. (2011); reproduced with permission from Elsevier

and toilet) contributed a maximum Cr load of 0.014 to 35.8 mg per week (Tjandraatmadja et al. 2010).

Chromium can be removed by several techniques. Presently coagulation followed by filtration is extensively used as a pre-treatment technique for treating the commercial wastewater. Ion exchange, reverse osmosis (RO) and lime softening are then followed in removing the dissolved chromium present in the wastewater. Figure 16.2 gives a layout of mass flow of chromium in a wastewater treatment system. The sludge treatment process helps in recovering 70% of chromium (Kilic et al. 2011). However the end- of-the-pipeline treatments usually increase environmental impact, due to the quantity of chemicals and energy used. Improved remediation systems such as green treatment technologies are being looked as a suitable alternative for treating chromium containing wastewaters.

16.2.3 Lead

Lead (Pb) is the fifth element in group 14 of the periodic table. It has an atomic number of 82, atomic weight of 207.2 and its common oxidation states are +2 and +4. The average concentration of Pb in the Earth's crust is 13 ppm, 2.6 to 25 ppm in soil and generally less than 1×10^{-4} g/L in groundwater. Lead is found in nature as PbO_2 in the brown to black mineral plattnerite. It is commercially produced from trilead tetroxide by oxidation with chlorine. Lead is used in batteries, ammunition, solder, piping, pigments, insecticides, alloys and also in gasoline as an anti-knocking agent. The USEPA has set the drinking Maximum Contaminant Level Goal (MCLG) to be 0. The MCL should be lower than 15×10^{-4} g/L (U.S. EPA 2004). The WHO's permissible limit of lead in the agricultural soil is 150 mg/kg (WHO 2006).

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The global consumption of lead in year 1998 was estimated to be around 6 million tonnes (European Commission 2002). Almost 75% of the contribution came from the batteries; lead compounds and extruded lead contributed around 9% and 6%, respectively. Ammunition and alloys contributed around 3% respectively (European Commission 2002). Australia ranks No.1 in the world in economic lead and is world's largest exporter with its bulk being exported to the United Kingdom. Lead recycling is also being extensively done in Australia with about half the lead consumed comes from the recycling plants. Domestic lead waste is mainly contributed by the old lead pipes, laundry and kitchen wastes. The commercial source of lead contamination contributed around 13.4×10^{-3} g/L in the industrial effluent of Germany. In Italy, around 6×10^{-3} g/L of lead was found in the effluent from ceramics and photo-ceramics (European Commission 2001). The metal and electrical industries in Greece contributed around 5×10^{-4} g/L of lead waste in the effluent from the industry (European Commission 2001).

Lead removal from wastewater is mainly done by coagulation, ion exchange and sand filtration. Additionally activated carbon, media filtration and reverse osmosis may be applied. Organo-metallic compounds of lead are difficult to treat as the lead is not free to precipitate. Generally organo-metallic compounds are oxidized to separate the lead and then adsorbed onto carbon to remove as organic complex.

16.2.4 Mercury

Mercury (Hg) is the third element in the group 12 of the periodic table. It has an atomic number of 80, an atomic weight of 200.59 and has valences of 1 and 2. Mercury is the only liquid heavy metal. The principal ore from which mercury is extracted is from the red sulphite (Cinnabar). Generally mercury occurs in Earth's crust on the average of about 0.08 gram per ton of rock. Native mercury occurs in isolated drops and occasionally found in larger fluid masses. Mercury is widely used in thermometers, manometers, float valves, relays and as alloys. Mercury amalgamated with silver is used as a filling in dentistry. The MCL of mercury is set to be 2×10^{-6} g/L by the U.S. EPA (2004).

The main source of mercury contamination in the effluent is from the thermometers, glass and electrical industries. In 1994, WRC report established that the mercury emissions in UK are much higher from industrial sources than domestic sources (European Commission 2001). In France, it was estimated that 73% to 80% of the waste in urban wastewater is from dental practices and amalgam filling corrosions (European Commission 2001). In Spain, majority of the mercury contamination came from the chloro-alkali production unit. In Australia, the southern coast of News South Wales has seen elevated Hg concentrations as a result of industrial activities. The Hg concentrations around Great Barrier Reef surface sediments have been found to be increased by 3-fold from pre-1850 levels (Haynes and Michalek-Wagner 2000). Mercury contamination in India is on the alarming level due to discharges from industries containing mercury levels $5.8 - 26.8 \times 10^{-5}$ g/L as against the prescribed WHO limit of 1×10^{-6} g/L (Srivastava 2003). The earthquake that rocked North Andaman had an estimated release of 50 kg of Hg from the east island lighthouse. This spill still poses health hazards to the locals and to fragile ecology of the entire region.

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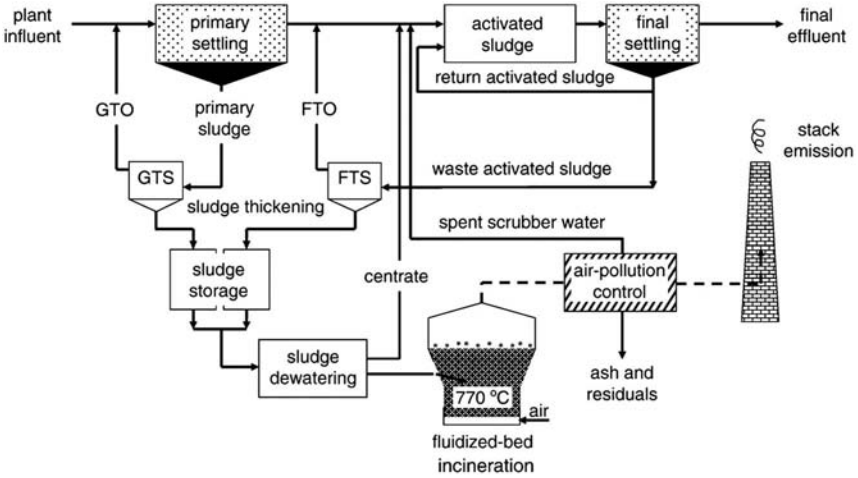

Figure 16.3. Schematic diagram showing the mass flow of mercury in a wastewater treatment plant

Note: GTO = Gravity thickened residual water, GTS = Gravity thickened sludge; FTO = Flotation thickened residual water; and FTS = Flotation thickened sludge

Source: Balogh and Nollet (2008); reproduced with permission from Elsevier

Mercury can be separated from waste by filtration, distillation or precipitated by using carbonate, phosphate or sulfide. Ion exchange may also be employed in treating mercury wastes. Prior to using ion exchange, the mercury must be first oxidized. Mercuric wastes which cannot be further processed or reused are generally incinerated at medium/high temperatures. A detailed insight of mass flow of mercury in a wastewater treatment plant has been shown in Figure 16.3. The plant discharges (includes plant effluent and incinerator stack exhaust) were found to be less than 5% of mass of mercury entering the plant. The activated carbon/baghouse control system for removal of mercury from incinerator offgas showed approximately 83% removal efficiency (Balogh and Nollet 2008.). This treatment process gives us an understanding on system design for removing Hg from wastewater and sequestering it in a controllable stream for secure disposal.

16.2.5 Pourbaix Diagram of Heavy Metals in Different Water Bodies

Pourbaix diagram, also known as Eh-pH diagram, maps out the possible stable forms of an element in an aqueous electrochemical system. The reduction potential of the environment and pH are a mandatory requirement to identify the speciation of a given element in natural water systems. At any given point on the diagram, we can identify the thermodynamically most stable form of the element at the corresponding E and pH. Figure 16.4 shows the Eh-pH diagrams of Arsenic, Chromium, Lead and Mercury, respectively (WOU 2015).

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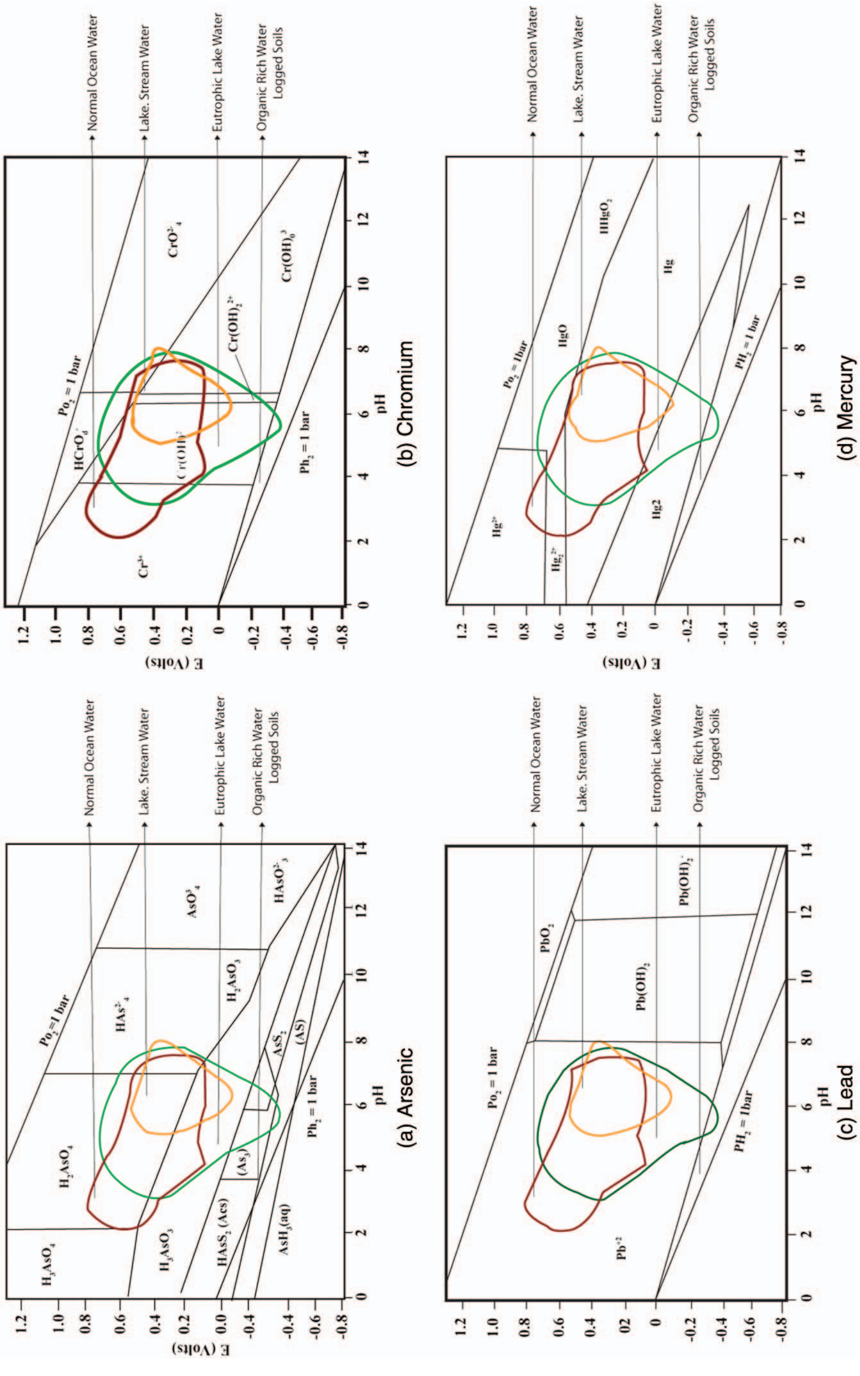

Figure 16.4. Pourbaix diagrams of heavy metals in different water bodies

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For a clean lake, the surface water is well aerated and the dissolved oxygen concentrations are high enough to make the potential, E reasonably high and close to the E° of oxygen. Conditions may approach anaerobic (actively reducing), approaching the lower boundary of the reduction of water to hydrogen for i) a lake highly polluted with organic reducing agents, ii) the bottom layer of a thermally stratified lake, and iii) a swamp. Organic rich waterlogged soils can generally be seen to have E° value below −0.2. This form of representation enables us determine the elemental form of mineral present in natural water bodies.

16.3 HEAVY METAL POLLUTION AND ITS IMPACTS

Heavy metals are widely used for various applications. The extent of its impacts depends on the type and concentration of heavy metal polluted. The impacts can be classified into two broad categories, i.e. environmental and health.

16.3.1 Environmental Impact

Heavy metals released by industry enter the fields and contaminate the soil. Their concentration in the environment is increased drastically which in turn surges the risk of groundwater pollution, augments toxic metal mobility, plant toxicity and metal contamination in the food chain. In soil, the metal mobility depends on two main factors: (1) water transfer through the soil; and (2) physical/chemical interaction between the metal and particles present in the soil. Acidic soil conditions provide a high potential for metal mobilisation as they reduce the chance of mechanisms like hydrolysis and precipitation.

Long-term accumulation of heavy metals in the soil can cause reduced plant growth as the concentration of heavy metals in plant tissues may go beyond the threshold value. For example, high concentration of lead is known to inhibit seed germination of barley plants. Phytotoxicity of cadmium is demonstrated by stunting, chlorosis, wilting, necrosis and reduction in photosynthesis by plants. High concentration of mercury in plants is also known to cause depressed root elongation and shoot growth. Chromium and arsenic have also known to cause leaf chlorosis during the late stage of growing.

Numbers of studies have been carried out on the aspects of soil microbial activities near industries which emit heavy metals. These studies were motivated by the concern that elevated heavy metal levels in soil could interfere with litter breakdown rates. Effects can take place via metal toxicity to soil bacteria, fungi, actinomycetes or arthropods. Metal toxicity can be attributed to the tight binding of metal ions to the sulfhydryl groups of the enzymes which are necessary for the biodegradation of the contaminants. Soils co-contaminated with organics and heavy metals are considered difficult to remediate because of the mixed nature of contaminants.

A report by Tyler et al. (1989) clearly suggests that a low degree of heavy metal pollution is sufficient to bring about measurable disturbances which ultimately

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reduce the productivity of the ecosystem. In the reports by Jackson et al. (1978) increased heavy metal concentration affected the soil nutrient pool cycling of the forest eco-system. There was also an increase in essential elements of soil leachate as a result of heavy metal impaction. Heavy metals in soil are also known to affect the mineralization of essential nutrients required by the plants.

16.3.2 Health Impact

Metals belong to a class of globally distributed pollutants due to their extensive use in industries and in the development of products for the millennia. They are notable for their wide dispersion and have a tendency to accumulate in living tissues of the human body which can be toxic even at very small levels of exposure. There are a few essential metals which are referred to as micronutrients, as they are required for normal functioning of the human body. However, these micronutrients can become toxic at high exposure levels. The Agency for Toxic Substances and Disease Registry (ATSDR) of U.S. Department of Health and Human Services has listed the heavy metals arsenic, chromium, lead and mercury as most toxic and hazardous (Hu 2002).

Exposure to these heavy metals can occur through a variety of ways. They can be inhaled as dust or fumes, ingested involuntarily through food or water, and also exposed to by direct physical contact. Once they are digested or absorbed, they get distributed in tissues and organs (Hu 2002). Excretion typically occurs through the kidneys and the digestive tracts, but metals tend to accumulate in certain specific storage sites for years or decades. Here we focus on the exposure and toxicity of the four main heavy metals discussed earlier.

16.3.2.1 Arsenic

Significant exposure to arsenic can occur through both anthropogenic and natural sources. Arsenic is widely distributed as a metalloid occurring in rocks, soil, water and air. Occupational exposure to arsenic occurs mainly through smelting of non-ferrous metals and energy production from fossil fuels. Other small sources of contamination are the manufacture and use of arsenical pesticides and wood preservatives. Inorganic arsenic is present in groundwater used for drinking in several countries all over the world (e.g. Bangladesh, Chile, China, India and parts of South-west U.S.A), and organic arsenic is found commonly in fish, which in turn give rise to human exposure (Järup 2003).

Arsenic concentration in rural air is found to be around <1 to 4 ng/m^3, whereas in cities the concentration may be as high as 200 ng/m^3. Higher concentrations (>1000 ng/m^3) have been measured around industrial sites (Järup 2003). General population exposure to arsenic is mainly through food intake and drinking water. Drinking water is the main source of inorganic arsenic. Inorganic arsenic is generally methylated in humans, and metabolites are excreted in the urine. Soluble arsenic compounds are easily absorbed from the gastrointestinal tract.

Arsenic once absorbed into the body undergoes some accumulation in soft tissue organs such as liver, kidney, lungs. Major accumulation is seen in the keratin

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rich tissues like hair, skin and nails. Arsenic in nails and hair can be useful indicators of its exposure. Inorganic arsenic is acutely toxic and can cause gastrointestinal symptoms, severe disturbances of cardiovascular and central nervous systems and can be fatal (Järup 2003). Chronic exposure can cause hyperpigmentation, peripheral nerve damage manifesting as numbness, tingling and weakness in hands and feet. There have also been reports on development of cancers, most notably skin, liver and lung. Drinking water arsenic concentrations of approximately $5–10 \times 10^{-5}$ g/L have led to skin cancer. WHO has set the permissible arsenic content in drinking water to be less than 1×10^{-5} g/L (WHO 2006).

16.3.2.2 Chromium

Chromium is widely present in the Earth's crust, predominantly in the trivalent chromium Cr (III) form. The hexavalent form of chromium Cr (VI) is generally of anthropogenic in origin. The enormous amount of chromium is produced through a wide range of activities, including production of chromates and dichromates, welding, chrome plating, welding, ferrochrome alloys and chrome pigment production. Global production of chromium in the year 2001 was estimated to be about 13.7 million tonnes. Cr (VI) released is expected to be reduced to Cr (III) by the biotic or abiotic process. The general population may be exposed to chromium by inhaling ambient air, or ingesting food and drinking water that contain them. Chromium may also enter through skin when exposed to products like wood preservatives, cleaning materials, textiles and leather tanned using chromium. Cr (III) is regarded as an important element and plays a crucial role in maintenance of metabolism.

The toxicity of chromium depends on the oxidation state, with Cr (VI) being more toxic than Cr (III). Cr (VI) is readily absorbed by inhalation and by oral routes. Inhaled Cr (VI) generally affects the respiratory tracts and can cause dyspnoea; on acute exposure, effects on kidney, gastrointestinal tract and liver have also been reported. Ingested Cr (VI) can affect the functioning of cardiovascular, gastro-intestinal, hepatic, renal and neurological systems. Due to corrosive nature of Cr (VI), dermal exposures can lead to dermal ulcers and, at high doses, systemic toxicity, leading to effects on the renal, haematological and cardiovascular system and death (Assem and Zhu 2007). Chronic exposure to Cr (VI) compounds can also cause allergic responses in sensitized individuals. Chronic exposure to Cr (III) resulted in weight loss, anaemia, liver dysfunction and renal failure. Cr (VI) is classified as Group 1 human carcinogen by the inhalation route of exposure and chromium metal (Assem and Zhu 2007). In blood, Cr (III) is bound to large molecular mass proteins. Cr (VI) has a better tendency to pass through plasma membranes. Generally the absorbed chromium is excreted primarily via urine. The half-life of chromium when given as potassium chromium is estimated to be 35–40 hours (Assem and Zhu 2007).

16.3.2.3 Lead

Lead exposure can occur through air and food roughly in equal proportions. Lead mining and introduction in mass production of plumbing equipment, solder used

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in food cans, paint and ceramic ware resulted marked rise in population exposures in the 20th century. Earlier lead in food stuffs originated from utensils used for cooking and storage, and lead acetate was previously used to sweeten port wine. The dominant source of lead emissions in ambient air has clearly been the use of lead organic compounds as an anti-knock agent in motor vehicle fuel. However, there has been a decrease in lead emissions in developed countries due to the use of unleaded petrol. Subsequently the blood lead levels in the general population have decreased. The worldwide lead production is approximately estimated to be 5.4 million tons annually and is expected to rise. The major occupational exposure to inorganic lead occurs in mines and smelters as well as welding of lead painted metal and in battery plants. Airborne lead can be deposited in the soil which can further concentrate on root vegetables (e.g., onion) and leafy green vegetables (e.g., spinach) and thus reaching humans via the food chain.

Almost 50% of the inorganic lead inhaled is absorbed in the lungs. Adults take up to 10–15% of lead from food, whereas children may absorb up to 50% via the gastrointestinal tract (Järup 2003). Lead in blood mainly is bound to the erythrocytes, and its elimination is slow, mainly via urine. Lead also gets stored in the skeleton of the human body. The half-life of lead is about 1 month in blood and 20–30 years in the skeleton. In adults, blood doesn't penetrate the blood-brain barrier as it is well developed. In children, the chance for lead entering into the blood-brain barrier is high as it is under developed, which makes them more susceptible to lead exposure and subsequent brain damage (Järup 2003). Tetramethyl and tetraethyl lead can penetrate the skin easily. They also can cross the blood-brain barrier in adults, which can further cause lead encephalopathy due to acute lead poisoning by organic lead compounds. Lead encephalopathy is characterized by sleeplessness and restlessness. Other symptoms of acute lead poisoning include headache, irritability, abdominal pain and various symptoms (Järup 2003). Long-term low-level exposure of lead to children can also result in diminished intellectual capacity. Acute exposure to lead has also known to cause proximal renal tubular damage. Few studies also report that certain genetic and environmental factors can increase the detrimental effects of lead on neural development.

16.3.2.4 Mercury

Mercury comes in a number of different chemical forms. In its pure form, metallic mercury is a liquid. The mercury compound cinnabar (HgS) was used in prehistoric cave paintings for red colour, and metallic mercury was used in ancient Greece as a cosmetic to lighten skin. Mercury was also used to cure syphilis and was used as diuretics (Järup 2003). Metallic mercury is used in thermometers, barometers and in instruments for measuring blood pressure. Mercury is also being widely used as amalgams in tooth filling. The largest occupational group exposed to mercury is the dental care staff. Mercury has become a widespread contaminant in the recent years. Almost half of the National Priority List toxic waste sites in the US contain mercury. Brazil has reported to a widespread mercury contamination due to excessive gold mining and deforestation. When

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deposited in soil, the inorganic mercury is converted to organic form such as methylmercury by microorganisms. This organic form is very stable and accumulates in the food chain. The general population is primarily exposed to mercury via the fish, particularly tuna, king mackerel, and swordfish as they can concentrate methyl mercury at high levels.

Acute mercury exposure by inhalation of mercuric vapours can lead to lung damage. Chronic poisoning is characterized by neurological and physiological symptoms such as tremor of the hands, excitability, memory loss, insomnia, timidity and depression. Metallic mercury is an allergen, which on contact can cause eczema. Mercury from amalgam fillings may also give rise to oral lichen. Dimethyl mercury is a supertoxic compound which can penetrate through skin and cause degeneration of the central nervous system. Methylmercury poisoning has a latency of one month. The earliest symptoms are paresthesias and numbness in the hand and feet. High doses may lead to death, usually 2–4 weeks after the onset of symptoms. The 1955 disaster in Minamata Bay, Japan was caused by methyl mercury poisoning from fish contaminated from mercury discharges in the surrounding area (Järup 2003). Mothers who were exposed to mercury gave birth to infants with mental retardation, retention of primitive reflexes, cerebellar symptoms, and other abnormalities. In the early 1970's, more than 10,000 people were poisoned by eating bread baked from mercury polluted grain. High dietary intake of fish has been hypothesized to increase the risk of coronary heart disease.

16.4 CURRENT REMEDIATION STRATEGIES FOR HEAVY METALS

Soil and water are the major sinks for heavy metals released into the environment by anthropogenic activities. They persist in the natural environment for an extended period as they are not biodegradable. Moreover, they also have the ability to accumulate in successive levels of the biological chain, thereby causing acute and chronic diseases. With the enactment of several water legislations and guidelines worldwide, heavy metals are listed as the environmental priority pollutants and are becoming one of the most serious environmental problems. Many methods are being currently employed for heavy metal ions removal. We shall look in detail of several important remediation techniques which are extensively used.

16.4.1 Chemical Precipitation

Chemical precipitation is one of the most commonly used processes in industry because of its simple mode of operation and inexpensive compared to other treatment methods. Generally in the precipitation process, the chemicals react with the heavy metal ions to form insoluble precipitates (Fu and Wang 2011). The precipitates are then separated by sedimentation or filtration. The treated water can be discharged or reused. The conventional precipitation process is done by using either hydroxide or sulphide.

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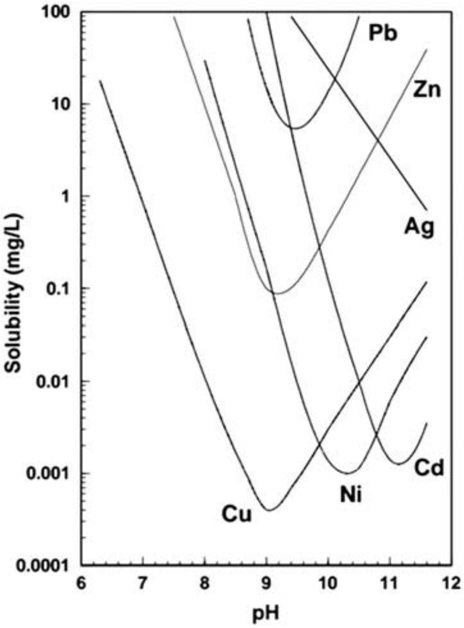

Figure 16.5. Solubility of metal hydroxides at different pH
Source: U.S. EPA (2003)

16.4.1.1 Hydroxide Precipitation

Hydroxide precipitation is commonly used due to its simplicity, low cost and ease of pH control. Metal hydroxides tend to precipitate in the pH range of 8.0–11.0 as their solubilities are minimized (Figure 16.5) which can further be removed by flocculation and sedimentation. Slaked lime or calcium hydroxide $Ca(OH)_2$ is the most commonly used industrial hydroxide precipitant. Sometimes the addition of coagulants like alum, iron salts and organic polymers enhance the removal of heavy metals from wastewater. Sodium hydroxide (NaOH) was studied in the removal of Cu (II) and Cr (VI) from wastewater by Mirbagheri and Hossein (2005). Although hydroxide precipitation is most sought-after, it still comes with few limitations. Hydroxide precipitation tend to generate large volumes of sludge which causes dewatering and disposal issues. Also when the wastes contain mixed metals, treatment using hydroxide precipitation can be a problem as the ideal pH of one metal can put another metal back into the solution. Finally, when complexing agents are present in wastewater, they will inhibit metal-hydroxide precipitation.

16.4.1.2 Sulfide Precipitation

Sulfide precipitation is also an efficient process for the treatment of toxic heavy metals. The main advantages of sulphides is the ability to precipate the heavy metals at low pH (which are dramatically lower than hydroxide precipitates),

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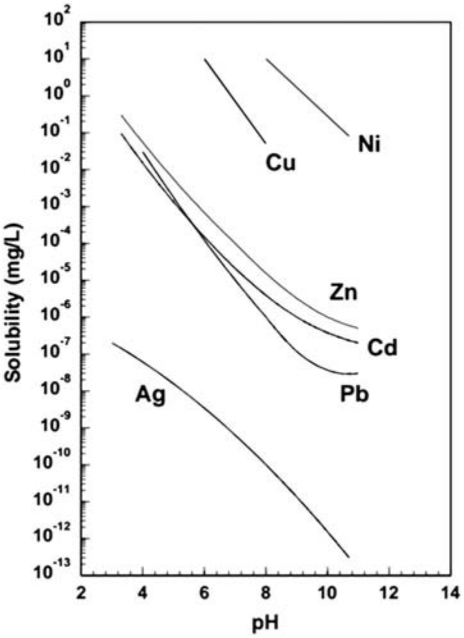

Figure 16.6. Solubility of metal sulfides at different pH
Source: U.S. EPA (2003)

and sulfide precipitates are not amphoteric (Figure 16.6). Also the sludge generated shows better thickening and dewatering characteristics than the corresponding hydroxide sludge. The major disadvantage of using the sulphide precipitation process is the generation of H_2S fumes at acidic conditions. So it is essential to perform the precipitation process in a neutral or basic medium. Also, the colloidal precipitates which are generated after sulfide precipitation process tends to cause separation problems during settling or filtration processes.

16.4.1.3 Heavy Metal Chelating Precipitation

Currently, the use of chelating precipitants to precipitate heavy metals from aqueous solutions is gaining popularity. Trimercaptotriazine, potassium/sodiumthiocarbonate and sodiumdimethyldithiocarbamate are the most commonly used heavy metal precipitants. Apart from these commonly used precipitants, precipitants specific for a given heavy metal are being developed. For example, a thiol based precipitant 1,3-benzenediamidoethanethiol ($BDET^{2-}$) was designed and synthesised by Matlock et al. (2002), specific for precipitating mercury. Potassium ethyl xanthate was employed to remove copper ions from wastewater (Chang et al. 2002). Similarly, dipropyl dithiophosphate was used successfully to remove lead, cadmium, copper and mercury (Xu and Zhang 2006).

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16.4.2 Ion Exchange

Ion exchange resins work on the principle of exchanging cations with the metals in wastewater. Their major advantages include high treatment capacity, high removal efficiency and fast kinetics. Among the materials used in the ion-exchange process, synthetic resins are commonly preferred as they are capable of removing heavy metals efficiently in the solution. Most common cation exchangers are strongly acidic with sulfonic acid groups ($-SO_3H$), and weakly acidic resins with carboxylic acid groups ($-COOH$). The general ion-exchange process can be understood by the simple equations as follows (Fu and Wang 2011):

$$nR-SO_3H+M^{n+}\rightarrow(R-SO^{3-})_nM^{n+}+nH^+(\text{Resins with}-SO_3H\,\text{group})$$

$$nR-COOH+M^{n+}\rightarrow(R-COO^-)_nM^{n+}+nH^+(\text{Resins with}\\ -COOH\,\text{group})$$

The uptake of heavy metals depends on various variables like pH, temperature, initial metal concentration and contact time. Low-cost naturally occurring silicate minerals are also being widely used to remove heavy metals.

16.4.3 Adsorption

Adsorption is one of the most widely used processes for treatment of wastewater containing heavy metals. It is an efficient and economical treatment process and offers flexibility in design and operation. Since adsorption in most cases is reversible, the adsorbents used can be regenerated by suitable desorption process. The different types of adsorbents currently being used are discussed in brief below.

16.4.3.1 Activated Carbon Adsorbents

Activated carbon adsorbents are predominantly used because of their large micropore and mesopore volumes resulting in high surface areas. Extensive research is being done on the use of activated carbon for removing heavy metals (Table 16.2). However with depleting coal resource, the cost of preparing coal-based activated carbon has increased considerably. Therefore, the development of activated carbon composites is being looked as an alternative. Additives like alginate, tannic acid, magnesium and surfactants are being used to develop activated carbon composite adsorbents for heavy metals (Fu and Wang 2011). Generation of activated carbon from different sources is also an alternative. Converting carbonaceous material into activated carbon for heavy metal removal has been reported. The use of activated carbon from eucalyptus bark and from poultry litter was also explored (Kongsuwan et al. 2009; Guo et al. 2010).

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Table 16.2. List of various activated carbon adsorbents used for adsorbing different heavy metals

Heavy metal	*Type of adsorbent*	*Optimum pH*	*Adsorption capacity (mg/g)*	*References*
Hg (II)	ACC	2.5–5.5	65	Babic et al. (2002)
Cr (VI)	GAC	N.A.	6.84	Monser and Adhoum (2002)
Cr (VI)	GAC - Filtrasorb	2	53.19	De Castro Dantas et al. (2001)
Cr (III)	GAC - Filtrasorb	> 4.5	30	Park and Jung (2001)
Zn (II)	GAC-C	7	18	Leyva Ramos et al. (2002)
Cd (II)	ACF	6	146	Rangel-Mendez and Streat (2002)
Ni (II)	Oxidized ACF	3.5–4	10	Shim et al. (2001)
Cu (II)	GAC	N.A.	38	Monser and Adhoum (2002)

Note: GAC = Granular Activated Carbon; ACC = Activated Carbon Cloth; PAC = Powdered Activated Carbon; ACF = Activated Carbon Fibrous

16.4.3.2 Carbon Nanotubes Adsorbents

Over the last two decades, Carbon Nanotubes (CNTs) have been widely studied for their excellent properties and applications. They possess high potential for removing heavy metals like lead, cadmium, chromium, copper and nickel from wastewater (Fu and Wang 2011). The results of these studies made CNTs as a promising candidate for adsorption of heavy metals. CNTs are broadly classified into two types, including (1) single-walled CNTs (SWCNTs) and (2) multi-walled CNTs (MWCNTs). The mechanism of heavy metals adsorption by CNTs can be ascribed to sorption-precipitation, electrostatic attraction and chemical interaction between the metal ions and the surface functional groups of CNTs.

Functionalised CNTs (oxidized by HNO_3, NaClO and $KMnO_4$) show better adsorption capacities of metal ions as compared to raw CNTs. The oxygenous functional groups are known to play an important role in adsorption of heavy metal ions. Both functionalised and non-functionalised MWCNTs showed a superior adsorption capability to that of activated carbon. Extensive use of CNTs can cause a serious risk to humans as they are eventually discharged to the water environment. Efforts are being streamlined to develop an environmental friendly adsorbent. One such example is calcium alginate immobilized CNTs which was developed and tested for removal of copper (Li et al. 2010).

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16.4.3.3 Low–Cost Adsorbents

Numerous studies have been conducted on the development of low-cost adsorbents. Agricultural wastes, industrial by-products and wastes/natural substances are the most commonly-studied low-cost adsorbents (Table 16.3). The use of kaolinite and montmorillonite has been reported successfully in heavy metal removal (Bhattacharyya and Gupta 2008). Industrial by-products like lignin, diatomite, clino-pyrrhotite, lignite, aragonite shells, natural zeolites, clay and peat have also been reported to have excellent adsorption capacity for heavy metals (Fu and Wang 2011). In a specific study the use of kaolinite clay obtained from Longyan, China was able to remove heavy metal ions like Pb (II), Cd (II), Ni (II) and Cu (II) from wastewater. The kaolinite clay was able to bring down the Pb (II) concentration from 0.160 g/L to 0.008 g/L (Jiang et al. 2010).

16.4.4 Membrane Filtration

Membrane filtration technology employs the use of different types of membranes for the removal of heavy metal ions with high efficiency, easy operation and space saving. Various membrane processes are used to recover heavy metals from wastewater. The most commonly used ones are ultrafiltration, nanofiltration, reverse osmosis and electrodialysis.

16.4.4.1 Ultrafiltration

Ultrafiltration is a membrane technique which removes dissolved and colloidal materials present in the solution at a low transmembrane pressure. Due to small size of the dissolved heavy metal ions, they tend to pass quickly through the UF membrane. In order to obtain high removal efficiency of heavy metal ions, the micellar enhanced ultrafiltration (MEUF) and polymer enhanced ultrafiltration (PEUF) were developed.

MEUF is a technique where surfactants are introduced into wastewater to form micelles which can bind with the metal ions to form large metal-surfactant structures. The micelles containing the metal ions can now be retained by the UF membrane. In order to get good retention of heavy metal ions, the surfactant with an electric charge opposite to that of targeted heavy metal ions has to be used. Sodium dodecyl sulphate (SDS) is the most commonly used anionic surfactant for the removal of heavy metal ions in MEUF. Metal removal efficiency by MEUF depends on the concentration of the metal and surfactants, solution pH, ionic strength and parameters related to membrane operation. In order to get a good rejection, the surfactant to metal molar ratio (S/M) is maintained above 5. Numerous studies have been conducted using synthetic wastewater. Rejection co-efficiencies up to 99% were obtained by maintaining the S/M ratio (Landaburu-Aguirre et al. 2010). Surfactant accounts for a large percentage of the operating costs of MEUF systems. Recovery of surfactants is done by using either acid or alkali treatment of the retentate. In a study by Li et al. (2009), the SDS micelles along with the heavy metals were separated by using EDTA. They were able to

Table 16.3. List of low cost adsorbents used for adsorbing different heavy metals

Heavy metal	*Type of adsorbent*	*Optimum pH*	*Adsorption capacity (mg/g)*	*References*
Cd (II)	Cocoa Shell	2.0	4.94	Meunier et al. (2003)
Cr (III)	Cocoa Shell	2.0	2.52	Meunier et al. (2003)
Ni (II)	Cocoa Shell	2.0	2.63	Meunier et al. (2003)
Zn (II)	Cocoa Shell	2.0	2.92	Meunier et al. (2003)
Cu (II)	Cocoa Shell	2.0	2.87	Meunier et al. (2003)
Ni (II)	Orange Peel	6–8	6.01	Annadurai et al. (2002)
Cu (II)	Orange Peel	6–8	3.65	Annadurai et al. (2002)
Zn (II)	Orange Peel	6–8	5.25	Annadurai et al. (2002)
Cr (VI)	Sawdust	2.0	15.82	Dakiky et al. (2002)
Cr (VI)	Maple Sawdust	5.0	5.1	Yu et al. (2003)
Cu (II)	Banana Peel	6–8	4.75	Annadurai et al. (2002)
Zn (II)	Banana Peel	6–8	5.80	Annadurai et al. (2002)
Ni (II)	Banana Peel	6–8	6.88	Annadurai et al. (2002)
Ni (II)	Hazelnut Shell	3.0	10.11	Demirbas et al. (2002)
Cr (VI)	Hazelnut Shell	1.0	170	Kobya (2004)
Cr (VI)	Activated alumina	4.0	1.6	Bishnoi et al. (2003)
Cr (VI)	Rice Husk	2.0	0.79	Bishnoi et al. (2003)
Ni (II)	Almond Husk	5.0	37.17	Hasar (2003)
Cr (VI)	Almond Shell	2.0	10.62	Dakiky et al. (2002)
Cu (II)	Coir Pith	4–5	10.22	Kadirvelu et al. (2001a)
Ni (II)	Coir Pith	4–5	91.63	Kadirvelu et al. (2001a)
Ni (II)	Coir Pith	5	62.50	Kadirvelu et al. (2001b)
Cd (II)	Sugar-cane pith	6.0	24.70	Krishnan and Anirudhan (2003)
Cd (II)	Cassava waste	4–5	18.05	Abia et al. (2003)
Cu (II)	Cassava waste	4–5	56.82	Abia et al. (2003)
Zn (II)	Cassava waste	4–5	11.06	Abia et al. (2003)
Ni (II)	Maize Cob	9	57.5	Selvakumari et al. (2002)
Cd (II)	Jackfruit	5	52.08	Inbaraj and Sulochana (2004)
Ni (II)	Red Mud	9	160	Zouboulis and Kydros (1993)
Ni (II)	Fly Ash Type	8.0	0.99	Bayat (2002)
Pb (II)	Iron slags	3.5–8.5	95.24	Feng et al. (2004)
Pb (II)	Steel slags	5.2–8.5	32.26	Feng et al. (2004)
Cu (II)	Iron slags	3.5–8.5	88.50	Feng et al. (2004)

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Table 16-3. List of low cost adsorbents used for adsorbing different heavy metals (Continued)

Heavy metal	*Type of adsorbent*	*Optimum pH*	*Adsorption capacity (mg/g)*	*References*
Cu (II)	Steel slags	5.2–8.5	16.21	Feng et al. (2004)
Cr (VI)	Bagasse	6.0	0.03	Rao et al. (2002)
Cr (VI)	Fly Ash	6.0	0.01	Rao et al. (2002)
Cr (VI)	Rice Husk Ash	3.0	25.64	Bhattacharya et al. (2008)
Zn (II)	Green Sands	5.5–6.0	32.46	Lee et al. (2004)
Zn (II)	Rice Husk Ash	5.0	14.30	Bhattacharya et al. (2006)
Hg (II)	Treated Rice Husk	5.6–5.8	9.32	Feng et al. (2004)
As (III)	Fly Ash Coal-char	2.2–3.9, 2.2–3.1	3.7–89.2	Pattanayak et al. (2000)
As (V)	Fly Ash Coal-char	7.3–9.3, 2.2–3.0	0.02–34.5	Pattanayak et al. (2000)

recover about 65% of the SDS after the treatment. A similar recovery study using H_2SO_4 was performed, and 58% of SDS was recovered.

PEUF is a technique where a water-soluble polymer is employed to complex metallic ions and form macromolecules having molecular weight higher than the molecular weight cut off of the membrane. The macromolecules are retained when they are pumped through the membrane. The retentate can then be treated to recover the metallic ions, and the polymeric agent obtained can then be re-used. Polymeric agents such as polyacrylic acid (PAA), polyetyleneimine (PEI) diethyleneimine cellulose and humic acid (Fu and Wang 2011) are widely used and have established to achieve selective separation and recovery of heavy metals with low energy requirements. Important parameters affecting the PEUF's performance include: pH, the type of metal and polymer used, the ratio of metal to polymer and the presence of other metal ions in the solution. The major advantages of using PEUF includes high removal efficiency, high binding selectivity and highly concentrated metal concentrates for metal reuse.

16.4.4.2 Nanofiltration

Nanofiltration (NF) is a membrane technology used broadly for removal of contaminants with low molecular weight. The benefits of using NF include ease of operation, reliability and comparatively low energy consumption as well as high efficiency of heavy metal pollutant removal (Fu and Wang 2011). The two commercially available NF membranes NF90 and N30F have been extensively

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studied and have proved to work well for heavy metal removal. NF composite membranes have also been developed as an alternative. Thin film composite polyamide NF membrane developed by Murthy and Chaudhari (2008) had am As rejection rate of 98% and 92% for initial concentrations of 5 and 250×10^{-3} g/L, respectively. NF membranes were also used for treating mine wastewater. In one study, the NF membrane was investigated in the recovery of silver from mining wastewater after the silver was taken into the solution as AgCN employing re-cyanidation and subsequent sedimentation and pre-filtration of wastewater. Silver recovered after hybrid cyanidation and membrane separation was found to be 29–59% (Koseoglu and Kitis 2009).

16.4.4.3 Reverse Osmosis

Reverse Osmosis is a membrane process which uses a semi-permeable membrane to purify the fluid while rejecting the contaminants. RO is an gradually becoming a popular wastewater treatment technique used in chemical and environmental engineering. Appropriate RO systems need to be employed to remove particular heavy metal salts. Sometimes RO systems are used in combination with other removal techniques to obtain higher efficiency. The major drawback of RO systems is its high power consumption due to the pumping pressures and membrane restoration.

16.4.4.4 Electrodialysis

Electrodialysis (ED) is a membrane technique where ions are separated across charged membranes from one solution to another using an electric field as the driving force (Fu and Wang 2011). Ion exchange membranes (either cation or anion exchange) are accompanied in most of the ED process. Treatment of hexavalent chromium was performed using an ED pilot plant with a set of ion-exchange membranes (Natraj et al. 2007). Results obtained were satisfactory in meeting the MCL of 1×10^{-4} g/L of chromium. A similar study was performed on the separation of Cu and Fe and water recovery from solutions in electrowinning operations (Cifuentes et al. 2009). ED was proved to be very effective in the removal of Cu and Fe from the working solution.

16.4.5 Coagulation and Flocculation

Coagulation is a precipitation technique where a coagulant/flocculant is added to form agglomerates with the metal ions, which are further separated by sedimentation and filtration process. The addition of coagulant generally destabilizes the colloids by neutralizing the forces that keep them apart. The commonly used coagulants for wastewater treatment are ammonium, ferrous sulphate, ferric chloride and polyaluminium chloride (PAC). A combination of coagulants is also being studied for heavy metal elimination. In a report by El Samrani et al. (2008), the use of two commercial coagulants, ferric chloride and PAC were tested for heavy metal removal, and was found that both the coagulants showed excellent removal as the residual concentrations of Cu, Zn, and Pb in the clarified water

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complied with the legislation of potable water. A different type of coagulant was developed by grafting a sodium xanthogenate group to polyethyleneimine, which can remove both the soluble heavy metal and insoluble substances as the existing coagulants were specific in action for the hydrophobic colloids and suspended particles (Chang and Wang 2007). This newly developed coagulant is an amphoteric polyelectrolyte and is able to coagulate the negatively charged species at low pH.

Flocculation is a technique where the polymers help in forming the bridges between the flocs and binds the particles into large aggregates or clumps. Once the aggregates are formed, they are removed or separated by filtration. Flocculants like PAC, polyferric sulphate (PFS) and polyacrylamide (PAM) are widely used in wastewater treatment. These commercially available flocculants are not effective in removing the heavy metals in wastewater. Macromolecule heavy metal flocculants are used as an effective alternative in treating wastewater having heavy metal contaminants. Chang et al. (2009) prepared a macromolecule heavy metal flocculant mercaptoacetyl chitosan by reacting chitosan with mercaptoacetic acid. This coagulant was able to remove turbidity and heavy metals present in the wastewater. Different macromolecule flocculants like Konjac-graft-poly (acrylamide)-co-sodium xanthate (Duan et al. 2010) and poly-ampholyte chitosan derivatives – N-carboxyethylated chitosans were also developed and studied for heavy metal removal (Bratskaya et al. 2009).

Heavy metals also have a tendency to form complexes with Humic acid (HA). Flocculating such bound complexes with coagulants/flocculants are also being investigated. In one study, HA bound heavy metal ions Pb^{2+} and Zn^{2+} have been successfully coagulated with the cationic polyelectrolyte polydiallyldimethylammonium chloride (Poly-DADMAC) (Hankins et al. 2006). Recently a new flocculation technique was proposed using thermosensitive polymers for removing the undesirable heavy metals and humic acid (Tokuyama et al. 2010). New tannin-based flocculant has also been commercially developed (Heredia and Martin 2009). Generally, coagulation-flocculation technique cannot completely treat the heavy metal from wastewater; therefore, they must be followed by another treatment technique.

In summary, this section discusses a few important heavy metal wastewater treatment techniques which are currently being used. These techniques have their inherent advantages and limitations. Heavy metal removal from wastewater has been traditionally carried out by chemical precipitation due to its simplicity and inexpensive capital cost. Chemical precipitation is used to treat high concentrated wastewater containing heavy metal and fails in treating the metal ion concentration when it is low. Ion exchange can be used to treat low metal ion concentration to an extent. However, after treatment, the ion-exchange resin must be regenerated by chemical reagents which can cause serious secondary pollution.

Membrane filtration technology can remove heavy metal ions with high efficiency, but its usage is limited due to high cost, process complexity, membrane fouling and low permeate flux. Using coagulation-flocculation, the sludge obtained has good sludge settling and dewatering characteristics. However, this

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method consumes a large amount of chemicals with an increase in sludge volume generation.

Adsorption is the most widely recognized method for heavy metals from low concentration wastewater containing heavy metals. Many low-cost adsorbents have also been developed and tested for heavy metal removal. The adsorption efficiency depends on the type of adsorbent used. Biosorption of heavy metals from aqueous solution is relatively a new process which is gaining popularity and has proven to remove the heavy metal from wastewater. Biosorption is based on adsorption of heavy metals onto naturally available biological sources. There has been a good appreciation of upcoming green technologies for wastewater treatment and has been well received commercially.

16.5 GREEN TECHNOLOGY FOR HEAVY METAL REMEDIATION

In recent years, there has been a strong drive to develop treatment technologies which are efficient and cause less deleterious effect on the environment. Bioremediation may offer one such green technology solution for heavy metal contamination. It is process where microorganisms/plants are used to detoxify the contaminated wastes that are present in the environment. There are different biological techniques which can be used to treat wastewater containing heavy metals. These techniques are cost-effective, non-invasive and efficient. The following green technologies namely Biosorption, Biostimulation, Bioaugementation, Bioleaching, Biosurfactants, Bioprecipitation, Vermicomposting and Phytoremediation have been discussed subsequently.

16.5.1 Biosorption

Biosorption is defined as adsorption of metals onto cell surface by physiochemical mechanisms. The dead cell and the metabolically inactive biomass concentrate the heavy metals present in the environment. This property can be attributed to the cell wall structure of the microorganisms. Recently the role of exopolysaccharides (EPS) in sequestration of heavy metals has been elucidated (Harish et al. 2012). Although not all biosorbents are systemically examined, a substantial amount of evidence has been collected and identifies ion exchange as the principle mechanism of metal biosorption. According to the dependence of cell metabolism, biosorption can be divided into metabolism dependent and non-metabolism dependent (Vijayaraghavan and Yun 2008). Biosorption can also be classified based on the location where the metal removed is found, being extra cellular accumulation/precipitation, cell surface sorption/precipitation and intracellular accumulation (Gaur et al. 2014). pH plays a crucial role in the biosorption process. pH determines the protonation and de-protonation of the binding sites and thus influence the availability of the site to the sorbate. By lowering the pH, the metal ions adsorbed can be released from the binding site. This property is used to recover the metal adsorbed and regenerate the biosorbent.

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16.5.2 Biostimulation

Biostimulation is a technique popularly used to promote the growth of indigenous microorganisms present in the contaminated site by supplementing them with the necessary nutrients, to enhance the activities of heavy metal removal (Abioye 2011). Along with supplements, necessary environmental conditions are provided for the efficient bio-removal. In one laboratory study, microorganisms were isolated from heavy metal contaminated environment and were biostimulated in minimal salt media. The biostimulated microbial consortium was then studied for removal of the heavy metals Cd, Cu and Fe and was observed to remove 98.5%, 99.6% and 100% respectively (Fulekar et al. 2012). Olaniran et al. (2009) investigated the effect of biostimulants namely glucose, kompel fertilizer and yeast in treatment of 1,2-dichloroethane (DCA) which was co-contaminated with heavy metals lead and mercury. It was found that the DCA degradation enhanced remarkably upon the addition of biostimulants and also expounded the potential of the biostimulation technology for effective remediation of soils co-contaminated with chlorinated organics and heavy metals.

16.5.3 Bioaugementation

Bioaugementation is another approach where the microorganisms capable of remediating the heavy metals are introduced into the contaminated environment to assist the indigenous microbes with the removal process. This might sometimes include the introduction of genetically modified microorganisms into the contaminated site (Abioye 2011). A list of different types of biosorbents used for adsorbing heavy metal ions has been given in Table 16.4.

16.5.4 Bioleaching

Bioleaching is the process of extracting heavy metals through excretion of organic acids or methylation reactions by the microorganisms (Olson et al. 2003). It can also be defined as the mobilization of metal cations from insoluble ores by biological oxidation or complexation processes (Rohwerder et al. 2003). Two main mechanisms, namely contact and non-contact, have been reported in the literature with regard to bioleaching. In contact mechanism, the cells attach to the surface of sulfide mineral ores. The electrochemical process from the dissolution of sulfide minerals takes place at the interface between the cell wall and the mineral sulfide surface. The mineral sulfide is directly oxidized by *At.thiooxidans* into soluble metal sulphate according to following equation:

$$\mathrm{MeS} + 2\mathrm{O}_2 \rightarrow \mathrm{MeSO}_4$$

where MeS is the metal sulfide.

Non-contact mechanism is generally exerted by phyoplanktonic bacteria which oxidizes the Fe (II) ions in solution (Rohwerder et al. 2003). The resulting

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Table 16.4. Biosorbents used for adsorbing heavy metals

Heavy metal ions	*Bacterial species*	*Biosorption capacity (mg/g)*
Pb	*Bacillus* sp.	92.3
Pb	*Corynebacterium glutamicum*	567.7
Pb	*Enterobacter* sp.	50.9
Pb	*Pseudomonas putida*	56.2
Zn	*Aphanothece halophytica*	133
Zn	*Streptomyces rimousus*	80.0
Zn	*Thiobacillus ferrooxidans*	172.4
Zn	*Pseudomonas putida*	17.7
Cu	*Bacillus* sp.	16.3
Cu	*Pseudomonas putida*	96.9
Cu	*Enterobacter* sp.	32.5
Cu	*Micrococcus luteus*	33.5
Cd	*Aeromonas caviae*	155.3
Cd	*Psedumonas* sp.	278.0
Cd	*Staphylococcus xylosus*	250.0
Cd	*Streptomyces rimosus*	64.9
Cr (VI)	*Aeromonas caviae*	284.4
Cr (VI)	*Staphylococcus xylosus*	143.0
Cr (VI)	*Psedumonas* sp.	95.0
Cr (VI)	*Bacillus thuringiensis*	83.3
U	*Arthrobacter nicotianae*	68.8
U	*Nocardia erythropolis*	51.2
U	*Bacillus subtilis*	52.4
U	*Bacillus licheniformis*	45.9
Th	*Bacillus megaterium*	74.0
Th	*Micrococcus luteus*	77.0
Th	*Bacillus licheniformis*	66.1
Th	*Arthrobacter nicotianae*	75.9

Source: Wang and Chen (2009); reproduced with permission from Elsevier

Fe (III) ions are reduced back to Fe (II) ions when in contact with the mineral surface and enter the cycle again. The following equations give us a clear understanding of the non-contact mechanism.

$$2FeSO_4 + 0.5\,O_2 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + H_2O$$

$$4Fe_2(SO_4)_3 + 2MeS + 4H_2O + 2O_2 \rightarrow 2Me^{2+} + 2SO_4^{2-} + 8FeSO_4 + 4H_2SO_4$$

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where M^{2+} is soluble metallic ion. In the first reaction *At.ferrooxidans* take active part whereas the second reaction takes place chemically without any involvement of bacteria.

Wong and Henry (1983) reported batch bioleaching with anaerobic digested sludge using *At.ferrooxidans* and $FeSO_4$ as energy source. Batch experiments after 8 days resulted in solubilization of 65%, 78%, 87%, and 0% of Cu, Ni, Zn, Cd and Pb respectively. Seth et al. (2006) investigated heavy metal removal using a continuous bioleaching process with elemental sulphur as an energy source. The continuous system was able to remove 50%, 33%, 48% and 74% of Cd, Cu, Ni and Zn respectively. Recently Wen et al. (2013) investigated the bioleaching capability of iron-oxidizing microorganisms isolated from Fuzhou Jingshaw sewage treatment plant in China. The results indicated a removal of 88.5%, 79.9%, 50.1% and 32.2% of Zn, Cu, Pb and Cr respectively. Also the leaching kinetics study indicated that the rate of metal soubilization in bioleaching was more effective than chemical leaching.

16.5.5 Biosurfactants

Surfactants are compounds which can lower the surface tension of the liquid in which it is dissolved by virtue of its hydrophilic and hydrophobic groups. Biosurfactants are surfactants obtained from biological sources.Decrease in surface tension of water makes the heavy metals more available for remediation (Hashim et al. 2011). Biologically produced surfactants like surfactin, rhamnolipids and sophorolipids were tested for removal of heavy metals such as Cu, Zn, Cd and Ni from contaminated sites (Wang and Mulligan 2004; Mulligan et al. 1999). Rhamnolipid was studied for its metal removal capacity both in liquid and foam forms (Wang and Mulligan 2004; Mulligan and Wang 2006). Rhamnolipid type I and type II was found to be suitable for heavy metal removal. Glycolipids or lipopeptides are the best examples of low-molecular-weight biosurfactants. The metals form complexes with the surfactants due to low interfacial tension and hence associating with the surfactant micelles. Cd showed a removal percentage of 73.2 and Ni showed 68.1 with the pH adjusted to 10. A similar study was also performed using rhamnolipids for extracting Cd (II) and Zn (II) from quartz. An average of 66.5% and 30.3% of Zn (II) and Cd (II) was removed at high saturation metal ion loadings of quartz (Asci et al. 2010).

16.5.6 Bioprecipitation

In-situ bioprecipitation is a process where the heavy metals are immobilized in ground water as precipitates in the solid phase (Hashim et al. 2011). The metal ions to be treated are trapped in the organic matrix of carbon source (such as molasses, lactate, acetate and composts) during fermentation process when injected into the aquifer. Bioprecipitation is a strategy employed mainly to treat groundwater. Heavy metal ions like Cu, Zn, Cd, Ni, CO, Fe, Cr and As were successfully treated using bioprecipitation. In-situ bioprecipitation process was assessed with bacterial sulphate reduction (BSR) with molasses as the carbon

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source and immobilization of a Zn plume in an aquifer (Janssen and Temminghoff 2004). The Zn concentrations were reduced from around 40×10^{-2} g/L to below 1×10^{-5} g/L. Satyawali et al. (2010) also investigated the stability of Zn and Co precipitates formed after ISBP in an artificial and natural solid matrix. In the artificial matrix, about 58% of Zn got mobilized with sequential pH change whereas in the natural matrix, the carbon source used affected the stability of metal precipitates of Zn and Co.

16.5.7 Vermicomposting

Vermicomposting is the process of composting mainly by earthworms which are present in the soil. Earthworms are important soil organisms and play an indispensable role in improving soil quality. Their activities like burrowing, feeding, excreting and metabolic redox material, improve both the soil texture and nutrition content. The functional groups −COOH and −CO released help in acidifying the soil and thereby activating the heavy metal (Wu et al. 2010). The earthworm's excretion also facilitates the complexion and chelation of metal ions. Due to a relatively low specific surface area and a small concentration, such removal become very difficult to be noticed. Different studies also prove that the effectiveness and efficiency of earthworm depend on outer conditions and may not be the optimum way of rapidly removing heavy metals.

16.5.8 Phytoremediation

Phytoremediation is a process of utilizing plants to partially or substantially remediate the contaminated soil, groundwater or wastewater. It is also referred as botano-remediation, green remediation, agro-remediation or vegetative remediation (Wuana and Okieimen 2011). Phytoremediation is economically viable, less disruptive, doesn't require new plant communities to recolonize the site and does not need disposal sites; it is more likely to be accepted as it aesthetically pleasing; it avoids transportation of the polluted media thus reducing contamination and has the potential to treat site having more than one type of pollutant. Depending on the type of contaminant and underlying process, phytoremediation is broadly classified as phytodegradation, phytoextraction, phytostimulation, phytovolatilization, and phytostabilization (Akpor and Muchie 2010).

Phytodegradation is the breakdown of organic contaminants by the internal and external metabolic process of the plant (Akpor and Muchie 2010). Plants generally adsorb, store and degrade the contaminants within the tissue. The exudates released by the plants also help to degrade the pollutants via co-metabolism.

Phytoextraction is a process where plants absorb, translocate, and store contaminants along with nutrients and water. This is primarily used for wastes containing metals. The process of phytoextraction is known to occur either continuously (natural) using hyperaccumulators or induced through the addition of chelates to increase bioavailability (Utmazian and Wenzel 2006). Different plants have varying abilities to uptake and withstand high levels of pollutants.

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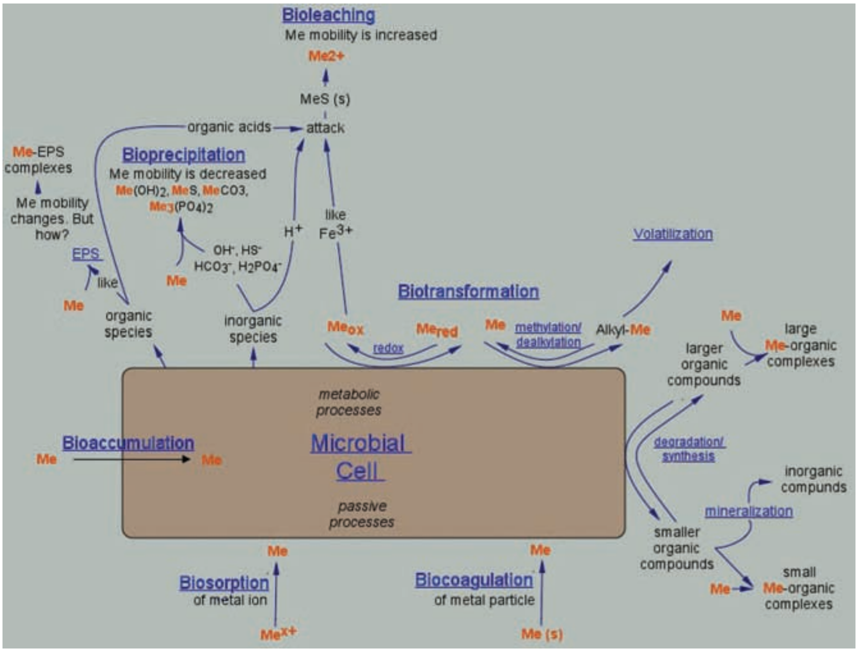

Figure 16.7. Microbial approaches towards metal remediation
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Phytostimulation is a process where microorganisms are stimulated to biologically degrade the wastes through release of natural substances such as nutrients by the plant roots. It is a symbiotic relationship between plants and micro-organisms for the degradation of contaminants. The release of organic substances and oxygen by plant roots increases the microbial activity in the rhizosphere leading to an increased microbial activity, which in turn results in stimulation of natural degradation of organic contaminants (Figure 16.7).

Phytovolatilization is the process wherein the contaminants present in the growth matrix of the plant is taken up and subsequently transformed and volatilised into the atmosphere through its leaves. The contaminant gets modified while it travels through the plant's vascular system and get vaporized from the leaves (Akpor and Muchie 2010). If the contaminant have good chemistry with the plant, they can get easily adsorbed at comparatively low concentrations and pass through the system and volatize into the atmosphere through their stomata.

The phytostabilization technique retains the contaminants in place and inactivates them by absorbing or accumulating onto the roots thereby limiting their mobility and hence reducing their availability in the food chain. Largely plants that grow under contaminated conditions are considered as phytostabilization agents even if they remove little or no contaminants. Plants used for the phytostabilization should be able to decrease the amount of water percolating through the soil matrix as that may result in the formation of a hazardous leachate and act as

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barrier to prevent direct contact with the contaminated soil, prevent soil erosion and distribution of toxic metals to other areas.

16.6 TOWARDS SUSTAINABLE WATER MANAGEMENT

Fresh water stored in various sources (or water bodies) such as lakes, rivers, groundwater aquifers are being polluted due to the discharge of nutrients, heavy metals, non-metallic toxins, persistent organics and pesticides, and microbial contents into those sources (Carr and Neary 2008). Population growth, urbanization and development and climate change are the main factors not only for the depletion of water quality in the above mentioned fresh water sources but also for the increase in the demand for fresh water. Sustainable management of freshwater has therefore become extremely important. In order to achieve sustainability, the quantity of freshwater in water bodies must be maintained without further deterioration. Green and other treatment technologies discussed in this chapter are essential in removing one of the pollutants namely heavy metals which would otherwise end up in fresh water bodies. Similar approach should be taken for other pollutants that are present in water.

Advancements in green remediation technology can drive the green growth in the water sector to achieve an effective and sustainable water management. Figure 16.8 shows a holistic approach to employ the available green remediation

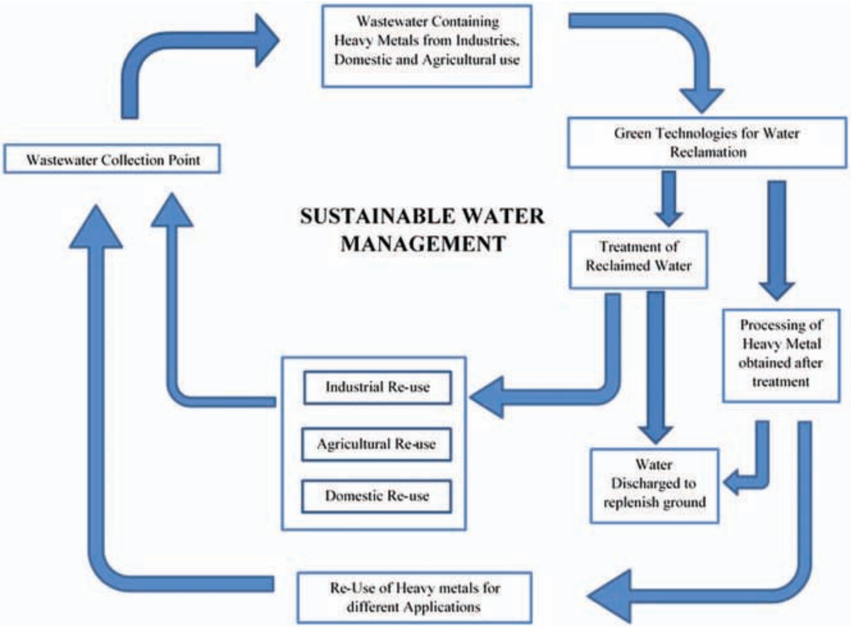

Figure 16.8. Holistic approach towards sustainable water management

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strategies in developing a water-efficiency program. The wastewater containing heavy metals is reclaimed using the green remediation technology and reused for industrial, domestic and agricultural purposes thereby reducing the need for fresh water. Discharging the treated water to the ground also help in the replenishment of groundwater where it is further cleansed by natural processes. Implementation of such integrated water management systems can increase the sustainable levels of different eco-systems and also help in providing water security.

16.7 CONCLUSION

With increasing population and climatic changes, there has been considerable stress on the available water resources in the recent years. By 2030, 47% of the world's population are expected to live in areas of high water stress (WWDR 2012). Sustainable water management has become the viable solution for the existing water woes. The different treatment techniques which have been discussed for wastewater containing heavy metals can help reuse the treated water thereby reducing the annual wastewater discharge. Green treatment technologies also offer a smarter option towards water sustainability and are being accepted globally. With the efficient utilisation of the available water, the per capita consumption can be brought down remarkably. Global water sustainability practices will form the backbone for good health, food production, clean energy and environmental sustainability for a prospective and secured future.

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CHAPTER 17

Micellar Enhanced Ultrafiltration (MEUF) and Activated Carbon Fiber (ACF): An Integrated Approach for Heavy Metal Remediation from Wastewater

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17.1 INTRODUCTION

Water contamination by heavy metals in the ecosystem is a major environmental problem encountered in many industrial areas. When heavy metal-contaminated wastewater is disposed and used for irrigation purpose, it may adversely affect the plants. Similarly, if it is mixed into municipal wastewater, it may inhibit the biological wastewater treatment processes as heavy metals can kill necessary bacteria required for the activated sludge process. Heavy metals can be found in varying concentrations in any natural source of water. In larger concentrations, these metals have detrimental health effects on human beings as most of them are carcinogenic. They also can cause lung, skin-related diseases, and other functional disorders. Moreover, heavy metals are cumulative toxins that the body cannot dispose of, so they accumulate to the harmful levels from the repeated exposure. Thus, it is an utmost requirement to treat wastewater before discharging it into the environment.

A wide range of methods are available for the removal of metal ions from aqueous solution such as ion exchange, solvent extraction, reverse osmosis (RO), precipitation, chemical oxidation and reduction, electrochemical treatment, etc. Each of these methods has its own advantages and disadvantages. Among them, membrane technology (MT) is advancing rapidly as a powerful tool to abate looming water crisis and improve water quality. Ultrafiltration (UF) is the

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pressure-driven membrane process which has a high flux and low energy requirement, compared to nanofiltration (NF) and RO. MEUF is a promising technique to remove lower molecular weight substances as it combines the efficiency of RO and high flux of UF (Bahdziewicz et al. 1999; Yang et al. 2003; Purkait et al. 2004). Micellar enhanced ultrafiltration (MEUF) is surfactant-based separation techniques in which solubilization of organic compounds into the non-polar interior of a micelle or electrostatic attraction of ionized metals and metal complexes to the charged surface of a micelle occurs. Surfactant, known as 'surface active agent' plays a crucial role in this process (Chai et al. 1997). Surfactant possesses peculiar nature in case of ionic surfactants. Its head is hydrophilic, and the tail is hydrophobic in nature.When ionic surfactants are dissolved in water at a critical micelle concentration (cmc), it aggregates with the orientation of head toward water and tail inside the spherical micelle. Micelle has a high electrical potential on the surface where charged hydrophobic groups are located (Baek et al. 2003). This characteristic of the surfactant is utilized for heavy metal removal in the MEUF process. The main feature of this process is to enhance retention coefficients of the inorganic contaminants by increasing the surfactant concentration to the CMC at which surfactants form micelle. Those micelles are much bigger than the size of monomer surfactants. Metals are attached on the micelle surface and form a single unit. When the solution is passed through the UF membranes, metals are together with the micelle due to its size. In the MEUF process, cationic surfactants are used for anionic metals removal and anionic surfactants are used for cationic metals removal.

Nonetheless, one of the major drawbacks of the MEUF process is the production of surfactant-rich effluent which needs further treatment before discharging to the environment. A remedial measure for this problem is an adsorption process, which has been economical and efficient method for removing trace heavy metal and organics from wastewater (Brasquet et al. 1999). The commonly used media for the adsorption are powdered activated carbon (PAC), granular activated carbon (GAC), and activated carbon fiber (ACF). ACF has a uniform micro-pore structure, faster adsorption kinetics and a lower pressure drop in comparison to PAC and GAC (Lu and Zheng, 2002; Park and Kim, 2004). In the MEUF-ACF hybrid process, MEUF can be effectively and efficiently used for heavy metals removal while ACF for the surfactant removal from the MEUF effluent. The MEUF-ACF hybrid process has been employed by various researchers for the heavy metals removal from the heavy metals contaminated wastewater. Thus, application of the MEUF-ACF hybrid process for the removal of heavy metals from wastewater has been reviewed in this chapter. In addition, this chapter seeks to define the various optimizing operating parameters of the MEUF and adsorption process separately in precise. However, special concern is given for the application of surfactant-based membrane separation processes and ACF for heavy metals removal. Also, this chapter depicts a clear picture regarding the concentration polarization (CP), micellization, critical micelle concentration (CMC), MEUF mechanism and surfactant types, including recovery of trace permeate surfactants and metal ions.

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17.2 MEUF MECHANISM

Micellar enhanced ultra-filtration (MEUF) is one of the viable alternative techniques as it has proven its ability in removing contaminants from wastewater. Surfactant is the main ingredient of the MEUF process. Fig. 1.0a illustrates the MEUF phenomenon, and Figure 17.1b shows a general structure of surfactant. In MEUF, the surfactant is added to the aqueous stream containing contaminants or solute (e.g. metal ion, organic materials, low molecular weight solute above its critical micelle concentration (CMC)) (Landaburu-Aguirre et al. 2009). When the surfactant concentration exceeding the CMC value, the surfactant monomers will assemble (Zeng et al. 2008; Chung et al. 2009) and aggregate to form large amphiphilic transparent micelles (Luo et al. 2010) having hydrodynamic diameter significantly larger than the pore diameter of ultrafiltration membrane (Chung et al. 2009; Huang et al. 2009; Misra et al. 2009; Yenphan et al. 2010). The contaminants or solute will entrap in micelles if they tend to strongly attracted by micelle surface and will solubilize in the micelle interior (Zaghbani et al. 2009a, b). Micelles containing solubilized contaminants with larger diameter than membrane pore size will be rejected by the membrane during the ultrafiltration process leaving only water, unsolubilized contaminants and surfactant monomers in permeate stream (Misra et al. 2009; Zaghbani et al. 2009a, b).

The principle of the MEUF process introduces the importance of surfactant's critical micelle concentration (CMC) for the selection of suitable surfactant concentration for the MEUF process. Critical micelle concentration (CMC) is defined as the concentration of surfactants which micelle starts to form spontaneously and it is one of the most important physical parameters of surfactants (Shi et al. 2011). The addition of surfactant into the water system will decrease water surface tension. As the concentration of surfactants increases, the surface will be covered by the surfactant hence the surface free energy (surface tension) will be reduced. Subsequently, the surfactants will start to aggregate, thus the contact area

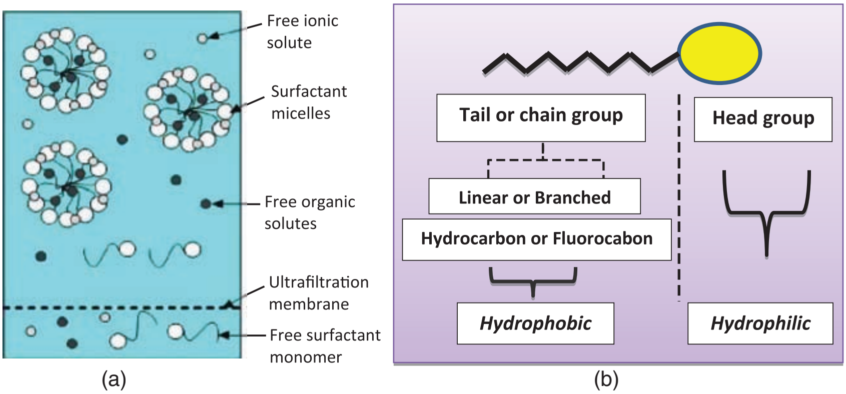

Fig. 17.1. (a) MEUF phenomenon, (b) General structure of surfactant

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of hydrophobic parts of the surfactant with water will be reduced. As a result, the system free energy will also decrease. Once the surfactant concentration reaches CMC, the air-water interface is assumed to remain saturated with the surfactant so that the surface tension becomes minimum at this state (Mittal 1996). The hydrophobic ends of the molecules in micellar aggregates tend to stick together while the hydrophilic ends protect the resulting micelles from external influences through repulsive forces. The aggregation number of micelles depends on the type of surfactant. The non-ionic surfactants usually constitute clusters of 1000 or more molecules (Baeurle and Kroener 2004), while ionic surfactants generally only manage to create clusters of 10-100 molecules, because their charges create electrostatic repulsions between head-groups which tend to break the particles apart (Baeurle and Kroener 2004; Misra et al. 2009).

Generally, micelle can be divided into two sections: the core of micelle which is composed of hydrophobic hydrocarbon chains and the surface of micelle which is composed of hydrophilic head groups and water of hydration (See Figure 17.2). The solubilization of solute into micelles occurs at four sites in micelle: at the micelle-water interface, between the hydrophilic head groups, in the palisade layer of the micelle and in the inner hydrophobic core of micelle. The palisade layer of micelles is located between the hydrophilic groups and the first few carbon atoms of the hydrophobic groups that comprise the outer core of the micelle interior (Xu et al. 2010). However, the solubilization of solute into surfactant micelles depends on how the material binds with the surfactant micelles. The binding mechanism of solute is based on the type of solute (organic, inorganic or metal ions).

In MEUF, metal cations and inorganic pollutants form a bond with the head of the ionic micelles surface which is oppositely charged via electrostatic interaction (Luo et al. 2010; Huang et al. 2009; Misra et al. 2009; Yenphan et al. 2010) but this is not applicable for MEUF of organic materials. In MEUF of organic contaminants, dissolved organic solutes will be solubilized in the palisade layer or the core of micelles (tail of the micelles) via Van der Waals' force (Luo et al.

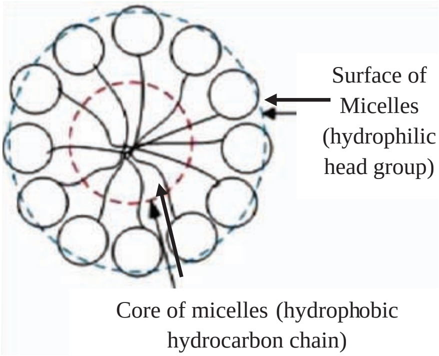

Fig. 17.2. Schematic representation of a spherical micelle

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2010; Misra et al. 2009; Yenphan et al. 2010). The extent of solubilization does rely on the characteristics of surfactant and the structure of the solute (Chung et al. 2009). Luo et al. (2010) proved that the removal of phenol using cetylpyridinium chloride (CPC) are higher as compared to octadecyltrimethyl ammonium bromide (OTAB) due to the rule of similarity and inter-miscibility since the CPC and phenol all possess an aromatic ring.

Selection of surfactant is very necessary to ensure the efficiency of the MEUF process. The chemical classification of surfactant is based on the nature of the hydrophilic head, with the subgroups based on the nature of hydrophobic tail. Basically, the surfactant can be classified into four types: anionic, cationic, nonionic, and amphoteric surfactant (Myers 2006). The MEUF of wastewater commonly can be classified into four categories: (i) MEUF using cationic surfactant; (ii) MEUF using anionic surfactant; (iii) MEUF using nonionic surfactant; and (iv) MEUF using mixed surfactant.

17.3 SURFACTANT

Surfactants are compounds that lower the surface tension of a liquid, the interfacial tension between two liquids, or that between a liquid and a solid. Surfactants can be used as detergents, wetting agents, emulsifiers, foaming agents, and dispersants. Surfactants are usually organic compounds that are amphiphilic, meaning they contain both hydrophobic groups (their *tails*) and hydrophilic groups (their *heads*). Therefore, a surfactant molecule contains both water insoluble (oil soluble) component and a water-soluble component. Surfactant molecules will migrate to the water surface, where the insoluble hydrophobic group may extend out of the bulk water phase, either into the air or, if water is mixed with oil into the oil phase, while the water soluble head group remains in the water phase. This alignment and aggregation of surfactant molecules at the surface acts to alter the surface properties of water at the water/air or water/oil interface.

Many surfactants can also assemble in the bulk solution into aggregates. Examples of such aggregates are vesicles and micelles. The concentration at which surfactants begin to form micelle is known as the critical micelle concentration (CMC). When micelles form in water, their tails form a core that can encapsulate an oil droplet, and their (ionic/polar) heads form an outer shell that maintains favorable contact with water. When surfactants assemble in oil, the aggregate is referred to as a reverse micelle. In a reverse micelle, the heads are in the core and the tails maintain favorable contact with oil. Surfactants are also often classified into four primary groups: anionic, cationic, non-ionic, and zwitter-ionic (dual charge).

17.3.1 Micellization

Micelles are formed at the CMC, which is detected as an inflection point when physicochemical properties such as surface tension are plotted as a function of concentration (Figure 17.3). The main reason for micelle formation is the

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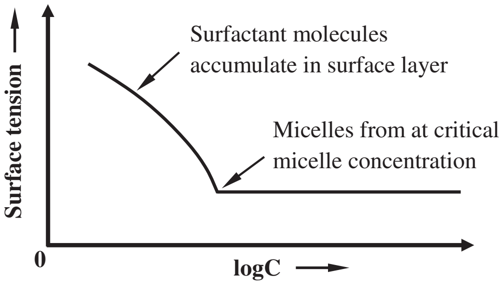

Fig. 17.3. Typical plot of the surface tension against the logarithm of surfactant concentration C, showing the critical micelle concentration (CMC)

attainment of a minimum free energy state. The main driving force for the micelles formation is the increase of entropy that occurs when the hydrophobic regions of the surfactant are removed from the water and the ordered structure of water molecules around this region of the molecule is lost. Most micelles are spherical and contain between 60 and 100 surfactant molecules (Sinko 2006).

17.4 MEMBRANE FOULING

Accumulation of the substances on the membrane surface or within the membrane pores, which results in the deterioration of the membrane performance is called as membrane fouling. In simple words, membrane contamination is referred as the fouling. It is the reduction of the flux through a membrane caused by the build-up of the contaminants. The fouling of the membrane can take place either at the surface (macro-fouling) or inside the pore (pore fouling or micro-fouling). Fouling can be reversible or irreversible.

The main problem in the MEUF process is 'membrane fouling' mainly caused by the concentration polarization and pore blocking (Zeng et al. 2008; Zaghbani et al. 2009a, b). The membrane fouling can be minimized by using optimum initial permeate flux, retentate pressure, and initial feed concentration of pollutant and surfactant. It can be regenerated by frequent backwashing with clean water or cleaning with chemicals like NaOH and HCl (Mittal 1996; Huang et al. 2009; Shi et al. 2011).

Membrane fouling hinders the performance of a membrane (Baeurle and Kroener 2004; Myers 2006). Koyuncu et al. (2001) reported that a high solute concentration at the membrane interface increased the risks of change in the composition of membrane material due to chemical attack. Those characteristics are dependent upon both membrane and foulants. Compounds that are rejected from the membrane surface forms a layer on the surface called a concentration polarization (CP).

Flux decline caused by the CP can be recovered by backwashing while fouling caused by microbial adhesion, gel layer formation, and solute adhesion cannot be

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recovered. In order to remove those flocs, it is important to clean the membrane periodically with chemicals (Luo et al. 2010). Generally, the blockages are more complicated with when the particles and pores are similar in both shape and size (Ahmad et al. 2006). Hlavacek and Bouchet (1993) stated that after pore blockage, further flux decline would be caused by the formation and growth of the cake layer on the membrane surface. Flux decline due to a pore blocking is sharp at the beginning; then it decreases gradually and reaches a steady state when the cake layer has grown to the equilibrium thickness (Myers 2006; Purkait et al. 2006).

17.4.1 Factors Affecting Membrane Fouling

Membrane cleaning is a method of removing foreign materials that have been already attached on the membrane surface. In the cleaning process, it should be kept in mind that the membrane should not be allowed to dry once it has made contact with pollutants. It is also necessary to clean the membrane as soon as possible. The following factors need to be considered with great attention while cleaning a membrane surface (Otoyo and Ogawa 2002).

When selecting cleaning conditions, one of the most important considerations is if the conditions for cleaning are compatible with membrane media and other components of the membrane filters and systems. Chemical compatibility of the membrane and other filter components and systems limits the type and the maximum allowable concentration of cleaning chemicals. Membranes made from materials with high chemical resistance allow more flexible selections of types and concentrations of cleaning chemicals in dealing with various types of fouling problems. The concentration of cleaning chemicals can affect both the equilibrium and the rate of reaction. Unlike reactions that occurred in the liquid phase, reactions between cleaning chemicals and fouling materials occur at the interface between liquid and a (solid) fouling layer. The concentration profile of cleaning chemicals within the fouling layer is a function of the concentration of cleaning chemicals in the bulk liquid phase. Therefore, the concentration of cleaning chemicals not only needs to maintain the reasonable reaction rate (kinetics), but also needs to overcome mass transfer barrier imposed by the fouling layer (Otoyo and Ogawa 2002).

In practice, the concentrations of cleaning chemicals are usually high enough to satisfy the kinetic need. It is the mass transfer that sets the lower boundary for the concentration of cleaning chemicals. Temperature can affect membrane cleaning by (1) changing the equilibrium of a chemical reaction, (2) changing the reaction kinetics, and (3) changing the solubility of fouling materials and/or reaction products during the cleaning. Generally, an elevated temperature promotes better membrane cleaning. At the same time, one should check the compatibility of membrane and other filter components regarding temperature while cleaning (Otoyo and Ogawa 2002).

Membrane cleaning involves the mass transfer of chemicals to the fouling layer and the reaction products back to the bulk liquid phase. Therefore, hydrodynamic conditions that promote contacts between cleaning chemicals and

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fouling materials during the cleaning are preferred. From mass transfer point of view, dynamic cleaning involving circulating cleaning solutions through the system can be more effective than simply static cleaning such as soaking. This may be particularly important for the fouling materials embedded in membrane matrix. In static cleaning conditions, the transport mechanism is primarily through diffusion. Maximizing concentration gradients of both cleaning chemicals and reaction products and shortening the distance of diffusion by bringing fresh chemicals close to the vicinity of the fouling materials would enhance the cleaning (Otoyo and Ogawa 2002).

17.5 OPTIMIZATION OF SURFACTANT-BASED MEMBRANE SEPARATION PROCESSES

The global trends toward more stringent regulation of effluent quality resulting from the treatment of wastewater regarding heavy metals contents have led to increased interest in the application of surfactant-based membrane separation i.e. the MEUF process effectively and efficiently. The mechanism of removing targeted contaminated ions by the MEUF process is based on adsorption of small contaminated ions to a large surfactant micelle which will be formed only when concentration of the surfactant is higher than its CMC, followed by the subsequent removal of ion-micelle complexes by an ultrafilter. Efficient use of the MEUF process relies upon various operating parameters that directly have impacts on the removal efficiency of this process.

17.5.1 Initial Permeate Flux

The flux decline remains the most serious problem for the efficient application of membrane separation processes due to concentration polarization (CP) and membrane fouling. The CP is caused by the accumulation of retained solutes such as micelles on the membrane surface where their concentration gradually increases. The micelles retained on the membrane surface generate a deposited layer on the membrane surface increasing the resistance against the trans-membrane flux and consequently, decreasing the permeate flux (Zaghbani et al. 2007). The accumulation of micelles over the membrane can continue until a gel layer concentration (Cg) is formed. At this point, a gel layer is formed and the permeate flux is zero, i.e. fouling will occur.

As surfactants on the membrane surface increase, there is a higher enhancement in metal removal, as concentration polarization (CP) on the membrane surface increases with the increase of permeate flux. As a result, the bulk surfactant (CPC/SDS) concentration at the surface becomes higher and enhances the chromate removal. Thus, average chromate removal efficiency was found to be 86% at the initial permeate flux of 54.6 L/m^2-h, while it was found to be 81% and 69% for the initial permeate fluxes of 43.7 L/m^2-h and 32.9 L/m^2-h, respectively (Bade and Lee 2008). Similarly, average copper

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removal was 55%, 51%, and 54% at an initial permeate flux of 1.31 m^3/m^2-d, 0.79 m^3/m^2-d, and 1.05 m^3/m^2-d, respectively (Bade and Lee 2007). Due to applied pressure, the pollutants adsorbed on the pore of membrane moved slowly to permeate during filtration (Ghosh and Bhattacharya 2006). Relative flux is an important parameter in filtration. The average relative flux was found to be 0.85, 0.65, and 0.55 for the initial permeate flux of 0.79 m^3/m^2-d, 1.05 m^3/m^2-d, and 1.31 m^3/m^2-d, respectively. With the increase of initial permeate flux, there was a sharp reduction in relative flux. Floc formation on the membrane surface hinders the permeate flux which can be minimized by selecting the optimum initial permeate flux. Maximum chromate removal and higher permeate flux were achieved at initial permeate flux of 1.05 m^3/m^2-d (40 mL/ min). And the similar case was obtained in copper removal (Bade and Lee 2007). Advantages of the MEUF process are high removal efficiency, high fluxes, and low energy costs. At the same time, flux decline remains the most serious problem for the efficient application of membrane separation processes due to concentration polarization and fouling (Huang et al. 1994; Juang et al. 2003; Purkait et al. 2005).

17.5.1.1 Factors Affecting Permeate Flux: Study of Concentration Polarization (CP) Phenomenon

Membrane nominal molecular weight limit (NMWL) and pressure are the two main parameters that positively affect the permeate flux. An increase in permeate flux with pressure indicates that the separation process is under pressure-controlled region (Metasamuuronen 2003). The interaction between NMWL and pressure also has a noticeable positive effect on the permeate flux. Thus, there is synergy between the NMWL and the pressure. This indicates that the effect of NMWL on permeate flux is dependent on the pressure value used and vice-versa.

Concentration polarization (CP) i.e., the absolute permeate flux decline, was reported to be more severe when increasing the surfactant feed concentration (Xu et al. 2007). At a high surfactant feed concentration, the surfactant concentration in the retentate is also high and, therefore, CP phenomenon is enhanced (Xu et al. 2007). It was reported that the increasing SDS feed concentration from 8.3 to 16.6 mM at identical conditions did not significantly decrease the absolute flux (Landaburu-Aguirre et al. 2009). As the increasing SDS feed concentration did not enhance CP and no significant flux decline was observed, so it was concluded that the CP phenomenon might be due to membrane characteristics rather than surfactant feed concentration (Landaburu-Aguirre et al. 2009).

The NMWL, pressure, and their respective interaction presented the largest influence on the permeate flux and a negligible effect on the rejection coefficient. Moreover, zinc and SDS feed concentrations and their interaction had a significant influence on the rejection coefficient and negligible effect on the permeate flux. Consequently, the use of high NMWL membranes with high pressure will provide high flux and will have a minimum effect on the rejection coefficient (Landaburu-Aguirre et al. 2009).

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17.5.1.2 Effect of Pressure on Permeate Flux

Both the permeate flux and surfactant (CPC) retention remains relatively constant with the varying range of applied pressures (Ghosh and Bhattacharya 2006). As the time progresses, the retentate side concentration (bulk + micelles) increases i.e. CPC surfactant retention percent increases with increase in applied pressure. Since the bulk monomer concentration is maintained at the CMC level, extra CPC monomers contribute towards the growth of separate small size micelles or increase the size of already existing micelles. These may also allow breakage of micelles into the dimmers and trimmers, which may pass through the membrane and reduce retention values as a function of time (Christian and Scamehorn 1989).

Surfactants under relatively larger concentration form micelles having a tendency to settle at the membrane surface. This eventually forms micelle aggregation layer (MAL), restricting the passage of smaller sized micelles through the membrane. At higher pressures, the resistance of MAL increases due to the compaction that also increases the retention of such broken micelles and hence increases retention percent of surfactant. The MAL provides an additional resistance and deters the passage of the free passage of free surfactant through the membrane. This phenomenon is strong at higher pressures due to compaction of micelle aggregation layer (MAL) (Ghosh and Bhattacharya 2006).

17.5.2 Retentate Pressure

It was found that metal removal efficiency was enhanced with the increase in the retentate pressure. Average copper removal was found to be 54%, 61%, and 63% for the retentate pressure of 1.4 bar, 1.8 bar, and 2.0 bar, respectively (Bade and Lee 2007). A similar result was achieved on the chromate (Gargi and Bhattacharya 2006). The increase of pressure enhances the gel layer thickness and the rejection metal-micelle complex. However, the specific flux decreased with the rise of the operating initial retentate pressure. Increased CP at a higher initial applied retentate pressure caused a faster reduction in the permeate flux. Therefore, a lower operating retentate pressure should be chosen to get a higher specific flux. Among the applied retentate pressures, the highest average specific flux of 0.52 m^3/m^2-d-bar was observed when the retentate pressure was 1.4 bar (Bade and Lee 2008). At the higher retentate pressure, compared to the energy applied, the flux reduction was found higher due to faster gel formation on the membrane surface. Based on the permeate flux, retentate pressure of 1.4 bar was the optimal retentate pressure (Bade and Lee 2008). In other experiment, Karate and Marathe (2008) revealed that the transmembrane pressure in cross flow system proportionally increases as the inlet pressure increases and correspondingly the rejection of both Ni^{2+} and Co^{2+} ions increases giving more than 99% rejection.

17.5.3 Operating Pressure (Transmembrane Pressure)

The trans-membrane pressure (TMP) is defined as the difference between the average feed/concentrate pressure and the permeate pressure. It is effectively the driving force associated with any given flux for low-pressure membranes. The

TMP of the membrane system is an overall indication of the feed pressure requirement, and it uses the flux to excess membrane fouling. It is a foremost requirement for an efficient removal of heavy metals from the wastewater that the optimum operating pressure should be maintained. It is because the metal concentration in the permeate is reduced by increasing the pressure (Purkait et al. 2004). It is mainly due to an increase of micelle aggregation layer (MAL) (Ghosh and Bhattacharya 2006). Urbanski et al. (2002) reported that the resistance of the membrane increased faster by increasing the input pressure. Permeate flux increased with increased trans-membrane pressure (TMP) and cross flow rate (Park et al. 1997; Purkait et al. 2005). It was also explained that at constant TMP, permeate flux increased with the increased of inlet pressure without affecting the permeate concentration (Fillipi et al. 1999; Aoudia et al. 2003; Ghosh and Bhattacharya 2006).

Ultrafiltration is a pressure-driven membrane separation process. Generally, a higher operating pressure gives a higher permeate flux. At low pressure, the flux increases with increasing pressure. However, the flux may not increase proportionally with pressure at high operating pressures. In this case, the flux reaches a plateau level. This behavior is usually explained by the reason that high operating pressures can lead to more micelle deposition on the membrane surface, which enhances the CP and the gel layer composition (Xu et al. 2007).

Therefore, it is noticed that the very high operating is not necessary for a high permeate flux as it also needs greater initial investments and operational costs. For commercial applications, the recommended operating pressure for the UF membrane system is below the 1.5 MPa. It was found that operating pressure did not show a significant effect on the metal rejection and on permeate flux (Rahmanian et al. 2010).

The effects of operating pressure on pure water flux, permeate flux and permeate chromate concentration in the both presence and absence of surfactant were demonstrated by Kamble and Marathe (2005). They observed that both fluxes varied linearly with the applied pressure, but the permeate flux rate was lower in the presence of surfactant. However, no significant effect was observed in the normalized flux if the pressure increased from 2 to 6 kg/cm^2. Meanwhile, the permeate chromate concentration decreased, and its removal percentage increased slightly. This was because the increase in applied pressure promoted the surfactant concentration polarization layer near to the membrane surface, and consequently resulted in increasing concentration of micelles in CP layer on which the metal ions are adsorbed. The flow of a solution of charged species across a membrane, under the effect of pressure gradient, also resulted in an unbalanced distribution of electrical charges at the upstream and downstream interfaces of the membrane. This distribution generated a streaming potential depending upon the pressure gradient. An increase in the TMP may lead to a better rejection of the metal ions (Azoug et al. 1997). Similarly, in the absence of surfactant (membrane effect only), both the fluxes varied linearly with the applied pressure. The permeate flux rate was slightly lower than the water flux rate because of the presence of chromate salt in the solution. Karate and Marathe (2008) has reported that the TMP in cross

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flow system proportionally increased as the inlet pressure increased and correspondingly the rejection of both Ni^{2+} and Co^{2+} increased, giving more than 99% rejection.

The operation of the membrane process at low trans-membrane pressure is an important issue for reducing the operating costs. Danis and Aydiner (2009) reported that with the increase in TMP, both rejection increases but transient flux decreases. And it was suggested to use the membrane with lower pore-size or the binary surfactant for the purpose of obtaining higher surfactant rejection at relatively low TMP. Moreover, the lowest fouling was achieved at low TMP because of more porous gel layer with the relatively bigger aggregates on the membrane surface. The fouling increased with the increase in TMP (Danis and Aydiner 2009).

17.5.3.1 Impact of Cross Flow Velocity

It was reported that with the increased membrane surface cross flow velocity or tangential flow filtration (TFF), the operating pressure (TMP) also increased. This is because the foulant on the surface was peeled off by the flow perpendicular to permeate directly; meanwhile, it was difficult for the foulants to settle perpendicularly due to high-velocity flow but it had the disadvantage of a greater return flow. However, when the membrane surface velocity was zero, i.e., dead-end flow or normal flow filtration (NFF), there was no cycle of raw water or peeling off the foulant from the membrane surface velocity. Thus, in case of cross-flow velocity, TMP can be controlled with great ease in compare to the dead-end flow. A similar result was reported by Wang et al. (2008).

During membrane filtration, a fouling layer is formed. So with the progress of membrane filtration, the TMP gradually increases, in the meantime, the permeated water quality of the membrane remains steady, which indicates that the fouling layer plays a filtration function as the membrane itself (Wang et al. 2008). Iqbal et al. (2007) demonstrated the comparison of dead-end and cross flow system on the removal efficiency of the arsenate and the flux. The removal in the cross flow was similar to that of the dead-end system, but the cross flow system showed a much less flux decline compared with the dead-end system.

17.5.3.2 Effects of Operational Conditions on TMP

The various operating conditions such as the raw water concentration, permeability, working time, backwash interval, and backwash pressure have a significant influence on the operating pressure or TMP. It was reported that in the case of high raw water concentrations, TMP pressure increases quickly in a short time (Wang et al. 2008). This is because, with increased raw water concentrations, the concentration of membrane surface solution increased and the fouling layer was gradually formed due to the function of CP. Therefore, permeated water resistance quickly increased which led to the increase of the TMP. It was reported that when the permeability was greater than 1.0 m/d, the TMP increased rapidly with the increased permeability as the increased permeability accelerates the accumulation

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of the membrane surface fouling layer (Wang et al. 2008). Further, they also reported that with the increasing backwash interval or permeation period, both the TMP and permeated water quality declined as the attachment on the membrane surface was peeled off by the effect of frequent backwash. Similarly, the backwash pressure affects the TMP only when the backwash pressure was high.

Moreover, it was reported that with the increase of operating time, the permeate flux decreased whereas the rejection factor was enhanced. This phenomenon was attributed to the fact that the surfactant accumulation on the membrane surface increases with the increasing operating time (Rahmanian et al. 2010).

17.5.4 Influence of S/M Ratio

It is obvious that the molar ratio of surfactant to the metal ions, i.e., the S/M ratio or the initial feed surfactant concentration has significant impacts on the metal removal efficiency in the MEUF process as the MEUF process is the viable surfactant-based separation process. The concentration of surfactant has the most significant positive effect. Thus, increasing the surfactant feed concentration enhances the rejection coefficient.

Further, initial metal feed concentration also shows an adverse effect on the rejection coefficient. This shows that MEUF is more efficient for the diluted heavy metal streams (Kertész et al. 2009). Higher surfactant retention was observed during initial stages of UF with surfactant concentration below CMC and also above CMC level. This is because during initial stages of UF, all the surfactant molecules are in the form of free monomers, the size of which is much smaller than the pore diameter of the membrane used (10,000 MWCO) (Ghosh and Bhattacharya 2006). With the increase in surfactant feed concentration, larger fractions of micelles are formed. Hence, the MAL thickness increases; as a result, the resistance offered by the MAL increases, and consequently, the permeate flux declines (Van Oers et al. 1992). Some authors have reported that under a stirred condition, a higher permeate flux would have been observed with an increase in surfactant feed concentration (Ghosh and Bhattacharya 2006). Accordingly, MAL thickness would have decreased, which in turn would have resulted in an increased flux.

The MEUF process involves the combined use of surfactant and UF membrane. Metal removal by MEUF can be accomplished by the complexes formed between metals and micelles and the entrapment of such complexes by the membrane. So, the MEUF process highly depends upon the surfactant concentration in the feed solution. Cationic surfactants have been used for anionic metal removal and vice-versa. Huang et al. (2010) reported that Cd^{2+}/Zn^{2+} concentration decreased from 50 mg/L to less than 1 mg/L at the SDS dosage of 2.15 mg/L (CMC of SDS). Baek and Yang (2004c) demonstrated that at the molar ratio of 1:5, 98% of chromate removal was achieved but when the CPC concentration was too high it decreased due to the increased Cl^- (Ghosh and Bhattacharya 2006).

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Chromate removal was increased from 98% to over 99% when the molar ratio of chromate to CPC was increased from 1:5 and 1:10 in UF membrane of 10,000 MWCO (molecular weight cut off) (Baek and Yang 2004b). Chromate removal increased with the increase of CPC in the feed solution, but the percent retention slightly decreased due to preferential adsorption of chloride when CPC concentration in the feed was too high. Significant chromate removal was also observed with cetyltrimethyl ammonium bromide (CTAB) (Keskinler et al. 1997). CPC was found effective in arsenate removal (removal efficiency = 86% to 94%) at the CPC concentration ranging from 5 to 10 mM (Iqbal et al. 2007). CPC concentration at the membrane surface reaches CMC due to CP even the feed solution concentration was less than CMC that in turn, resulted higher surfactant removal efficiency (Gzara and Dhahbi 2001; Ghosh and Bhattacharya 2006; Li et al. 2006).

Aoudia et al. (2003) reported that feed SDS concentration of less than CMC has a Cr^{3+} removal efficiency of 33%, but 99% removal was observed at CMC. At the lower SDS concentration, zinc removal was also not effective. The removal was only 46% and 53% at SDS concentration of 1 mM and 3.4 mM. Various researchers used anionic surfactants such as SDS and sodium dodecyl benzene sulphonate (SDBS) for cationic heavy metals removal. The molar ratio of SDS to copper of 1:5 and SDS concentration equal to CMC was efficient for copper removal (Liu and Li 2005). They reported copper removal efficiency of 93% at 8.5 mM of SDS concentration. An efficient arsenic (V) removal, i.e., removal efficiency of 98%, was also achieved with the larger molecular weight cut-off (MWCO) membrane at the feed CPC concentration of 1–3 mM (Beolchini et al. 2007).

Surfactant-based MEUF has been successfully employed to remove multivalent metal ions. Huang et al. (1994) reported that two important parameters controlled the removal efficiency of metals: surfactant concentration and the surfactant to metal molar ratio (the S/M ratio). To achieve the maximum metal removal efficiency (greater than 90% for most of the metals investigated), the surfactant concentration has to be higher than the CMC of the surfactant (Fillipi et al. 1999). Chang et al. (2007) reported that the surfactant to metal ratio controlled the removal efficiency of metals. Huang et al. (2007) reported 97% of zinc removal at the molar ratio of SDS to zinc of 24.4. They reported the gel layer concentration of CTAB and CPC were 0.6 M and 0.53 M, respectively. Comparing efficiency of SDS and SDBS, SDBS was found to be more efficient for heavy metals as well as organics removal (Chai et al. 2007; Huang et al. 2007). Similarly, the effect of feed cetyltrimethylammonium bromide (CTAB) on the normalized flux through the membrane and removal percentage of Cr(VI) was reported by Kamble and Marathe (2005). Gold removal efficiency was found 100%, 99.9%, and 89%, respectively using CPC, POESA, PONPE10 surfactants (Akita et al. 1997).

Akita et al. (1999) mentioned an efficient removal of cobalt (90%) over nickel (50%) with anionic surfactant PONPE10 and extractant EHPNA. Ghosh and Bhattacharya (2006) explained that permeate flux reduced due to the formation of MAL on the membrane surface. With a view of the permeation flux, CMC of SDS (8 mM) was the appropriate SDS concentration (Xu et al. 2007). Permeate flux

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reduction was higher at the lower SDS concentration (below CMC) than higher SDS concentration (above CMC) due to the adsorption phenomenon and the interaction between ionic species and membrane with opposite charge. The CMC of surfactant can be affected by the changes in temperature, pH, presence of non-ionic surfactant, and inorganic salt. In an aqueous medium, ionic surfactants have much higher CMC than non-ionic surfactant containing equivalent hydrophobic groups (Rosen 1978).

The size of micelle has an important role in the removal efficiency. Xu et al. (2007) reported that at CMC of SDS, the micelle has a regular size of 5.07 nm. But beyond the CMC value the size of micelle decreases and shape of it also changes. Linear molecule passes through a membrane whereas globular molecules of the same molecular weight may be retained (Trivunac and Stevanovic 2006).

Karate and Marathe (2008) reported that at a very low S/M ratio (equal to 3) where SDS concentration was 6 mM which is less than its CMC (8 mM), rejection of Ni^{2+} and Co^{2+} was found to be 94% and as the S/M ratio increased, the rejection percentage also increased. This is because SDS is a long chain molecule. Even in a monomer form, it can be rejected by the membrane due to stearic hindrance. In the dead-end system, maximum rejection was obtained at the S/M ratio equal to 10 whereas for the cross flow system, the S/M ratio is 7. This means the surfactant requirement is reduced in cross flow continuous UF. The increment in surfactant concentration from 0 to 20 mM results in the reduction in normalized flux, which indicates that CP is most severe at higher surfactant concentration. No gel layer or gel concentration (Cg) was observed. Gel concentration is the extreme case of CP, at which the retentate concentration reaches a maximum value close to 500 mM (in case of cationic surfactants) and 600 mM (in case of anionic surfactants). The permeate flux becomes zero (Scamehorn et al. 1994).

Micelles continuously form and break at any concentration of the solution. At higher surfactant concentrations, either smaller surfactant aggregates of micelles (n-mers) are formed and/or the spherical micellar shape changes into cylindrical shape (Sadaoui et al. 1989; Scamehorn et al. 1994). Landaburu-Aguirre et al. (2009) showed that, at SDS feed concentration range from 8.3 mM to 14.0 mM, higher the surfactant concentration, the higher retention of heavy metals is achieved. In addition, when SDS feed concentration was further increased to 16.6 mM, no further increase in retention was observed. Therefore, increasing the SDS feed concentration enhances the retention of heavy metals until the certain limits. This is ascribed to the fact that the electrostatic interaction between the anionic micellar surface and the metals cation depends on the ion charge and concentration (Chhatre and Marathe 2006). At first, when increasing the SDS feed concentration, a higher fraction of surfactants will be in micellar form. This will increase the surface charge; hence more divalent heavy metals will be adsorbed on the micellar surface displacing the sodium counter ions. This ion exchange will consequently enhance heavy metal retention. However, at diluted heavy metal feed concentration up to 16.6 mM, the sodium counter-ions concentration might increase to an extent that the adsorption of sodium counter-ions is favored

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(Chhatre and Marathe 2006). Similarly, they also reported that the optimum S/M ratios for the removal of zinc and cadmium were 27.8 and 28.4, respectively. In order to obtain the high efficient retention of heavy metals, the surfactant feed concentration has to be large enough to create micelles and available binding sites. Rahmanian et al. (2010) demonstrated that the Zn^{2+} rejection was observed when the SDS concentrations were below the CMC. This behavior was observed due to the CP effect which hindered the ions permeation through the membrane pores. The CP is an important characteristic of all ultrafiltration (UF) systems. Some level of CP may have a beneficial effect in terms of permeate and rejection. When the SDS concentration reaches the CMC level at the CP layer, many SDS monomers begin to form large numbers of big-size micelles at the CP layer. Furthermore, the surfactant concentration in the layer adjacent to the membrane surface is higher than that of the bulk solution. Actually, the true rejection of the solute does not depend on the initial SDS concentration in the bulk solution while it is a function of the SDS concentration at the CP layer. Similar justification in case of cadmium ions has been reported by Fang et al. (2008).

Guntae and Lee (2011) observed that average lead removal efficiency was 98.8% at the molar ratio of 1:20 and the lead removal efficiency was almost constant to 99.5% and 98.6% at the molar ratio of 1:80 and 1:100, respectively. So, it can be inferred that the lead removal efficiency was higher for a higher initial SDS concentration (Guntae and Lee 2011).

17.5.5 Solution Acidity/Basicity

It has been reported that the MEUF process is not practical when the synthetic wastewater is intensively acidic (Rahmanian et al. 2010). The pH values have a pronounced effect on the metal removal as higher metal removal efficiency was obtained with the higher pH value (in case of anionic surfactant like SDS) whereas lower metal removal efficiency was obtained with the higher pH value (in case of cationic surfactant like CPC). Previous researchers have shown that chromate removal increased with the increase of acidity in the feed solution (Juang et al. 1997). But the flux increases with the increase of feed solution pH.

The Zn^{2+} rejection factor increases gradually with an increase in solution pH at fixed SDS and Zn^{2+} concentrations of 6 mM and 100 mM, respectively (Rahmanian et al. 2010). This was due to the competition between H^+ trapped on the micelle surface with the metal ions. At low pH (acidic condition), there are more H^+ ions compared with basic condition ($pH > 10$). Consequently, the effective binding sites are occupied by the hydrogen ions. But in solutions with high pH, there are fewer ions with the same charge. As a result, Zn^{2+} rejection increased. Further, they reported that the increasing the solution pH had very little effect on the permeation fluxes. This phenomenon was ascribed by the reason that the shape and aggregation number of micelles changes with the increase of the feed solution pH and pore blocking can be more intense. Cadmium removal increased sharply at pH less than 9 and increased to 99% at pH 11 with 8 mM SDS (Xu et al. 2007). Copper removal sharply dropped at the lower pH (Bade and Lee

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2007). Various researchers presented similar trend of the effect of pH on zinc and cadmium removal (Trivunac and Stevanovic 2006).

Some authors have reported that poly-sulfone membranes can be operated in a wide pH range of 1.0–13.0 (Kamble and Marathe 2005). They further stated that the maximum binding of Cr(VI) and its maximum rejection were observed at pH range of 5.5–6.5, this was because the most active forms i.e., $HCrO_4^-$ and CrO_4^{2-} prevailed in that pH range. Juang et al. (2003) reported that cationic heavy metals (Mn^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}, and Cr^{3+}) removal reached over 80% with SDS as the pH increased from 2.0–12.0. At the lower pH, lower heavy metals removal efficiency was, due to the competition between H^+ ions and cationic metal ions on the anionic micelle surface of SDS. But, there was no effect of pH on the removal efficiency for Sr^{2+} and Cr^{3+}. Cadmium rejection increased from 83% to 99% when pH increased from 3.0–11.0 in the feed solution containing cadmium (100 mg/L) and SDS (8 mM) (Xu et al. 2007). Viera et al. (2001) reported that Ca, Mg and Fe removal efficiencies were 55%, 53%, and 74%, respectively at the pH of 4.0–5.0 with PEI membrane. But, the removal efficiencies were reduced by 10% over or below this pH range. Geocol et al. (2004) expressed a different view on the effect of pH. In CPC enhanced ultrafiltration, with the increase in pH (5.5–8.0), arsenic leaching decreased (0.02−0 mg/L) when 10 kDa poly-sulfonate (PS) membrane was used with 0.221 mg/L of the initial arsenic concentration. The increase in the removal was mainly due to the formation of di-anionic arsenic at the higher pH. The less removal at the low pH was mainly due to the arsenic in the mono-ionic form. But the flux decreased with the increase in removal due to concentration polarization. A similar effect of pH on arsenate removal was observed for cationic surfactants CPC, CTAB and Octadecylamine acetate (ODA) (Iqbal et al. 2007). However, at a higher surfactant concentration, due to the availability of a larger number of binding sites, the removal was not significantly reduced even the pH was low.

The rejection of Ni^{2+} and Co^{2+} remained nearly constant in a broad pH range of the feed solution between 3 and 10 (Karate and Marathe 2008). This was corroborated as the concentration of H^+ ions becomes greater than the feed concentration of Ni^{2+} and Co^{2+}, so Ni^{2+} and Co^{2+} ions have to compete with the Na^+ and H^+ ions for their binding sites with the SDS micelles. Samper et al. (2010) revealed that the permeate flow rate was similar for all pH values studied, except in the case of pH 2.1, for which it was slightly higher due to the negative charges of linear alkylbenzene sulfonate (LAS) and sodium dodecyl sulfate (SDS) molecules. They further reported that Ni^{2+} retention (100%) occurred at the pH of about 10.0, which could be a result of the appearance of precipitate. Under the basic conditions (pH 10.0), the elimination yields of Ni(II) were higher as Ni(II) formed precipitate of $Ni(OH)_2$ under this condition. Similarly, at other pH values, particularly from the pH value 2.0–8.0, Ni(II) retention decreased gradually. Regarding the surfactant retention, the lowest retention was produced at a pH of around 2.0 in all cases. Highly acidic conditions (pH 2.1) gave the membrane a less negative zeta potential. This led to the greater repulsion of free Ni(II) cations and consequently, the cations were forced into the bulk of the solution.

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Guntae and Lee (2011) reported that the lead removal efficiency increased with the increase of pH in feed solution at CMC of SDS surfactant. At lower pH, lead had to compete with the H^+ ions to get the micelle surface, so less amount of lead was adsorbed due to the competition with the H^+ ions in acidic solution. This sort of similar phenomena was explained for SDS in copper removal (Bahdziewicz et al. 1999). The effect of pH depended on the type of metal used in the solution whether H^+ ions and OH^- ions competed with the metal or not during the electrostatic adsorption on micelle (Bahdziewicz et al. 1999). The chromate removal efficiency increased in the acidic condition, so the chromate removal efficiency was between 87% and 69% at the pH range of 6.5–9.0 (Bade and Lee 2008). At higher pH, chromate had to compete with OH^- ions to get adsorbed on the CPC micelle, therefore, lower chromate removal was observed at the higher pH value.

17.5.6 Influence of Initial Metal Feed Concentration

The initial feed metal concentration significantly influences the efficiency of the MEUF process. Kamble and Marathe (2005) demonstrated the effect of feed chromate concentration on normalized flux and removal percentage of the chromate in the absence of surfactant (membrane effect). They observed that there was no significant effect on the normalized flux because of the absence of surfactant. Similarly, in the absence of surfactant and with devoid of significant chromate adsorption on the membrane, no rejection of Cr(VI) was expected. Since the poly-sulfone membranes carried a negative charge, the membrane charge effect was probably responsible for the separation. But in the presence of the surfactant (CTAB), the increase in chromate concentration from 0.1 mM to 1 mM resulted in a slight decrease in the normalized flux and the rejection of chromate was excellent (above 99%). As the feed metal concentration increased, the number of free metal ions in the solution also increased proportionally because of the equilibrium between the adsorbed ions and free metal ions in the bulk solution, thus the chromate concentration in the retentate increases and also the permeate chromate concentration also increases proportionally. A similar result was presented by Karate and Marathe (2008). They observed that the increase in concentration of unbound Ni^{2+} and Co^{2+} was proportional with the increase in the feed metal concentration and hence, the permeate concentration also increased but the rejection considerably dropped down to about 99%. The reduction in rejection at higher feed concentration could be attributed to the lack of availability of binding sites. It was reported that the increase in nickel concentration did not significantly affect the SLES rejection (64.2–70%) while remarkable increases in nickel rejection could be obtained (Danis and Aydiner 2009). Furthermore, Bade and Lee (2008) observed the permeate concentrations of 0.24 mg/L, 0.33 mg/L, 0.71 mg/L, and 1.27 mg/L for the corresponding initial chromate concentration of 10 mg/L, 15 mg/L, 20 mg/L, and 29 mg/L, respectively. It implied that the chromate removal decreased with the increase of its initial concentration at one CMC CPC surfactant while CPC removal increased. It

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was mainly due to more competition among chromate ions to get the binding surface with micelle. Similar results on chromate removal were presented by other researchers (Gzara and Dhahbi 2001). They further demonstrated that the CPC removal from the 100 kDa MWCO membrane was 49%, 55%, 72%, and 73%, respectively for the respective initial chromate concentration of 10 mg/L, 15 mg/L, 20 mg/L, and 29 mg/L. The CPC removal increased at the higher initial chromate concentration due to the formation of more micelle with the presence of counter ions (Bade and Lee 2008).

The CPC removal in the absence of the chromate was only 40% at one CMC of the CPC and the removal increased to 80% in the presence of chromate in similar condition. Zhang et al. (2007) reported that the increase of the initial Zn^{2+} concentration, the Zn^{2+} rejection decreased gradually, and the permeate Zn^{2+} concentration increased synchronously. The efficient removal of Zn^{2+} at the low Zn^{2+} feed concentrations is a critical feature of MEUF. Similarly, the copper removal efficiency was 98% for the initial copper concentration of 0.31 mM while 96% for 1 mM concentration (Bade and Lee 2007). They reported that copper concentration in the permeate increased with the increase of initial copper concentration mainly due to less micelle surface area available for the electrostatic adsorption of higher copper concentration.

Das et al. (2008) observed a significant decline in permeate flux when increasing the concentration of divalent metal counter ions at fixed feed surfactant concentration. They reported that in the presence of metal ions, positively charged metal ions bridged more than one negatively charged micelles, leading to a formation of gel layer on the membrane surface at a lower concentration of surfactants. Further, the increase in cation concentration such as heavy metals cations released the repulsive forces between the head groups, and the formation of micelles became easier i.e. the CMC decreased (Samper et al. 2009). When decreasing the CMC of the surfactant, more surfactant monomers would be in the micellar form and, therefore, the surfactant concentration in the retentate would be increased enhancing the flux decline (Huang et al. 2009). Landaburu-Aguirre et al. (2009) reported that smaller zinc feed concentration, the higher retention of heavy metals was achieved. When the heavy metal feed concentration was 0.5 mM, the retention achieved was up to 99% but at the higher heavy metal feed concentration (3 mM), retention dropped to 94%. When increasing the heavy metal feed concentration, the zeta potential of the micelles increased as the surface charge density decreased (Fang et al. 2008). Therefore, the reduction in retention at higher metal feed concentrations might be due to the lack of available binding sites. Consequently, MEUF is more efficient in solutions with the diluted metal concentrations.

17.5.7 Thermal Influence on Micellization

The peculiar feature of surfactants is that they have the capacity to aggregate in solutions and thus, various physical properties of the surfactant solutions change abruptly within the narrow concentration range, which is popularly known as

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critical micelle concentration (CMC), above which micelles exist in the solution. For ionic and amphiphilic surfactants, micellization is affected by temperature as the hydrophobic and head group interactions change relative to temperature (UCLA 1994). Both the pure water flux and the permeate flux vary linearly with the temperature (Kamble and Marathe 2005). This is ascribed as the temperature has a marked and positive influence on both the fluxes. Within the framework of resistance theory, the flux is inversely proportional to the viscosity of the solvent. The temperature also plays very crucial role in the optimization of the MEUF process for the heavy metals removal as CMC of surfactant is a function of temperature (Zeng et al. 2008). The CMC of surfactant is a function of temperature (Kowalska et al. 2006). The CMC of SDS increases with the increase of temperature due to the de-micellization process because of the disruption of the palisade layer of the micelle. Thus, surfactant ions start detaching from micellar bulks. At the temperature of 25°C, 40°C, and 45°C CMC of SDS is 2,257 mg/L, 2,445 mg/L, and 2,706 mg/L, respectively (Kowalska et al. 2006). If the CMC exceeds the solubility of the surfactant at a particular temperature, then the minimum surface tension will be achieved at the point of maximum solubility, rather than at CMC. The temperature at which the solubility of an ionic surfactant becomes equal to the CMC is known as the “kraft point” (Rosen 1978). The resistance of surfactants increased with the kraft point. Urbanski et al. (2002) reported that SDS showed a higher additional resistance compared with cetyltriammonium bromide (CTAB) and APG. It is because of higher kraft point for CTAB. They reported the kraft point of 25°C and 21°C for CTAB and CPC, respectively. Zeng et al. (2008) further stated that with the increase of temperature, CPC monomer increased in the solution. Thus, the hydrophobic tails of CPC monomers interacted with poly-sulfone membrane (hydrophobic) resulting in the adsorption of CPC on the membrane surface and in its pores. They also elaborated that at high temperatures, the CPC micelle easily dissociated and decreased micelle number and its size which resulted in the passage of more CPC monomers. Another reason of the passage of CPC at permeate was due to the thermal expansion of the membrane. With the increase of temperature, permeate flux increased due to decreased viscosity and thermal expansion of membrane material. The increased flux resulted in a higher CP (Kowalska et al. 2006).

Kamble and Marathe (2005) reported that the maximum operating temperature in case of the poly-sulfone membrane was 75°C. They further reported that at higher temperatures, normalized flux increases due to a decrease in viscosity of the solution. The permeate chromate concentration, however, increased, which could be related to the CMC variation with the temperature. The CMC of CTAB was reported to increase with the temperature (Sadaoui et al. 1989). Unlike nonionic surfactants in which the log CMC is a linear function of inverse temperature (Becher and Schick 1967), ionic surfactants are known to display a U-shaped behavior in a CMC-temperature plot (Kang et al. 2001). Similarly, the CMC of octadecyl trimethyl ammonium chloride (OTAC) was reported to be the one order of magnitude smaller than that of ammonium dodecyl sulfate (ADS) at each

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temperature variation as the OTAC has a longer hydrocarbon chain than ADS (Kang et al. 2001). They further revealed that the micellization of ADS and OTAC was entropy-dominant at low temperatures and enthalpy-dominant at the high temperature.

17.5.8 Reduction of Surfactant's Critical Micelle Concentration

17.5.8.1 Non-Ionic Surfactant and Ionic Strength Increment

Non-ionic surfactants consist of a hydrophilic (lyophilic) head without charge. These surfactants are effective in the removal of oily soil. Most non-ionic are more tolerant to water hardness, effective at low concentration since they have sufficient cold water solubility and low CMC value (Kang et al. 2001). However, the use of non-ionic surfactants alone via MEUF is suitable only for removal of organic contaminants. The ionic (cationic or anionic) components have the tendency to create a bond with the head of the ionic micelles surface which is oppositely charged via electrostatic interaction. Theoretically, less removal of ionic contaminants via MEUF can be expected using non-ionic as a surfactant. Yenphan et al. (2010) studied on removal of Pb2+ ion using Triton X-100 (TX-100) and nonyl phenyl ether (NP12) as non-ionic surfactants and found that the Pb^{2+} ions removal were insignificant, about 9% to 18% for TX- 100 and 30% to 37% for NP12. They believed the removal of ions was due to the complex formation between the Pb^{2+} ions and ethylene oxide (EO) groups of TX-100 and NP12. To prove the non-ionic surfactants is quite suitable for removing organic contaminants via MEUF, Chung et al. (2009) had performed their study on removal of toxic organic tri-halomethane (chloroform) using polyethylene glycol alkyl ether as non-ionic surfactant via MEUF and observed that more than 80% of chloroform was removed from the wastewater.

In the MEUF process, the use of surfactant in the feed solution should be minimized from the economic and secondary pollution point of view. The use of surfactant can be reduced by reducing the CMC. One way is to reduce CMC of surfactant by using non-ionic surfactant (Yurlova et al. 2002). In the mixture of surfactant, hydrophilic parts of non-ionic surfactant counterbalanced the charge of ionic hydrophilic groups (Lee et al. 2005). It resulted in a decrease of charge density at the surface of micelle leading to diminishing of the electrical potential. Eventually, it enhanced the formation of micelle at a lower CMC, but the removal efficiency decreased slightly. Chromate removal reduced from 93.7% to 84.8% with the increase of Tween-80 from 10 mM to 25 mM in CPC and chromate solution (Liu and Lee 2004). With the increase of metal/SDS ratio, both SDS and Cd^{2+} removal decreased (Xu et al. 2007). Similar results of reduction in Cr^{3+} removal with nonylphenol ethoxylate (NPE) (Aoudia et al. 2003), zinc removal with NPE were observed (Fillipi et al. 1999). Jonsson and Jonsson (1991) compared the retention of the non-ionic surfactant and ionic surfactant. They reported a low removal of Triton X-100 but a quite high

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removal of SDBS and CTAB at the SDBS and CTAB concentration below the CMC. In terms of surfactant removal, the trend was opposite to that for heavy metals. CPC removal increased from 91% to 99% with Tween-80 due to the formation of more micelle, hence less CPC monomer passed to permeate. Yurlova et al. (2002) reported a different view that, at less than CMC of SDS, the addition of OP-10 improved the removal efficiency of nickel from 88% to 96%. But at or over CMC of SDS, no improvement in nickel removal was observed. Liu and Li (2005) reported that copper removal efficiency increased from 15% to 70% in the presence of 3.01 mM of Triton-X in SDS solution of 2.15 mM (less than CMC). No significant effect on copper removal and permeate SDS concentration was observed when Triton-X concentration (CMC = 0.2 mM to 0.43 mM) was less than 0.1 mM. Copper removal efficiency decreased from 90% to 88% when non-ionic surfactant Triton X-100 was added with SDS fraction of 0.7 (Lee et al. 2005). Fillipi et al. (1999) reported that, by the addition of non-ionic surfactant, both Zn^{2+} and organic TBP removal efficiency was increased in the negatively charged membrane. Permeate flux decreased by non-ionic surfactants in micelle solution; it was mainly due to the higher viscosity of non-ionic surfactant OP-10 (Yurlova et al. 2002). The viscosity of pure Triton-X was 240 centipoise at 25°C, which was 0.89 only for pure water. An increase in Triton-X concentration had a bigger impact on hydraulic resistance than the increase in copper concentration (Li et al. 2006). Contrarily, the addition of complexing agent has no effect on flux since complex of metal and chelating agent passed through the UF membrane (Kim et al. 2006).

Metal is removed through adsorption onto surfactant micelles, which form at the surfactant concentrations greater than its CMC, followed by the subsequent removal of metal-micelle complexes by UF. Huang et al. (1994) indicated that two important criteria, namely surfactant concentrations of greater than its CMC and the surfactant to metal molar ratio (the S/M ratio) of greater than a certain value, i.e. the critical S/M ratio, had to be met to achieve an efficient metal efficiency by MEUF. For SDS which had CMC of 8.27 mM, the critical S/M ratio was 5 to obtain metal removal efficiency of greater than 99% for the most of metals investigated (Huang et al. 1994).

To treat industrial wastewaters containing very low metal concentrations using MEUF, meeting above mentioned criteria makes the process less attractive. For instance, treating wastewater containing Cu(II) concentration of 0.2 mM (the median Cu(II) concentration in the wastewaters from electroplating industry in Taiwan according to the survey by the Eco-Technology Development Center, CTCI Foundation, Taipei (Taiwan)), meeting the critical S/M ratio of 5 will acquire only 1 mM of SDS concentration. To overcome this problem, one can increase ionic strength of the solution or add non-ionic surfactant as the CMC value of a surfactant can be reduced by increasing ionic strength of the solution or adding non-ionic surfactant (Fillipi et al. 1999). Increasing the ionic strength will increase the concentrations of total solids and conductivity in the effluent. On the other hand, the addition of non-ionic surfactant can be a very effective way to lower the CMC of SDS without increasing the total solids content.

17.5.8.2 Electrolyte Concentration

Generally, salts are used in electroplating and metal finishing industry for making buffer solutions, and hence can be easily found in industrial wastewater effluents. The presence of electrolyte can decrease the CMC of ionic surfactants because the electrolyte can weaken the repulsive forces between the head groups, which are typically fighting against the aggregation of surfactant monomers. Therefore, micelles can form readily in the presence of the electrolyte (Scamehorn et al. 1988; Xu et al. 2007). Thus, the addition of salt in surfactant solution is another way of reducing CMC of surfactant. Xu et al. (2007) further explained that the electrical double layer was compressed due to the increased electrolyte concentration, resulting in the reduced electrostatic attraction between ions and the micelles. As(V) replaced Cl^- ions in CPC and arsenic solution, the As(V) bound tightly with CPC ions and decreased the electrical charge on the surface and reducing CMC (Geocol et al. 2004). As a result, non-trapped metals passed through the membrane leading to the lower rejection (Juang et al. 2003; Geocol et al. 2004). Gzara and Dhahbi (2001) reported the decrease of chromate (CrO^{2-}) removal from 1 mM to 0.15 mM when NaCl concentration increased from 1 mM to 500 mM. Aoudia et al. (2003) reported that Cr^{3+} removal was also reduced with the addition of NaCl. In contrary, the addition of NaCl has an adverse effect on the reduction of metal removal and the formation of metal chloride. Basar et al. (2004) explained that with the increase of NaCl from 2 mM to 100 mM, CTAB rejection increased from 68% to 98%. On the contrary, LABS rejection rate decreased slightly from 38% to 34% at the salt concentration of 2 mM and 100 mM, respectively. Sampler et al. (2009) also reported the similar result of reduction of heavy metals (Cd^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}) when NaCl was added in the surfactant SDS and alkyl benzene sulfonate (LAS).

Using the MEUF process to remove the heavy metals would not be as effective when the high concentrations of dissolved salts were present. As the chromate rejection rate of higher than 81% was obtained, indicating that an adequate separation of metal ions can be attained by the MEUF process in the presence of NaCl (Kamble and Marathe 2005). Xu et al. (2007) reported that cadmium removal efficiency decreased from 95% to 75% at NaCl concentration of less than 20 mM. It could be due to the competition between Cd^{2+} and Na^+ ions to get the micelle surface, and due to the formation of complexes of Cl^- and metal. The relative flux also decreased with the increase of salt concentration. Akita et al. (1997) reported that in the process of removal of gold by the MEUF process; permeate flux reduced by the addition of NaCl; however, it tended to lower the surfactant leakage. Azoug et al. (1998) reported that at the SDS concentration of less than CMC, the SDS entirely dissociate into free ions, Na^+ and DS^-. They further added that membrane resistance was highly influenced by free ions

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dodecyl sulfates (DS^-) and sodium (Na^+), very slightly by negatively charged spherical micelles, and weakly by rod-like aggregates.

Karate and Marathe (2008) reported that the effect of electrolyte which is NaCl on the Ni^{2+} and Co^{2+} rejection efficiency. The rejection efficiency decreased with the increase in NaCl concentration from 10 mM to 100 mM and reached a constant low value of 88%. This was attributed as with the increase in the concentration of counter-ions due to salt addition the concentration of Na^+ ions in the stern layer increased and the probability of Ni^{2+} and Co^{2+} ions being found in the vicinity of micelles reduced. Therefore, one can expect the rejection coefficient to decrease with the increase in the salt concentration. Also, they reported that Cl^- ions could form the complexes with the metal ions. Adamczak et al. (1999) reported that the presence of $NaHCO_3$ reduced the permeate flux in the MEUF process containing SDS and hydrophobic oxyethylated methyl dodecanodate. Similarly, both the rejections and transient flux decrease with the increasing of electrolyte concentration, and sodium lauryl ether sulfate (SLES) rejection was not significantly affected by the low NaCl concentration (Danis and Aydiner 2009). It was also shown that the increased electrolyte concentration did not cause any significant change in the flux at the end of the processing time.

For relatively more economical or feasible removal of metal ions from wastewater, the MEUF process should be employed as tending to prevent the existence of the gel layer or to provide the formation of highly porous gel layer. It was reported that increase in the electrolyte content of solution increases both the membrane fouling and the specific gel resistance (Danis and Aydiner 2009). This is because of the formation of relatively smaller aggregates in a less porous layer on the membrane surface. The presence of Na^+ ions promoted the formation of micellar structures with lower size. The fouling and the flux decline occurred simultaneously under the effect of mechanisms such as intermediate blocking, gel layer formation, complete blocking, and adsorption in the pores. Despite a partial decrease in pore blocking by bridging with increasing of the electrolyte concentration, the increment in effects of the gel layer on the membrane fouling brought about a considerable reduction in both the rejections and the flux. Some author reported that the permeate SDS concentration decreased with the increasing Triton-X concentration (Li et al. 2006).

Kamble and Marathe (2005) demonstrated that the effect of feed NaCl concentration on the normalized flux through the membrane and removal percentage of chromate. They further added that with the increased NaCl concentration in the feed, the normalized flux initially increased and then slightly decreased. With the NaCl concentration increased from the 0 mM to 100 mM, the removal percentage of chromate decreased from 99.9% to 81.9%.

17.5.9 Ultra-Filter Membrane Type and MWCOs

The pressure works as the driving force, i.e., increasing the pressure, the higher flux will be achieved. Consequently, using the higher pore-sized membrane, a

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higher flux will be observed (Kertész et al. 2009). Permeate flux was highly influenced by the hydrophobic and hydrophilic behavior of membrane material and adsorbate. Jonsson and Jonsson (1991) indicated that flux reduction was much higher in the hydrophobic membranes than that in hydrophilic membranes. Kim et al. (1998) also reported on the reduction of flux in the hydrophobic membrane. Byhin and Jonsson (2002) further added that hydrophobic membranes reduced flux at a concentration below the CMC, whereas hydrophilic membranes did not reduce the flux at below CMC of non-ionic surfactant Triton X-100.They further explained that the decrease in permeate flux was more with the hydrophobic membrane than hydrophilic membrane, even though, the pore diameter was the same for both the membranes. The type of membranes such as hydrophilicity or hydrophobicity has a higher effect on permeates flux than by TMP. In their experiment, they found that increasing TMP by two folds there was an increment in permeate flux by two times in aqueous solution whereas it was only 1.5 times with the hydrophobic membranes for non-ionic surfactant TitronX-100. Fernandez et al. (2005) reported that decrease in the flux of SDS solution with CA membrane was due to interaction with the positive ions of the membrane caused by pH less than the iso-electric point.

Larger pore sized membranes caused an earlier development of CP and reduced the release of surfactant at the permeate (Beolchini et al. 2007). Baek et al. (2003b) observed higher rejection of CPC (>98%) with YM3 and YM10 ultrafilter of 3000 and 10,000 MWCO at the molar ratio of 1:10 (Baek et al. 2003b). Chromate removal was higher (>99%) with 3000 MWCO membrane than with 10,000 MWCO membrane (98%) at the chromate to CPC molar ratio of 1:10 (Baek and Yang 2004b). Chromate removal efficiency with 100 KD UF membrane was 98% while it was 97% with 300 KD membranes at the molar ratio of chromate to CPC of 1:5 (Bade and Lee 2008). Metal rejection can vary depending on the nature of membrane whether they are hydrophilic or hydrophobic. Kim et al. (1998) stated that polyethylene glycol (PEG) membrane increased rejection with the increase in the hydrophobicity of surfactant in the hydrophilic membrane cellulose acetate (CA). The hydrophilic part of micelle or monomer tried to adsorb on the hydrophilic membrane surface, in comparison with hydrophobic membrane surface (Juang et al. 2003). Ferella et al. (2007) further added that micelle adsorbs preferably on the hydrophilic surface of polyamide membranes rather than the hydrophobic surfaces of ceramic or poly-sulfone membranes. Cationic surfactant dodecylamine removal was found higher on the hydrophobic ceramic membrane due to the formation of lumps (Ferella et al. 2007). Byhlin and Jonsson (2002) stated that Triton X-100 at a concentration below CMC, the rejection was constant for both hydrophobic and hydrophilic membranes. But at the concentration over CMC, the permeation leveled off for hydrophilic membrane (regenerated cellulose) while it still remained high for the hydrophobic (polyether sulfone, i.e., PES) membrane. They further explained that there was no removal of non-ionic surfactant Triton X-100 from hydrophilic material below CMC but at or above CMC, there was higher percentage removal.

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Yurlova et al. (2002) reported that the best retention of Ni(II) ions was obtained when the OPMN-K membrane was used when the surfactant SDS used in an amount equal to the CMC. But the other membranes under study i.e., UPM-10 and UPM-20 did not give such perfect results (the aforementioned membranes: OPMN-K, UPM-10 and UPM-20 were made of polymers which pore size ranges from 5 to 20 nm). Similarly, the removal of arsenate using membrane with MWCO 3 kDa was slightly higher than those with MWCO 10 kDa, especially at the lower concentration of the surfactant (Iqbal et al. 2007).

17.5.10 Co-Existing Metal Cations

Various researchers reported that metal removal in the MEUF process was inhibited in the presence of other inorganic pollutants. Baek and Yang (2004a) reported that, in the treatment of inorganic pollutants, the presence of higher valence ions inhibited the removal of low valence ions. In the co-existence of various pollutants, higher valence pollutants were saturated first and lower valence pollutants later. In their study, chromate removal was inhibited in the presence of ferricyanide while the higher valence ferricyanide removal remained unchanged in octadecylamine (ODA) solution (Baek and Yang 2004b). In single-pollutant system, the order of removal was nitrate < chromate < ferricyanide. The same was true for the multi-pollutant system (Baek and Yang 2004a). In the coexistence of multi-pollutants, the quantity of surfactant required increased, in comparison with that in the single pollutant system for achieving similar removal efficiency. Iqbal et al. (2007) had shown that a small quantity of nitrate and phosphate (0.01 mM) reduced arsenate removal by 7% to 8% due to competition to get binding sites on cationic CPC micelle. Channarong et al. (2010) explained that there was no significant effect on Zn^{2+} and Ni^{2+} removal in the MEUF process on the co-existence of both the metals. In other experiment, Guntae and Lee (2011) reported that the lead removal efficiency was affected by the co-existing heavy metals such as copper and nickel. It was demonstrated that copper significantly affected the lead removal while nickel did not show any significant effect.

17.5.11 Influence of Conductivity

The metal retention gradually decreases whereas the surfactant retention increases with the increase in the conductivity. A similar result was revealed by Samper et al. (2010). They reported that the best retention of Ni^{2+} was achieved at low conductivities. This was because of more Na^+ ions in solution as the conductivity increased, resulting in greater competition between Na^+ and Ni^{2+} ions for the surfactant. Hence, as the concentration of Na^+ ions became greater than that of Ni^{2+}, the majority of micelles would coordinate with Na^+. As regards surfactant retention, when the conductivity increased from 200 to 6,000 μS/cm, the retention of surfactant increased. When the conductivity increased above 6,000 μS/cm, the surfactant retention remained constant. This was ascribed to the fact that as the solution conductivity increased, the value of the CMC diminished. Similarly,

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in all cases, the flow rate decreased as the conductivity increased (Samper et al. 2010).

17.5.12 Co-Existing Anions

With an addition of nitrate and phosphate ($[NO_3^-] = 0.45$ mM, $[PO_4^{3-}] = 0.01$ mM), the removal efficiency of arsenate from aqueous solution was decreased by 7% to 8% when CPC was used and it was reduced by 4% to 6% with the surfactants CTAB and ODA (Iqbal et al. 2007). The decrease in the arsenate removal can be explained by the consumption of the available binding sites of the micelles and reduction in electrostatic repulsion (Ergican et al. 2005). In another experiment, Tung et al. (2002) revealed that copper removal was enhanced in the presence of phenol while phenol removal was only 27% due to its relatively high hydrophilic characteristics.

17.6 OVERCOMING MAJOR LIMITATION OF MEUF PROCESSES

Overcoming the major limitations of the MEUF process lies in the realm of metal ions and surfactants recovery from the retentate and permeate. MEUF using anionic surfactants at concentrations much higher than CMC has proven to be very effective in removing the metals from aqueous streams. Since anionic surfactants have a relatively high CMC, large quantities of surfactant must be used to bring about an adequate separation. Consequently, the economic viability of the MEUF process strongly depends on the recovery (or recycling) ability of the surfactants from the retentate and permeate (Samper et al. 2009). An additional limitation of the MEUF process is the inevitable leakage of surfactant monomers through the UF membrane. Previous studies indicated that the permeate concentration of the surfactant was nearly equal to the surfactant concentration in the retentate or the surfactant CMC. Clearly, this may increase the cost of the separation process or make the process effluent unacceptable (Aoudia et al. 2003).

Retentate is the concentrated solution of the surfactants and heavy metals retained by the membrane, whereas the liquid that passes through the ultra-filter membrane is termed as permeate. As surfactant accounts for a significant portion of operating costs and can cause secondary pollution as well, it is essential to recover and reuse the surfactant from the retentate and permeate stream so far as possible from the environmental and economic point of view. Basically, three methods can be employed for the separation of metal ions from simulated retentate and permeate of the MEUF process: (a) acidification followed by ultrafiltration (UF); (b) use of a chelating agent followed by UF; and (c) precipitation by ferric- and ferrocyanide followed by centrifugation. In general use, it is considered that acidification is the simplest and most efficient process for surfactant recovery. However, ferricyanide has a potential applicability because of the rapid precipitation with metal ions and selectivity (Kim et al. 2006).

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Secondary pollution generated due to the formation of highly concentrated surfactant at the retentate is one of the prime concerns in the MEUF process (Baek et al. 2003b). Thus, the separation of surfactant from bulk solution is one of great concerns for reuse purposes. Canizares et al. (2002) mentioned the possibility of regeneration of water soluble polymer by changing the pH of the solution. The acidic/basic behavior of the functional groups make it possible for the further dissociation of already formed macromolecular complexes by their protonation. Hiraide and Itoh (2004) reported that copper in the MEUF retentate was leached from micelle with 4 mol/L of nitric acid. When pH of the aqueous medium reduced, polymer regeneration and recovery of the metal were achieved by a second UF process. Nitric acid, sulfuric acid or hydrochloric acid recovered 84% SDS from retentate solution and have separation efficiency over 95% for cadmium and copper after ultra-filtration (Kim et al. 2006). Juang et al. (2003) mentioned the recovery of surfactant using 6 N NaOH solution until precipitation reaction occurred. They repeatedly used the remaining solution after removing the precipitates by centrifuge at 5,000 rpm. Chelating agents can make good complexation with metal in retentate solution. After complexation, the chelating agent and metal can be well separated from the solution by ultrafiltering the solution. Kim et al. (2006) added iminodiacetic acid (IDA), ethylenediaminetetraacetic acid (EDTA), citric acid for in the MEUF retentate solution, then filtered it through ultrafilter membrane. The membrane rejected the surfactant while 82.5%, 99.9%, and 100% of copper were passed through the membrane, respectively for the solution IDA, EDTA, and citric acid. Similarly, EDTA showed higher removal efficiency of 75.7% for cadmium removal from the MEUF retentate solution.

17.7 OPTIMIZATION OF ADSORPTION PROCESSES

Surfactant and heavy metal ions from the industrial and municipal wastewaters represent an important category of contaminants. That is the reason why both the aforementioned contaminants are the matter of serious concerns due to their toxicity to various forms of life, from human beings to the environment as a whole. Many techniques have been used and developed to remove the surfactants and metal ions from wastewaters. These include ion exchange, solvent extraction, reverse osmosis, precipitation, chemical oxidation and reduction, filtration, electrochemical treatment, floatation coagulation, biodegradation and adsorption. However, biodegradation suffers from optimization problems while ion exchange and chemical oxidation are considered to be high-cost methods. Electrochemical processes suffer from three main problems: (1) high cost and unstable anodic materials; (2) effluent cannot be discharged in the presence of high chloride concentration; (3) low coulombic efficiency. Furthermore, floatation and coagulation methods have a low efficiency. More sophisticated techniques like solvent extraction, biosorption, and ultrafiltration are either expensive or cannot cope with the high concentrations of contaminants. All these methods have significant

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disadvantages such as incomplete removal, high energy requirements, and production of toxic sludge or other waste products that require further disposal (Saleh 2006). Amongst, adsorption process has been the most frequently applied method in the industries.

A number of researchers have utilized an extensive variety of adsorbents to remove heavy metal ions and surfactants from aqueous solutions. Some of the recent developments include adsorbents like cement kiln dust, NaS_2 treated granular activated carbon, activated carbon derived from carica papaya seed, activated carbon derived from polyacrylonitrile (PAN) fiber, activated carbons derived from coconut and seed hull of palm tree, olive cake, herbaceous peat, carbon aerogel, iron-oxide coated sand, sawdust, Ca-kaolinite, fithian illite, fly ash, baggage, activated carbon-zeolite composite, zeolite-A, fertilizer plant waste slurry, modified clay, bio-sorbents like cassava waste, areca, and so on.

An optimum dose of ACF for the surfactant adsorption varies depending upon the initial surfactant concentration, i.e., the higher the initial surfactant concentration, the higher is ACF dose for the adsorption and vice-versa. At the higher ACF dose, active sites available for the surfactant adsorption is high, thus higher surfactant removal was achieved. Saleh (2006) had also presented similar results for the CPC adsorption onto charcoal. At a higher CPC concentration, the adsorption is decreased after reaching the optimum dose, but at a lower concentration, it decreases abruptly after the optimum adsorption.

Within the certain range, adsorption of surfactant increases with the increase in the temperature within that range. Tan et al. (2007) demonstrated a similar result where basis dye adsorption to oil palm, activated carbon fiber increased at a higher temperature condition. The higher removal with the increase of temperature could be due to increased intraparticle diffusion into the pores of ACF at the elevated temperature. At a higher temperature, there was a possibility of chemical adsorption as well (Hiraide and Itoh 2004; Tan et al. 2007). An increase of adsorption with an increase of temperature indicates that the adsorption is endothermic. The adsorption mechanism may be physical or chemisorptions. If an adsorption decreases with an increase in temperature, the adsorption is physical adsorption. If the adsorption increases with the temperature, the adsorption is chemisorptions (Saleh 2006; Tan et al. 2007).

Various researchers had revealed the fact that the adsorption percentage decreased with an increase of surfactant concentration. However, the amount of the surfactant adsorbed per gram was increased within a certain concentration range (Bade and Lee 2007; Bade and Lee 2008). Erdem and Ozverdi (2005) had illustrated the lower percentage of lead removal with the increase in initial surfactant concentrations. Moreover, various experiments conclude that an adsorption decreased with an increase in pH within a certain range of surfactant concentrations.

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17.8 MEUF-ACF: AN INTEGRATED APPROACH

Micellar enhanced ultra-filtration (MEUF) is a powerful treatment process developed to remove heavy metals from wastewater, which combines ultrafiltration with surfactant technology. In other words, MEUF is the surfactant-based separation techniques based on the solubilization of organic compounds into the non-polar interior of a micelle or electrostatic attraction of ionized metals and metal complexes to the charged surface of a micelle, i.e., the metal removal by MEUF can be accomplished by forming complexes between metals and micelles and entrapment of complexes by the membrane. The addition of a surfactant to the MEUF system results in releasing some of the surfactants in permeate. Thus, the residual surfactant needs to be treated by another process so as to prevent the secondary pollution, which is good from the economic as well as environmental point of view. Adsorption technology is a common method for the removal of surfactants from aqueous solution and also for the adsorption of residual heavy metals present in permeate in the suitable adsorbent like activated carbon fiber (ACF). As a matter of fact, the MEUF process alone can remove metal to the greater extent, and its efficiency is further enhanced by the integrated approach of using the adsorbent like ACF. Similar results were reported by various authors (Bade and Lee 2008). The CPC removal efficiency of the MEUF-ACF process was found 39% higher than MEUF alone. The chromate removal efficiency was 98.6% and 99.5% respectively for the molar ratio of 1:5 and 1:10 while CPC removal efficiencies were 60.7% and 76.2% respectively. The MEUF-ACF hybrid process improved the removal efficiency of chromate to 98.8% and CPC to 99.9% at the molar ratio of 1:5 (Bade and Lee 2008). A similar result was reported by the other researchers in case copper (Bade and Lee 2007). Similarly, it was reported that over 95% of the SDS from MEUF effluents was removed by two sets of ACF unit at different pH conditions (Guntae and Lee 2011). Thus, the MEUF-ACF hybrid process can be the best alternative for to combat the burning issue of heavy metals pollution of this modernized, industrialized, and concretized world.

17.9 CONCLUSION

To comply with increasing stringent states environmental legislation, the MEUF-ACF hybrid process is the best alternative to combat hazardous heavy metals contaminated wastewater due to higher removal efficiency. The MEUF process is effective for removal of both inorganic and organic contaminants. It has been employed for removal of various sorts of heavy metals, but still ample research has not been done yet regarding it. As the MEUF process generates the surfactant-rich effluent, which is major bottleneck of this process, adsorption technology using ACF as adsorbent is the best remedial measure to overcome this problem.

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CHAPTER 18

Electrocatalytic Membrane Reactor for Industrial Wastewater Treatment: Sustainability and Prospects

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18.1 INTRODUCTION

Industrial wastewater has become a global issue due to its high concentration of pollutants, especially refractory organic compounds (Shannon et al. 2008). Membrane technology has attracted considerable attention in industrial wastewater purification over the past decades owing to its high flexibility regarding water quality and low investment costs. However, inherent membrane fouling caused by concentration polarization and pore blocking leads to low plant reliability and limits wide industrial application in wastewater treatment (Baker 2010). In recent years, with the ever-increasing interest in finding innovative solutions for the efficient treatment of industrial wastewater, applications of electrochemical oxidation have been thoroughly investigated (Martınez-Huitle and Ferro 2006). The inherent advantages of the electrocatalytic oxidation include that the main reagent, the electron is a clean reagent;there is little or no need for addition of chemicals; and no secondary pollution is generated. Therefore, electrocatalytic oxidation has been considered a competitive candidate for industrial wastewater treatment due to its low toxicity and high efficiency. Nevertheless, high operating cost seriously hinders its extensive applications due to the massive energy consumption (Yin et al. 2010).

Membrane-based separation and transport of the pollutant from or toward the reactor increase efficiency of removal and maximize the synergistic effects of

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the reaction and separation. In addition, the membrane used to immobilize a homogeneous catalyst could realize the catalyst recovery, regeneration, and reuse in successive catalytic runs. Electrocatalytic membrane reactor (ECMR) integrated electrochemical oxidation and membrane separation into a single processing step offers an innovative solution to tackle the challenging issues of membrane fouling and high operating cost of traditional electrochemical oxidation in industrial wastewater treatment (Balster et al. 2004). As reported by Yang et al. (2011), ECMR was generally assembled using a tubular conductive electrocatalytic membrane as anode and a stainless steel tube surrounding the membrane as cathode which were connected by a DC regulated power supply. An electrocatalytic membrane was prepared by a nanocatalyst (such as nano-TiO_2) loading the conductive membrane (such as carbon membrane) (Yang et al. 2011). In the ECMR operation, once the membrane anode was electrified, excitation of the nanocatalystled to holes in the valence band and electrons in the conduction band at the nanocatalyst surface. The obtained electrons and holes not only electrochemically decompose H_2O into O_2 and H_2, which induced gas and liquid microflows to reduce concentration polarization and avoid membrane fouling, but can also react with the adsorbed H_2O and O_2 on the TiO_2 surface to generate reactive intermediates such as ·OH, O_2^-, $HO_2\cdot$, and H_2O_2. Those can indirectly decompose the organic foulants on the membrane surface or in the pores into CO_2 and H_2O or biodegradable products. The synergistic effect between membrane separation and electrocatalytic oxidation in the ECMR results in the high performance of pollutant removal as well as antifouling of the membrane (Yang et al. 2011; Zaky and Chaplin 2013).

This chapter focuses on the application of ECMR in wastewater treatment. The concept and types of electrocatalytic membrane materials applied in wastewater treatment are introduced. Design optimization of ECMR for wastewater treatments such as oil water treatment, phenolic wastewater, and dyeing wastewater treatment is discussed. The mechanism of ECMR for wastewater treatment is explored.

18.2 SOURCES/CHARACTERISTICS OF REFRACTORY INDUSTRIAL WASTEWATER

Nowadays, the worldwide production and use of chemical compounds have increased tremendously. Many of these compounds find their way into the environment (e.g., refractory wastewater contaminated with medicine, dyestuffs, pesticides discharged from chemical industries). Refractory wastewater is mainly discharged from coking plants, pharmaceutical factories, refineries, dye factories, etc., and is of a high density of pollutants, poor biodegradability and high toxicity. Table 18.1 provides the typical pollutants and their environmental problems.

The refractory wastewater is recognized as the organics of incomplete and slow degradation, which also includes some organic metabolites. These refractory

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Table 18.1. Typical refractory industrial wastewater contaminates

Industry	*Characteristics of Wastewaters*
Pharmaceuticals	Dissolved and suspendedorganics, including somesurfactants and biological agent
Organic reagent	Dissolved organics, e.g., acids, aldehydes, phenolics and emulsified oils
Petroleum refining	Phenolics and emulsified oils
Plastics andresins	Dissolved organics, including acids,aldehydes, phenolics, cellulose,alcohols, surfactants and oils
Explosives	Organic acids, alcohols, and oils
Rubber and textiles	Dissolved and suspended organics, fats and oils
Leather tanning/ finishing	Dissolved/suspended organics, fats and oils, organic nitrogen

Table 18.2. Problems associated with wastewater pollutants

Pollutant	*Environmental Problem*
Surfactants	Toxicity to aquatic life
Mercaptans,chlorine	Toxicity; odor
Sulfides; sulfates	Toxicity; odor; low pH
Heavy metals	Toxicity to flora, fauna, humans
Toxic compounds	Toxicity to flora, fauna, humans
Phenoliccompounds	Toxicity to flora, fauna, humans; odor
Cyanides	Toxicity to flora, fauna, humans

pollutants can deposit easily into the organisms and have potential to be the main sources of water pollution. Table 18.2 provides the wastewater pollutants and the environmental problems. These refractory pollutants mainly contain cycloparaffin, surfactants, sulfides, halohydrocarbon and organic dyestuff, etc. The common characteristics of these refractory pollutants are toxic, complicated compounds, high chemical oxygen demand (COD) and non-biodegradable. Untreated refractory wastewater severely pollutes the environment and harms human health.

In biological systems for treatment of refractory wastewater, the external environmental conditions (temperature, pH, etc.) usually do not reflect the optimum conditions of biological treatment. Generally, enzymes obtained from the microorganism are unable to decompose these complicated compounds because the chemical compounds in the refractory wastewater are harmful to microorganisms and inhibit the growth of microorganisms. Thus, the organics could not be degraded rapidly. In general, the biological treatment systems are very complicated because of the characteristics of the refractory wastewater, and

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these characteristics can be classified into three major categories, i.e., physical, chemical, and biological characteristics. Each of them is described as follows:

Physical Characteristics. The most important physical properties of refractory wastewater are high solids content, pungent odors and high turbidity (Namour and Muller 1998). The detailed analysis is discussed below:

- The solids content in industrial wastewater varies considerably, depending on the process generating the wastewater. Typically, suspended solids carry a significant portion of organic material, thus significantly contributing to the organic load of the wastewater. Hence, an effective solids removal can significantly contribute to wastewater treatment.
- Odors in refractory wastewaters are typically the result of the emission of gases from the anaerobic decomposition of organic matter contained in the waste. The odorous compounds in wastewater are organic amines and sulfides. For example, hydrogen sulfide is generated under sulfidogenic conditions by desulfobacter hydrogenophilus (using acetate as electron donor):

$$CH_3COO^- + SO_4^{2-} \rightarrow 2CHO_3^- + HS^- \qquad \text{(Eq. 18.1)}$$

$$HS^- + H^+ \leftrightarrow H_2S \qquad \text{(Eq. 18.2)}$$

- The refractory wastewaters have a high turbidity. Turbidity is a measure of the cloudiness of water–the cloudier the water, the greater the turbidity. Turbidity in water is caused by suspended matter such as clay, silt, and organic matter and by plankton and other microscopic organisms that interfere the passage of light through the water. Turbidity is closely related to total suspended solids (TSS), but also includes plankton and other organisms.

Chemical Characteristics. The most important parameters used to characterize the chemical properties of wastewater are organic and inorganic compounds. The most important chemical properties of refractory wastewater are a high concentration of organics and salts (Namour and Muller 1998). The detailed analysis is discussed below:

- The typical high concentration refractory wastewater, such as coking wastewater, pharmaceutical wastewater, printing and dyeing wastewater, and petrochemical wastewater, contains almost 3000–5000 mg/L COD. The COD in some workshop sections even exceed 10000 mg/L. Even after the wastewaters from different workshop sections were mixed, the COD was still up to 2000 mg/L (Wu et al. 2007).
- Generally, the refractory wastewater contains high salt content, which further challenges the process of water purification. For example, typical antibiotic wastewater has about 2000 mg/L, and sometimes 15000 mg/L, of sulphate (Elmolla and Chaudhuri 2011).

Biological Characteristics. The most important biological properties of refractory wastewater are high concentrations of contaminants, their diversity

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and their biotoxicity. For example, coking wastewater contains not only high concentrations of ammonia nitrogen, but also polyphenols, polycyclic aromatic hydrocarbon (naphthalene, anthracene, benzopyrene, etc.), cyanide and sulfide (Lai et al. 2007). Similarly, antibiotic wastewaters contain various bio-recalcitrant and toxic compounds, such as residual antibiotics,intermediate metabolites, surfactant and organic solvent, etc. (Elmolla and Chaudhuri 2011).

On the basis of the discussion above, it is very important to use an efficient and green technology to treat refractory industrial wastewater.

18.3 TYPES OF ELECTROCATALYTIC MEMBRANE MATERIALS

The development of electrocatalytic membrane is a potentially transformative technology that integrates physical separation with electrochemical oxidation. It has many prospective applications in wastewater treatment, owing to its efficiency of wastewater recycling. The current types of electrocatalytic membrane materials are mainly based on conductive porous membrane or electrodes with the loading of some nanocatalysts on the surface. In recent years, a number of electrocatalytic membrane used in wastewater treatment include carbon, TiO_2/carbon, Ti_4O_7, TiO_2 and Ti/boron-doped diamond (BDD) (Yang et al. 2011; Chaplin et al. 2013; Li et al. 2011). Physical and electrochemical characteristics of each type of electrocatalytic membrane is presented as follows:

TiO_2/Carbon Electrocatalytic Membrane. Yang et al. (2011) used a nano-TiO_2 loaded conductive porous carbon membrane as a separation barrier and anode; they used a tubular stainless steel as a cathode and assembled an ECMR with a self-cleaning function. A tubular carbon membrane was employed as the conductive membrane substrate because of its significant mechanical strength, good chemical stability and especially specific conductivity.As a versatile material, TiO_2 is widely used as a catalytic layer of electrodes in treating various industrial wastewater. This is because TiO_2 is excellent in oxidation and reduction, chemically stable, non-toxic, and cheap. Herein, TiO_2 as the electrocatalyst and hydrophilic agent was coated onto the membrane by the sol-gel approach to preparing a TiO_2/carbon membrane to enhance the electron transfer and improve the membrane permeability. For example, the resistance of the TiO_2/carbon membrane was 22 Ω/cm^2, which was much smaller than that of an original carbon membrane (83 Ω/cm^2).

The morphology of TiO_2/carbon membrane characterized by TEM is shown in Figure 18.1a. The original carbon membrane consisted of a uniform graphite-like carbon structure. The average pore size was approximately 0.40 μm obtained by the recommended method. The porosity measured was 32.6% according to the criterion method of China National Standards. TiO_2 particles, which were anatase crystallites with an average crystal size of around 7.8 nm, were well distributed on the membrane surface (Figure 18.1b).

Ti/BDD Electrocatalytic Membrane. Li et al. (2011) considered incomparable electrochemical advantages of the boron-doped diamond (BDD) film electrode

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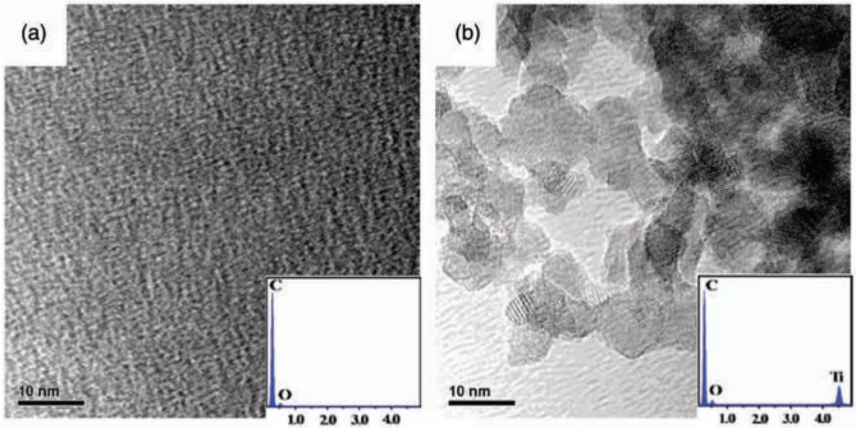

Figure 18.1. High-resolution TEM images: (a) original carbon membrane; (b) TiO_2/carbon membrane

Source: Yang et al. (2011); reproduced with permission from John Wiley and Sons

over conventional electrode as BDD could decompose fouling pollutants deposited on the surface and inner pores of membrane. A new composite membrane Ti/BDD, made by depositing chemical vapor deposition (CVD) boron-doped diamond film on titanium (Ti) membrane to modify porous titanium surface.

As shown in Figure 18.2a, the surface topography of Ti substrate is porous. Its surface is rough, and its internal interconnects form a random three-dimensional network structure. The roughness of the porous Ti membrane surface would increase the surface area and surface energy and provide energy to maintain sp3 carbon structure. Thus, this contributes to the deposition process of diamond nucleation on its surface as well as the growth of diamond (Pleskov et al. 2005) so as to improve nucleation density of diamond film on Ti substrate. Figure 18.2b demonstrates the surface topography of Ti/BDD composite membrane. The pore size of porous Ti substrate became small owning to deposition of BDD. The diamond film covered around the pores evenly. The diamond grains on Ti substrate are spherical shape polycrystalline composed by many small balls, which have the surface like orange peel (Chen et al. 1990).

In addition, the electrochemical performance of the Ti/BDD composite membrane electrode was investigated using cyclic voltammetry (CV). It was found that characteristic voltammetry features of polycrystalline diamond electrodes deposited on porous Ti showed a wide potential range (−1.8 V to +2.2 V) for water stability and low background current.

Ti_4O_7/BDD Electrocatalytic Membrane. More recently, Chaplin et al. (2013) proposed a porous tubular Ti_4O_7 membrane, which is known as substoichiometric titanium dioxide. The conversion of TiO_2 to Ti_4O_7 was accomplished at temperatures above 900 °C and under a H_2 atmosphere. The electrical conductivity of Ti_4O_7 ($166\ \Omega^{-1}\ cm^{-1}$) is many orders of magnitude greater than TiO_2 ($\sim 10^{-9}\ \Omega^{-1}\ cm^{-1}$). The morphology of the Ti_4O_7 membrane surface was

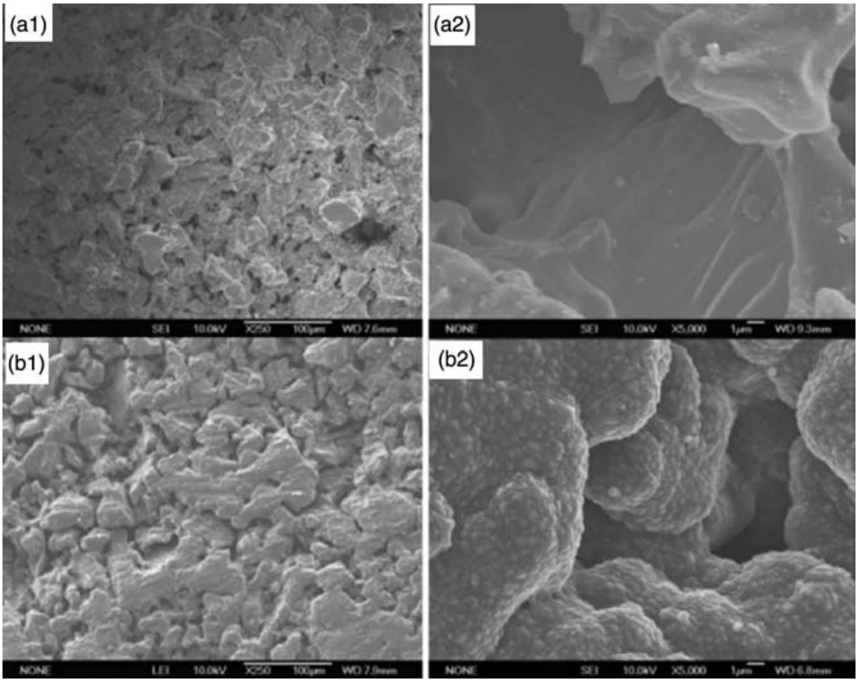

Figure 18.2. SEM of Ti/BDD composite membrane and Ti substrate: (a1) the surface topography of Ti substrate (x250); (a2) the surface topography of Ti substrate (x5000); (b1) the surface topography of Ti/BDD composite membrane (x250); (b2) the surface topography of Ti/BDD composite membrane (x5000)
Source: Li et al. (2011); reproduced with permission from Elsevier

characterized using SEM which showed surficial pore sizes approximately ranging between 1 μm and 6 μm (Figure 18.3). Micron-sized pores dominated the Ti_4O_7 membrane pore volume, which facilitated water transport through the Ti_4O_7 membrane at low applied pressures. Ti_4O_7 membrane with a porosity of 30.7 ± 2.8% (error bars represent 95% confidence intervals), specific surface area of $2.78 \pm 0.7\ m^2\ g^{-1}$, and median pore diameter of 1.7 ± 0.02 μm (based on pore volume data) was obtained. Total surface area of the Ti_4O_7 membrane used in the filtration experiments was $494 \pm 124\ m^2$. The total specific surface area of the micropores was $0.19 \pm 0.01\ m^2\ g^{-1}$, yielding a total microporous surface area of $33.7 \pm 1.8\ m^2$. Further, a porous substoichiometric titanium dioxide (Ti_4O_7) tubular as an anode was used in the filtration mode in order to create a reactive electrochemical membrane (REM) for wastewater treatment. The results showed that 99.9% p-methoxyphenol removal in the permeate, with calculated current efficiencies over 73% at applied current densities of 0.5–1.0 mA/cm^2.

In conclusion, these electrocatalytic membranes have been successfully designed and manufactured for industrial wastewater treatment. It exhibited excellent performance towards wastewater treatment.

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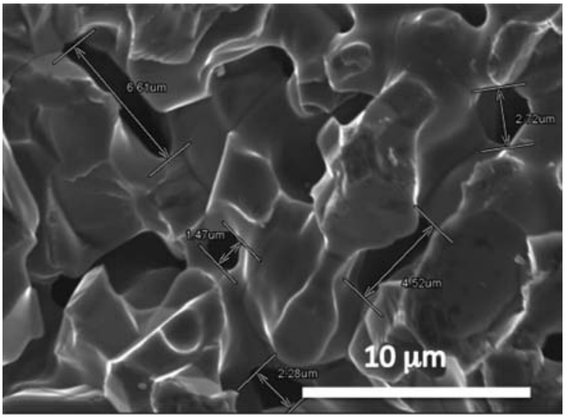

Figure 18.3. SEM image of Ti_4O_7 membrane
Source: Zaky and Chaplin (2011); reproduced with permission from American Chemical Society

18.4 DESIGN OPTIMIZATION OF ECMR IN WASTEWATER TREATMENT

The treatment efficiency of the ECMR is crucially affected by the operating parameters, such as electrode spacing, current density, residence time, the concentration of electrolyte, pH values and temperature, etc. The effect of each parameter on the treatment efficiency of ECMR is further introduced as follows:

Current Density. The current density ($mA{\cdot}cm^{-2}$) is defined as the ratio of the current (mA) to the filtration area of the membrane (cm^2). It represents the rate of electrode reaction, namely the electron transfer rate between the reactant and the electrodes (Santos et al. 2002). When the current density was increased, the rate of electron transfer increased, thus resulting in an increase in the reactive intermediates such as $\cdot OH$, O_2^-, $HO_2\cdot$, and H_2O_2 (He et al. 2009), which could indirectly decompose the organic foulants on the membrane surface or in the pores into CO_2 and H_2O or biodegradable products. However, an enormous current density would exacerbate the hydrogen and oxygen evolutions in the solution, leading to the decrease of COD removal (Marsen 1993). In addition, on the basis of the energy consumption, the energy cost increased linearly with the increase of the current density. Thus, an appropriate current density is crucial for the efficient and sustainable operation.

Electrode Spacing. The electrode spacing is defined as the distance between the anode and cathode electrodes. The electrode spacing mainly affects on the resistance and the distribution of the electric field in the electrolytic cell, thus affecting the reaction rate and energy cost. In general, the reaction efficiency and the power density increased with a decrease in distance between the electrodes (Ghangrekar and Shinde 2007). However, the COD removal for the ECMR to treat

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wastewater first increased, then decreased with an increase in the electrode spacing. The reason was that when the electrode spacing was smaller, the excited electrons aggregated on the surface of the electrode, thus leading to electroflotation and restraining the degradation reaction (Matsumoto 2004). On the other hand, a massive electrode spacing results in an increase in mass transfer resistance and a decrease in the reaction rate. Meanwhile, the obtained electrons and holes react with the adsorbed H_2O to trigger hydrogen and oxygen evolution reactions. The tiny bubbles of hydrogen and oxygen gases generated from water electrolysis restrained the contact between the organic matter and ·OH, leading to a decrease in COD removal.

Concentration of Electrolyte. It is of great importance for adding electrolyte into the wastewater with poor conductivity. On the one hand, increasing the concentration of electrolyte in the electrocatalytic system could increase the number of ions and promote electron transfer (Comninellis 1994). The COD removal of the ECMR increased with an increase in the concentration of electrolyte. On the other hand, the larger concentration of electrolyte increases interactions between ions and then reduces the conductivities (Fujishima and Honda 1972). In addition, it could further intensify hydrogen and oxygen evolution reactions on the surfaces of electrodes. Thus, too large concentration of electrolyte actually decreased the COD removal of organic matters.

Residence Time. As a critical parameter in ECMR, residence time is relative to the reaction time and degradation efficiency of organic matters. The residence time is defined as the ratio of the volume of membrane pore (cm^3) to the flow rate of solution (mL/min) (Li et al. 2013). It represents the reaction time between the foulants and the excited ·OH on the surface of the electrode (Mehmet et al. 2011). But the catalytic efficiency could not increase linearly with an increase of the residence time. On the one hand, the higher residence time can fully decompose the foulants into CO_2 and H_2O or biodegradable products. On the other hand, too long resident time intensified the concentration polarization on the membrane surface (Myint et al. 2011). It could reduce the diffusion of organic molecules onto the membrane surface per unit time, thus resulting in the decrease of degradation efficiency. Meanwhile, a higher resident time would result in potentially high capital cost and a large reactor footprint.

pH. In general, pH influences the catalytic activity of heterogeneous catalysis in wastewater treatment (Corma et al. 2007). The optimum pH value is mainly related to the electrocatalyst. For example, when the titanium dioxide (TiO_2) is used as a catalytic layer of the electrodes in phenolic wastewater treatment, the optimum pH value ranges from 5.8 to 6.8. This behavior is attributed to the amphoteric character of TiO_2 (Calza and Pelizzetti 2001). In electrocatalysis, the adsorbed H_2O molecules on TiO_2 catalyst is dissociated to generate hydroxy radical, leading to the coverage of chemically equivalent metal hydroxyl groups (Ti-OH) on the surface of TiO_2 (Eq. 18.3–18.4). The isoelectric point (pI) of common TiO_2 is 6.3 (Jaffeezia-renault and Pichat 1986). When the pH was less than pI, there mainly existed $TiOH_2^+$ on the

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surface of TiO_2. When the pH was higher than pI, there was more Ti-OH to be transformed into TiO^- on the surface of TiO_2. A variety of negatively charged intermediates including maleic acid, oxalic acid, etc. would be generated in the degradation process of phenol. The negatively charged intermediates were easily adsorbed by TiO_2 catalyst at pH < pI, owing to the electrostatic interaction between the charged surface of TiO_2 and the protonated intermediates. Hence, a relatively high COD removal efficiency was achieved in an acidic condition.

$$\mathrm{TiOH_2^+} \leftrightarrow \mathrm{TiOH} + \mathrm{H^+} \mathrm{pH} < \mathrm{pI} \qquad \text{(Eq. 18.3)}$$

$$\mathrm{TiOH} \leftrightarrow \mathrm{TiO^-} + \mathrm{H^+} \mathrm{pH} > \mathrm{pI} \qquad \text{(Eq. 18.4)}$$

Temperature. The reaction temperature plays a key role in the reaction. A higher reaction temperature promoted the collision between reactants and catalyst, resulting in the increase of the reaction rate (Simon and Gogotsi 2008). However, the increasing temperature is not preferred for COD removal. The reason is that too high temperature would induce the aggravation of the oxygen evolution reaction in the membrane anode (Liu and Vecitis 2012). The gas bubbles generated on the membrane would reduce the active electrode surface area and hindered the interfacial oxidation between pollutants and catalyst (Bermejo et al. 2008). Indeed, a high temperature would increase the energy cost. Moreover, the dissolved oxygen in the solution decreased with the continuous increase of temperature, resulting in the decrease of the reactive intermediates ·OH.

In order to optimize the ECMR processes, it is desirable to develop an acceptable process in shortest possible time using a minimum number of laborers, hours, and raw materials. Response surface method (RSM) was proposed to determine the influences of individual factors and their interactive influences. RSM is considered to be an effective means to design experiments that help to reduce the number of experimental trials, to evaluate the relative significance of variables and their interactions, and to build models. Recently, Zhang (2012) successfully employed the RSM to determine optimum parameters during treatment of 200 mg/L oil wastewater. It was found that the COD removal rate was 97.5% at the current density of 0.31 mA/cm^2 and the residence time of 3.8 min. Furthermore, Guan et al. (2013) optimized the operating parameters of the ECMR for the treatment of 940 mg/L phenolic wastewater by (RSM) (Figure 18.4). Figure 18.4 shows that two variables of residence time and current density have a significant effect on the COD removal efficiency of phenolic wastewater. The removal rate of COD would be 82.23% at the optimized conditions: current density of 0.33 mA/cm^2, the residence time of 4.77 min, pH of 5.56, and temperature of 36.6°C. Thus, the ECMR exhibited high treatment efficiency for the refractory industrial wastewater under optimum operating conditions.

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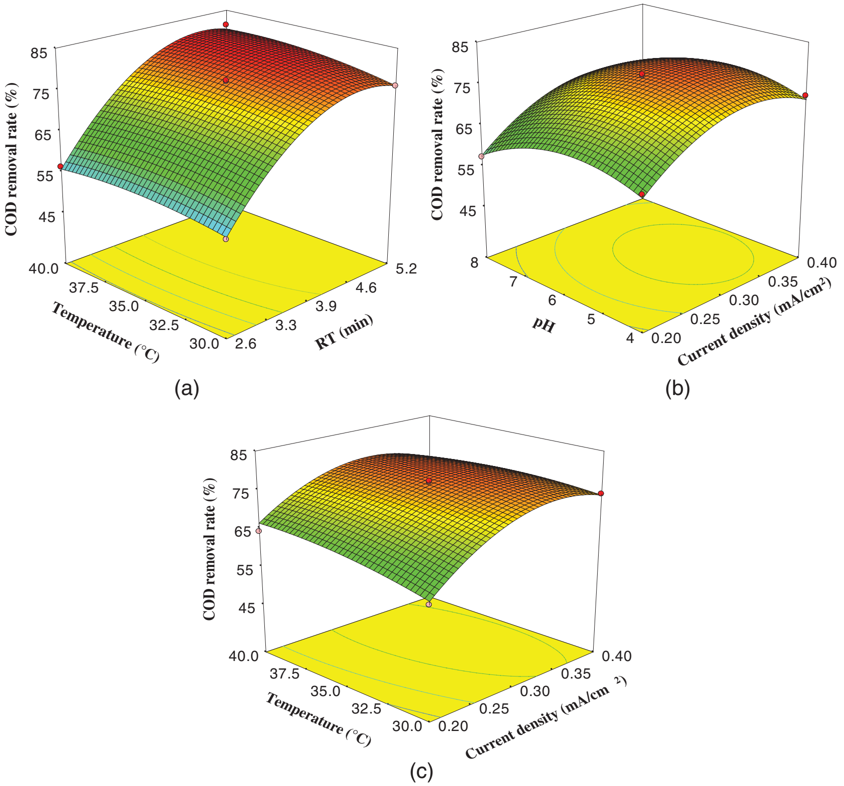

Figure 18.4. 3D surface map of COD removal rate under different conditions (a) the temperature and residence time (RT); (b) the pH and current density; (c) the temperature and current density

Source: Guan et al. (2013); reproduced with permission from *Journal of Water Sustainability*

18.5 ECMR FOR INDUSTRIAL WASTEWATER TREATMENT

To investigate the properties of electrocatalytic membrane, this section describes the ECMR for the treatment of oily, phenolic and dyeing wastewater. Before introducing the technologies, some terminologies concerned by electrochemical process engineers are reviewed.

Kinetic Analysis. The most frequently referred terminology besides potential and current may be the current density (i), i.e. the current per area of the electrode (Santos et al. 2002). It determines the rate of a process. The next parameter is current efficiency (CE), i.e. the ratio of current consumed in producing a target product to that of total consumption (Da Silva et al. 2003). Current efficiency indicates both the specificity of a process and also the performance of the electrocatalysis involving surface reaction as well as mass transfer. A parameter termed liquid hourly space velocity (LHSV) is used to describe the relationship

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between electrocatalytic residence time in ECMR and the COD removal efficiency (Weekman and Nace 1970). LHSV is the ratio of volumetric feed rate per hour to the catalyst volume. Herein, LHSV (h^{-1}) is defined as the ratio of the hourly volume of permeate (mL/h) to the volume of membrane reactor (cm^3). These relevant parameters can be calculated with the following equations (Simond et al. 1997).

The removal rates of compound i from the permeate ($r_{P,i}$) is calculated as:

$$r_{P,i} = J(C_{F,i} - C_{P,i}) \tag{Eq. 18.5}$$

where J is the permeate flux (L/m^2-h); $C_{F,i}$ and $C_{P,i}$ are the concentration of the feed and permeate, respectively (mmol/L). The percent removal (R_i) in the permeate is calculated as follows:

$$R_i = \frac{(C_{F,i} - C_{P,i})}{C_{F,i}} * 100 \tag{Eq. 18.6}$$

The current efficiency of the permeate ($CE_{p,i}$ (%)), current directed toward oxidation of the substrate that passes through the electrocatalytic membrane, is calculated as:

$$CE_{P,i} = \frac{JF_Z(C_{F,i} - C_{P,i})}{j} * 100 \tag{Eq. 18.7}$$

where j is the applied current density (A/m^2). The current efficiency related to the oxidation of compounds recycled in the feed ($CE_{F,i}$ (%)) is calculated as:

$$CE_{F,i} = \frac{F_Z r_{F,i}}{j} * 100 \tag{Eq. 18.8}$$

where $r_{F,i}$ is the removal rate in the feed determined by linear regression of concentration profiles with time. The overall current efficiency ($CE_{O,i}$ (%)) is determined by summation of $CE_{P,i}$ and $CE_{F,i}$. The overall current efficiency for COD removal (CE_{COD} (%)) is calculated as:

$$CE_{COD} = \frac{FV(COD_{ox,f})}{8jA\Delta t} * 100 \tag{Eq. 18.9}$$

where $COD_{ox,f}$ is the concentration of COD oxidized during a given experiment ($g\,L^{-1}$); V is the solution volume (L); Δt is the time of the experiment (s); and 8 is a dimensionless conversion factor. The space-time yield, Y_{ST}, of a reactor is defined as the mass of product produced by the reactor volume in unit time with

$$Y_{ST} = \frac{iaM}{1000zF} CE \tag{Eq. 18.10}$$

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Table 18.3. Sources of oily wastewater

Industrial process	*Oil concentration (mg/L)*
Hot rolling	20
Cold rolling	700
Aluminum rolling	5000–50000
Cold rolling coolant	2088–48742
Can production (forming)	200000
Food processing (fish and seafood)	520–13700
Rendering	14–3551
Metal finishing	4000–6000
Tanning waste, hide curing	40200
Wool scouring	1605–12260
Petroleum refinery	10–3200

Source: Cheryan and Rajagopalan (1998); reproduced with permission from Elsevier

The space-time yield gives an overall index of a reactor performance, especially the influence of the specific electrode area (A).

18.5.1 Treatment of Oily Wastewater

Oily wastewater is generated in many industrial processes, such as petroleum refining, petrochemical, food, leather and metal finishing (Table 18.3). These oily waters are mainly in the form of oil-in-water (O/W) emulsions that pose a significant problem in facilities attempting to stay in compliance with discharge limits. Typical limits for oil and grease discharges range from 10 to 15 mg/L for mineral and synthetic oils and 100–150 mg/L for those of animal and vegetable origin (World Bank 1999).

The conventional treatment methods such as gravity separation and skimming, dissolved air flotation, demulsifying, coagulation and flocculation are frequently inefficient to solve the problem, especially when the oil droplets are finely dispersed and their diameters are less than 20 μm. Therefore, some new technologies have been developed. Among them, membrane separation and electrochemical technique have enjoyed great popularity for the treatment of oily effluents over the last 30 years and are becoming a promising technology.

The membrane separation technology has several advantages including high oil removal efficiency, low energy cost, no chemical additives and small space occupancy. In past years,many studies of membrane separation for oily wastewater treatment have been reported (Li et al. 2006), particularly in ultrafiltration (UF) and reverse osmosis (RO) with organic membranes and inorganic ceramic membranes. However, inherent membrane fouling caused by concentration polarization and pore blocking leads to low plant reliability and limits wide industrial application in oily wastewater treatment.

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Apart from membrane technology, electrochemical technologies, with their low toxicity and high efficiency, have been considered competitive candidates for industrial wastewater treatment. Using electricity to treat water was first proposed in England in 1889 (Webster 1889). The application of electrolysis in mineral beneficiation was patented by Elmore in 1904 (Elmore 1904). Electrocoagulation (EC) with aluminum and iron electrodes was patented in the United States in 1909. The EC of drinking water was first applied on a large scale in the United States in 1946. Electrochemical water or wastewater technologies did not find wide application worldwide then because of the relatively large capital investment and the expensive electricity supply.

Nowadays, electrochemical and membrane technologies have reached such a state that they are not only comparable to other technologies in terms of cost but also are more efficient and more compact. For some situations, electrochemical and membrane technologies may be the indispensable step in treating wastewaters containing refractory pollutants. In order to overcome membrane fouling and high electricity cost, the development of an ECMR is a potentially transformative technology that integrates physical separation with electrochemical oxidation.

Electrocatalytic and Separation Properties. Recently, Yang et al. (2011) used the ECMR to treat 200 mg/L of oily water under 2.0 V supply voltage and 10.0 mA. The electrocatalytic membrane in an ECMR showed the excellent antifouling performance compared to the carbon membrane and TiO_2/carbon membrane. The permeate fluxes of both the original carbon membrane and the TiO_2/carbon membrane declined rapidly with increasing operation time, especially in the case of the former, due to heavy membrane fouling caused by concentration polarization and pore blocking. The permeate flux decreased to 19.4% of the pure-water flux (122.6 $L/m^2 \cdot h \cdot bar$) for the original carbon membrane and 48.8% of the pure-water flux (401.3 $L/m^2 \cdot h \cdot bar$) for the TiO_2/carbon membrane after 200 min of operation. At the same time, the removal rates of oil and COD were 68.0% and 58.6% for the original carbon membrane and 78.6 and 83.7% for the TiO_2/carbon membrane, respectively (Figure 18.5B). However, the electrocatalytic membrane in the ECMR showed only a slight drop of 9.6% in permeate flux (Figure 18.5A). The removal rates of oil and COD were up to 86.2% and 94.4%, respectively (Figure 18.5B). After 200 min of operation, the permeate flux of the electrocatalytic membrane was 15.2 and 1.85 times higher than those of the original carbon membrane and TiO_2/carbon membrane, respectively. The electricity consumption for this membrane reactor was 0.166 kW·h per ton of water. It indicates that the electrocatalytic membrane has very strong antifouling ability. It also implies that there is a synergistic effect between membrane separation and electrocatalytic oxidation in the ECMR.

The gas chromatography-mass spectrometer (GC-MS) was used to investigate the synergistic effect of ECMR. GC-MS analyzed the composition of feed and permeate as shown in Table 18.4. Table 18.4a shows that the oil feed included about 28 kinds of organic matters. 14 and 10 kinds of organic substances remained in permeate obtained from original carbon membrane and TiO_2/carbon membrane (Table 18.4a and b). The rejection of TiO_2/carbon membrane was a little bit

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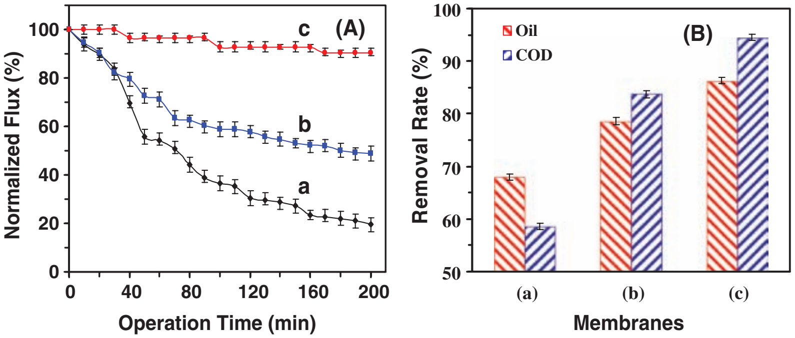

Figure 18.5. (a) Changes in the permeate flux of membranes; (b) removal rates of oil and COD: (a) original carbon membrane; (b) TiO_2/carbon membrane; (c) electrocatalytic membrane in ECMR

Source: Yang et al. (2011); reproduced with permission from John Wiley and Sons

Table 18.4(a). Composition analysis of oil feed and permeate of original carbon membrane

	Area (%)		
Peak	*Oil feed*	*Permeate*	*Library/ID*
1	2.7135	2.7135	Octane, 4-methyl-
2	1.7927	1.7927	p-Xylene
3	6.4087	6.4087	Benzene, 2-ethyl-1,4-dimethyl-
4	3.7546	3.7546	Benzenemethanol,. alpha.,.alpha.-dimethyl-
5	4.5852	4.5852	Hexane, 3,3-dimethyl-
6	11.6208	11.6208	Phytol
7	3.8652	3.8652	Tetradecane
8	7.5098	7.5098	Naphthalene, 1,2,3,4-tetrahydro-1,4-dimethyl-
9	8.0311	8.0311	13-Tetradecenal
10	9.2394	9.2394	Oxalic acid, cyclobutyl heptadecyl ester
11	8.3499	8.3499	Nonahexacontanoic acid
12	17.6942	17.6942	Hexadecane
13	9.6308	9.6308	Heptafluorobutyric acid, n-pentadecyl ester
14	4.804	4.804	Didodecyl phthalate

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higher than that of original carbon membrane. It was related to the enhanced hydrophilicity of TiO_2/carbon membrane as previously indicated. By contrast, only a small amount of three small molecules remained in permeate obtained by the electrocatalytic membrane and might be the products of electrocatalytic oxidation (Table 18.4c). The contents of which could be calculated from the

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Table 18.4(b). Permeate composition analysis of TiO_2/carbon membrane

Peak	*Area (%)*	*Library/ID*
1	29.3096	o-Xylene
2	3.2056	p-Xylene
3	5.6609	Propanoic acid, 2-methyl-, 3-methylbutyl ester
4	20.6489	Benzene, 1,3-diethyl-
5	17.375	Benzene, 1,4-diethyl-
6	11.8454	Benzene, 1,2-diethyl-
7	3.0267	2,6-Dimethylphenyl isocyanate
8	2.777	Ether, hexyl pentyl
9	2.522	Oxalic acid, allyl nonyl ester
10	3.629	Didodecyl phthalate

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Table 18.4(c). Permeate composition analysis of electrocatalytic membrane in ECMR

Peak	*Area (%)*	*Library/ID*
1	85.4525	dimethyl-
2	5.6889	Benzene, 1-isocyanato-4-methyl-
3	8.8585	N-Methyl-o-toluidine

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peak areas of permeate and were negligible as compared with that in the feed. Therefore, it further confirmed that the higher electrocatalytic activity of electrocatalytic membrane would decompose the foulants into CO_2 and H_2O, or small biodegradable products.

To further investigate the removal efficiency of ECMR, the ECMR was extensively used to treat 200 mg/L, 500 mg/L, and 1000 mg/L oily wastewater under different liquid hourly space velocities (LHSV) (Yang et al. 2012). As shown in Figure 18.6, the COD removal rate was 91.0% at a LHSV of 21.6 h^{-1} during the treatment of 1000 mg/L oily water. Although the COD removal rate decreased from 100% to 93.1% with an increase in the oily concentration from 200 to 1000 mg/L at a LHSV of 7.2 h^{-1}, there was no remarkable effect of the oily concentrations on the COD removal rate during ECMR operating. Further, Figure 18.6 shows that the COD removal rate was influenced by the LHSV in the ECMR. The removal rate increased with the decrease of LHSV values. The COD removal rate was 100% with a LHSV of 7.2 h^{-1} and 87.4% with a LHSV of 21.6 h^{-1} during the treatment of 200 mg/L oily water (Figure 18.6). Their corresponding residence time (reciprocal of LHSV) was about 0.14 and 0.05 h in a unit reactor volume, respectively. Apparently, the ECMR with a lower LHSV

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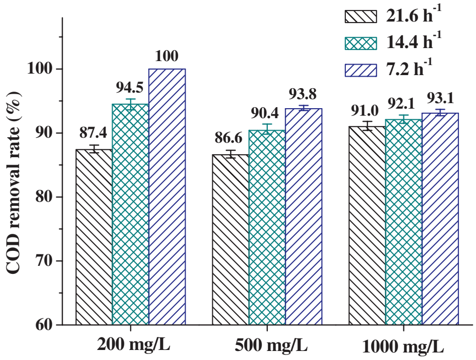

Figure 18.6. COD removal rates by the electrocatalytic membrane with different LHSV values in the treatment of 200 mg/L, 500 mg/L and 1000 mg/L oily wastewater

Source: Yang et al. (2012); reproduced with permission from American Chemical Society

or a longer residence time would provide a complete degradation of organic pollutants. The electricity consumption for this membrane reactor was 0.11, 0.17, and 0.33 kw·h per ton of water with a LHSV of 21.6, 14.4, and 7.2 h^{-1} under the above conditions, respectively. The reason for this phenomenon was that a lower permeate flux leads to a longer residence time. The longer the residence time is, the longer the oxidation process is. Hence, the more completely the pollutants are degraded. This was ascribed to the synergistic effect between membrane separation and electrocatalytic oxidation in the ECMR. The mechanism of ECMR for wastewater treatment would be particularly discussed in Section 18.6.

During the preparation of electrocatalytic membrane, a coal-based carbon membrane was employed as the conductive membrane substrate because of its significant mechanical strength, good chemical stability, and specific conductivity. However, the hydrophobic properties of coal-based carbon membranes result in low permeate flux which hinders their application in organic wastewater treatment and separation. To improve their hydrophilicity, Chen et al. (2013) used different acids to modify the coal-based carbon membranes so as to enhance its permeability. It showed that the hydrophilicity of coal-based carbon membranes modified with H_2O_2 and HNO_3 had been improved by increasing the content of surface oxygen groups such as hydroxyl groups and carboxylic groups, etc. The pure-water fluxes of coal-based carbon membranes modified with H_2O_2 and HNO_3 increased by 128.6% and 71.5%, in comparison with the original carbon membrane. In addition, there were little changes in the oil and COD rejection of the modified carbon membrane, which almost reached 95% and 88%, respectively.

18.5.2 Treatment of Phenolic Wastewater

Phenols and their derivatives are well known for their bio-recalcitrant and acute toxicity (Ahmed et al. 2010). The major sources of phenols in wastewater are the

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processing and manufacturing industries engaged in oil refining, coal tar processing, petrochemical production, coke manufacture, plastic industry, textile processing, leather processing, insecticides production, manufacture of dyes and dyeing, glass production, etc. Further, their variety, toxicity, and persistence can directly impact the health of ecosystems and present a threat to humans through contamination of drinking water supplies e.g., surface and ground water. Thus it has become a challenge to achieve the complete removal of persistent organic pollutants from wastewater effluent to minimize the risk of pollution problems from such toxic chemicals and to enable its reuse. Consequently, considerable efforts have been devoted to developing a suitable purification method that can easily destroy these bio-recalcitrant organic contaminants.

The choice of treatment depends on effluent characteristics such as the concentration of phenol, pH, temperature, flow volume, biological oxygen demand, the economics involved and the social factor like standard set by government agencies. In the last 20 years, several physicochemical and biological treatments have been suggested to efficiently remove these compounds such as adsorption with bone char or zeolites, stripping with air or steam, membrane technologies, wet air oxidation or biological treatments with pure or mixed cultures of microorganisms (Dosta et al. 2011). But the conventional wastewater purification systems also generate wastes during the treatment of contaminated water, which requires additional steps and cost.

During the past decades, electrocatalytic oxidation with low toxicity and automatic control has been considered as a competitive candidate for industrial wastewater treatment (Zhu et al. 2007). Electrochemical oxidation is an emerging advanced oxidation process, where water is oxidized to OH· on the anode surface. These OH· react unselectively with a wide range of recalcitrant organics, often at diffusion-limited rates.

Recently, Guan et al. (2013) used ECMR to treat phenolic wastewater using TiO_2/carbon electrocatalytic membrane as the porous electrode materials. In this study, a synthetic phenol wastewater as the feed was prepared by mixing 10.0 mmol/L phenol and electrolyte (Na_2SO_4) with the concentration of 15 g/L. A systematic experimental design based on the response surface methodology was used to optimize the operating conditions of ECMR. The removal rate of COD obtained by the model would be 82.23% at the optimized conditions: current density of 0.33 mA/cm^2, residence time of 4.77 min, pH of 5.56, and temperature of 36.65°C. The COD removal rate obtained by the experiment was 82.31%. The experimental results were in good agreement with the predicted value obtained.

To investigate the electrocatalytic properties of ECMR, the phenolic wastewater with different concentrations (2.0, 5.0, and 10.0 mmol/L) was treated by ECMR at the optimal operating conditions obtained. The results showed that the COD removal efficiency decreased from 92.12% to 82.31% with an increase in the phenol concentration in wastewater from 2.0 to 10.0 mmol/L, which was resulted from the utilization efficiency of reactive intermediates (Zhou and He 2008). In addition, the EC declined sharply from 1.45 to 0.32 kWh/kg COD with an

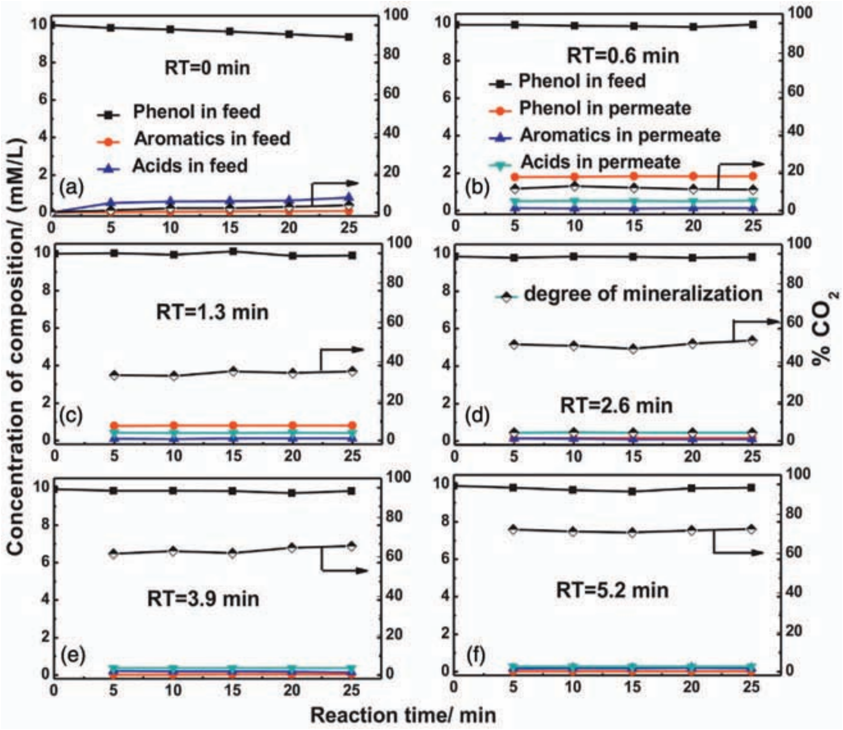

Figure 18.7. The effect of residence time on the degradation of substances during the phenolic wastewater treatment by ECMR

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increase in the phenol concentration from 2.0 to 10.0 mmol/L. This phenomenon could also be explained by the utilization efficiency of reactive intermediates. A higher phenol concentration promotes the collision between reactive intermediates and reactants, leading to the increase of the electrocatalytic efficiency.

Besides, Wang et al. (2014) further investigated the ECMR efficiencyand the changes on the concentrations of degraded intermediates with residence time using High-performanceliquid chromatography (HPLC), so as to illustrate the mechanism of phenol degradation. Results showed that the main intermediate products of phenol degradation included benzoquinone and organic acids. The efficiency and the degraded intermediates could becontrolled by the main parameters of ECMR such as residence time, current density, etc. (Figure 18.7).

As shown in Figure 18.7, when the residencetime (RT) was 0 min, the ECMR is similar to a conventionalelectrocatalytic reactor.Although aromatics and organic acid weregenerated from the phenol degradation during the ECRM operationat the residence time of 0 min, their concentrations were quitelow during the operation of 25 min.An interesting phenomenon wasthat the concentration of

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phenol and aromatics in the permeategradually decreased with increasing RT (Figure 18.7). Especially, the concentration of phenol in the permeate decreases from 2 to 0 mM/L when RT increased from 0.6 to 5.2 min (Figure 18.7b–f). This is to say thatphenol was completely or partly mineralized into CO_2 at an RT of 5.2 min, leading to the generation of the maximum CO_2 concentration (Figure 18.7f). Therefore, during the ECMRoperation under the conditions of 10.0 mmol/L phenolic wastewater, pH of 6, current density of 0.3 $mA/cm^2$and residence time of 5.2 min, the achieved phenol removal rate and complete mineralization fractionwere 99.96% and 72.4%, respectively.

Unlike the depositing TiO_2 photocatalyst on aconductive porous membrane surface as anode, Zaky and Chaplin (2013) used a porous substoichiometric titanium dioxide (Ti_4O_7) tubular as anode to treat p-methoxyphenol (p-MP). Firstly, according to the mass transfer analysis, mass transfer rates obtained in the filtration mode is the order of a 10-fold increase compared to that in the traditional flow-through mode. Secondly, the oxidation experiments with p-methoxyphenol showed that the reactive electrochemical membrane was active for both direct oxidation reactions and formation of hydroxyl radicals (OH·). The compound removal occurred by electro-assisted adsorption and subsequent oxidation. In addition, on the basis of the experimental data, a preliminary mechanism for p-MP removal during REM filtration experiments is proposed. Electro-assisted adsorption was the primary removal mechanism at potentials where OH· did not form. At higher potentials (>2.0 V), where OH· concentrations were significant, p-methoxyphenol removal occurred by a combination of electro-assisted adsorption and OH· oxidation. Thus, these removal mechanisms resulted in 99.9% p-methoxyphenol removal in permeate, with calculated current efficiencies >73% at applied current densities of 0.5–1.0 mA/cm^2. Indeed, details are needed about the validity of this model for the oxidation of other refractory organic compound.

18.5.3 Treatment of Dyeing Wastewater

Textile processing industries nowadays are widespread sectors in developing countries. Among the various processes in the textile industry, dyeing process uses a large volume of water for dyeing, fixing and washing processes. Thus, the wastewater generated from the textile processing industries contains suspended solids, high amount of dissolved solids, unreacted dyestuffs (color) and other auxiliary chemicals that are used in the various stages of dyeing and processing. The conventional method of textile wastewater treatment consists of chemical coagulation, biological treatment followed by activated carbon adsorption. The conventional coagulation process generates a huge volume of hazardous sludge and poses a problem of sludge disposal. The biological treatment of textile wastewater showed low degradation efficiency because of the presence of biologically inert high-molecular-weight dyestuffs. Hence, many investigators are studying Advanced Oxidation Processes (AOPs) as alternative techniques for destruction of dyes and many other organics in wastewater and effluents (Stasinakis 2008).

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Table 18.5. Advanced oxidation processes available in dyeing wastewater

Photocatalysis degradation	*Titanium dioxide*
Ozone	Catalytic oxidation
Hydrogen peroxide	Fenton's reactions

The main mechanism of AOPs function is the generation of highly reactive free radicals. Hydroxyl radicals (OH·) are effective in destroying organic chemicals because they are reactive electrophiles (electron preferring) that react rapidly and nonselectively with nearly all electron-rich organic compounds. A great number of methods are classified under the broad definition of AOPs (Table 18.5). Most of them use a combination of strong oxidizing agents (e.g., H_2O_2, O_3) with catalysts (e.g. transition metal ions) and irradiation (e.g., ultraviolet, visible light). Among different available AOPs producing hydroxyl radicals, photocatalysis degradation, titanium dioxide/UV light process, hydrogen peroxide/UV light process and Fenton's reactions seem to be some of the most popular technologies for wastewater treatment as shown by the large amount of data available in the literature. However, these advanced oxidation processes are often limited to the less COD removal and low efficiency.

In recent years, electrocatalytic oxidation with low toxicity and automatic control has been considered a competitive candidate for industrial wastewater treatment. Several researchers have studied the feasibility of electrochemical degradation of textile dyes using various electrode materials for wastewater treatment. Electrochemical degradation of different dye compounds was studied using titanium-based DSA electrodes (Szpyrkowicz et al. 2000), platinum electrode (Sanromán et al. 2004), diamond and metal alloy electrodes (Rivera et al. 2004) and boron-doped diamond electrodes (Chen et al. 2003). However, high energy consumption hinders their extensive application.

Recently, the ECMR assembled using a nano-TiO_2 loading microporous carbon membrane as an anode and a tubular stainless steel as a cathode was extensively used for the treatment of dyeing wastewater. In this study, a synthetic dyeing wastewater as the feed was prepared by mixing 200 mg/L methylene blue and electrolyte (Na_2SO_4) with the concentration of 10 g/L at the current density of 0.3 mA/cm^2 and residence time of 3.9 min. The treatment of methylene blue solution with the electrocatalytic membrane was shown in Figure 18.8. As shown in Figure 18.8, clearly, the decolorization rate of the dye wastewater was nearly up to 100%; The characteristic peaks of thiophene oxazine compounds (290 nm) and the chromophore (667 nm) completely disappeared after being treated with ECMR. It indicated that the electrocatalytic membrane had excellent performance for the degradation of organic matter in methylene blue solution. In addition, after 600 min operation, the removal rate of the chromophore remained 99.9%, and that of thiophene oxazine compounds decreased slightly from 99% to 94%. It exhibited good anti-fouling ability for dye wastewater.

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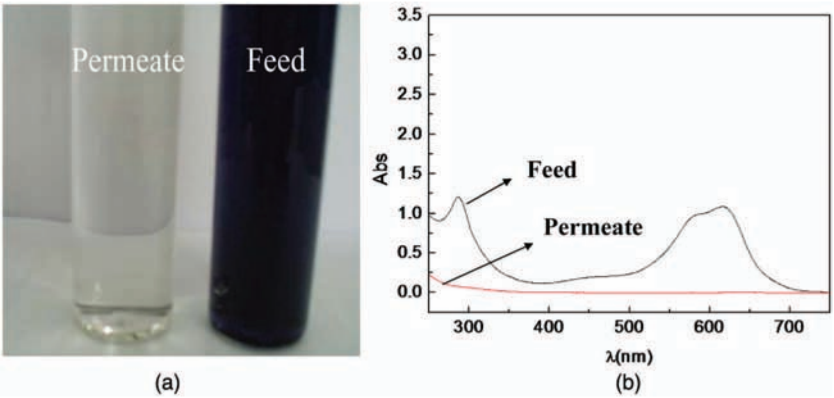

Figure 18.8. The treatment of methylene blue solution with the electrocatalytic membrane: (a) color changes; (b) ultraviolet spectra of feed and permeate

18.6 MECHANISM OF ECMR FOR WASTEWATER TREATMENT

A mechanism for the electrochemical oxidation of organics in the ECMR is based on intermediates of oxygen evolution reaction in aqueous media. The process involves anodic oxygen transfer from H_2O to organics via hydroxyl radicals formed by water electrolysis. During the operation of the ECMR, the organic pollutants in the wastewater can occur directly at the anodeof ECMR through the generation of physically adsorbed "active oxygen," such as $\cdot OH$, O_2^-, $HO_2\cdot$ and $H_2O_2\cdot$ or chemisorbed "active oxygen" (oxygen in the oxide lattice, MO). This process is usually called "anodic oxidation" or "direct oxidation," and the course of the anodic oxidation was described by Comninellis (1994). A mechanism of the electrochemical conversion/combustion of organics on oxide anode (M) was presented by several researchers (Vlyssides et al. 2004; Martinez-Huitle and Ferro 2006; Wang et al. 2012).

In the first step (Eq. 18.11), the oxidation of water molecules resulted in the formation of adsorbed hydroxyl radicals ($^{\cdot}OH$). M in all equation is the metallic oxide on oxide anode. In the second step (Eq. 18.12), the adsorbed hydroxyl radicals may interact with the anode, forming a higher oxide MO (oxygen in the oxide lattice).With active electrodes, the redox couple MO/M acts as a mediator in the oxidation of organics (Eq. 18.13).This reaction is in competition with the side reaction of oxygen evolution owing to the chemical decomposition of the higher oxide (Eq. 18.14).The oxidative reaction via the surface redox couple MO/M (Eq. 18.13) may be much more selective than the reaction involving hydroxyl radicals (Eq. 18.15).With a non-active electrode, weak interactions exist between the hydroxyl radical and the electrode surface. In this case, the oxidation of organics is mediated by hydroxyl radicals (Eq. 18.15) and may result in fully oxidized reaction products such as CO_2. In the above schematic equation, R is a fraction of an organic compound containing no heteroatom, which needs one

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oxygen atom to be entirely transformed into CO_2. This reaction competes with the side reaction of hydroxyl radicals to oxygen (Eq. 18.16) without any participation of the anode surface.

$$M + H_2O \rightarrow M(\cdot OH) + H^+ + e^- \qquad \text{(Eq. 18.11)}$$

$$M(\cdot OH) \rightarrow MO + H^+ + e^- \qquad \text{(Eq. 18.12)}$$

$$M + RO \rightarrow MO + R \qquad \text{(Eq. 18.13)}$$

$$MO \rightarrow M + 1/2O \qquad \text{(Eq. 18.14)}$$

$$M(\cdot OH) + R \rightarrow M + mCO_2 + nH_2O + H^+ + e^- \qquad \text{(Eq. 18.15)}$$

$$M(\cdot OH) \rightarrow M + 1/2O_2 + H^+ + e^- \qquad \text{(Eq. 18.16)}$$

The electrochemical activity and chemical reactivity of adsorbed $^{\cdot}OH$ are strongly linked to the strength of the M-$^{\cdot}$OH interaction.Generally, the weaker the interaction, the higher the anode reactivity for organics oxidation. This model assumes that the electrochemical oxidation is mediated by hydroxyl radicals, either adsorbed at the surface (in the case of active electrodes) or free, in the case of the non-active ones.

As mentioned in the introduction section, the ECMR integrates electrochemical oxidation and membrane separation into a single processing step and thus, offers an innovative solution to tackle the challenging issue of membrane fouling and high operating cost of traditional electrochemical oxidation in industrial wastewater treatment (Yang et al. 2011, 2012). For instance, a simple strategy employed an ECMR with a self-cleaning function has been designed for 200 $mg{\cdot}L^{-1}$ oily wastewater treatment (Figure 18.9). It presents a high efficiency in the treatment of wastewater as a result of the synergistic effect between membrane separation and electrocatalytic oxidation.

To prevent membrane fouling, the TiO_2/carbon membrane acts both as a filter and an anode during electrolysis.In ECMR operation, once the membrane anode is electrified, excitation of TiO_2 leads to holes in the valence band and electrons in the conduction band at the TiO_2 surface (Eq. 18.17).The obtained electrons and holes electrochemically decompose H_2O to O_2 and H_2 (Eqs. 18.18 and 18.19) (Fujishima and Honda 1972; Service 2009), which induce gas and liquid microflows to reduce concentration polarization and avoid membrane fouling (Cui et al. 2003), In addition, the obtained electrons and holes can react with the adsorbed H_2O and O_2 at the surface to generate reactive intermediates such as $\cdot OH$, O_2^-, $HO_2\cdot$, and H_2O_2, (Eqs. 18.20–18.23) (Zaky and Chaplin 2013), which can indirectly decompose the organic foulants on the membrane surface or in the pores to CO_2 and H_2O or biodegradable products, and thus achieve a

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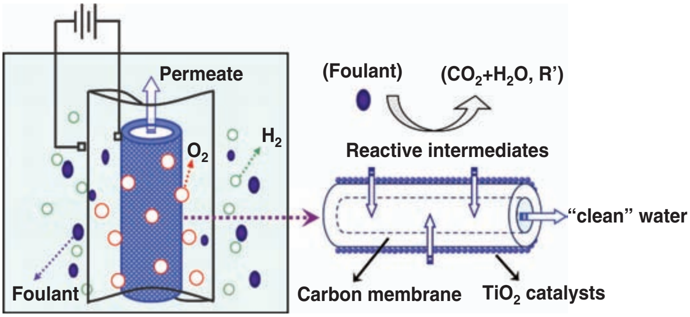

Figure 18.9. Scheme of ECMR
Source: Yang et al. (2011); reproduced with permission from John Wiley and Sons

self-cleaning effect of the electrocatalytic membrane.Simultaneously, CO_2 bubbles also induce microflows to strengthen the antifouling effect.

$$TiO_2 + ev \rightarrow TiO_2(h^+ + e^-) \qquad \text{(Eq. 18.17)}$$

$$H_2O + 2\ h^+ \rightarrow 1\ /\ 2O_2 + 2\ H^+ \qquad \text{(Eq. 18.18)}$$

$$2H^+ + 2e^- \rightarrow H_2 \qquad \text{(Eq. 18.19)}$$

$$H_2O + h^+ \rightarrow \cdot OH + H^+ \qquad \text{(Eq. 18.20)}$$

$$O_2^- + H^+ \rightarrow HO_2\cdot \qquad \text{(Eq. 18.21)}$$

$$2HO_2\cdot \rightarrow H_2O_2 + O_2 \qquad \text{(Eq. 18.22)}$$

$$O_2^- + H_2O_2 \rightarrow \cdot OH + OH^- + O_2 \qquad \text{(Eq. 18.23)}$$

18.7 CONCLUSION

In this chapter, we point out the validity ofthe ECMR for the treatment of differentrefractoryindustrial wastewater, including oily, phenolic, and dyeing wastewater.In consideration of the specific reactivity of different organic substrates, dedicated tests should be carried out in order to identify the most suitable experimental conditions during the ECMR operation. The reason is that the operation parameters of ECMR including current density, residence time, pH and temperature and their mutual interactions have a significant influence on the performance of the ECMR. The mechanism of ECMR for wastewater treatment

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suggests that the organic pollutants in wastewater would be decomposed into CO_2 and H_2O or biodegradable products through the generation of physically adsorbed "active oxygen," such as $\cdot OH$, O_2^-, $HO_2\cdot$ and $H_2O_2\cdot$ or chemisorbed "active oxygen" (oxygen in the oxide lattice, MO) at the anodesof ECMR. Obviously, the inherent advantages of the electrocatalytic oxidation include: a) the use of a cleaning reagent–the electron; b) little or no need for addition of chemicals; and c) no secondary pollution being generated. Most importantly, the function of self-clean in the ECMR provides an innovative approach to tackling the challenging issue of membrane fouling, which is unavoidable during the application of the membrane technology. The ECMR would have broad potential applications in industrial wastewater purification.

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CHAPTER 19

Water Reclamation by Heterogeneous Photocatalysis over Titanium Dioxide

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19.1 INTRODUCTION

The term “photocatalysis” refers to a chemical transformation or the acceleration of a chemical reaction in the presence of light and a photocatalyst (Kisch 1989). The various types of photocatalysts listed in the literature can be classified into three groups (Sakata 1989):

1. Dye molecules used as homogeneous photocatalysts;
2. Semiconductors used as heterogeneous photocatalysts (HP); and
3. A combination of dye and semiconductor species known as dye sensitised photocatalysts.

In HP, reactions occur at an interface of a solid/liquid (for aqueous pollutants) or of a solid/gas (for gaseous pollutants). Photocatalytic reactions are initiated by the absorbance of photons that drive subsequent redox reactions on the irradiated (activated) surface of the photocatalyst. Consequently, the adsorption of pollutants on the photocatalyst is very important for their photodegradation, although photodegradation also can occur at small distances from the irradiated surface, due to the diffusion of reactive species (Kikuchi et al. 1997; Tatsuma et al. 2001). The photocatalyst is involved in the reactions but is not consumed, chemically altered,

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or transformed. The most popular semiconductor used in HP is titanium dioxide (TiO_2) for being relatively inexpensive, chemically stable, and non-toxic.

The use of HP as a green technology in environmental remediation has been well studied to explore the benefits and tackle the challenges in this field (Chen et al. 2000; Fujishima et al. 2007). The removal of indoor odours by immobilised TiO_2 films under weak UV illumination (Ohko et al. 1997), the bactericidal effect of TiO_2 under low intensity UV-illumination (Kikuchi et al. 1997), the self-cleaning TiO_2 surfaces (Minabe et al. 2000), and the photocatalytic decomposition of endocrine-disrupter chemicals in water (Ohko et al. 2002) are few examples of using HP in environmental applications.

The growing importance of wastewater reuse and the resulting need to remove recalcitrant pollutants from effluents have impacted the science and engineering of water treatment, to generate significant research interest in this area (Ollis and Serpone 1989; Herrmann et al. 1993; Gaya and Abdullah 2008; Shon et al. 2008; Lee et al. 2009; Chong et al. 2010; Okour et al. 2010; El Saliby et al. 2011). The widely used conventional biological wastewater treatment technologies have limited ability to remove certain pollutants, such as pharmaceuticals, personal care products, and pesticides from water. Therefore, new treatment methods, chiefly advanced oxidation processes are gaining popularity in solving pollution problems created by such emerging pollutants. The application of HP in water treatment has been considered an effective way to eliminate harmful pollutants either by their complete mineralisation or partial degradation that allows successive biological treatment. The major advantages of HP can be summarised as follows:

1. Full degradation (mineralisation) of contaminants, even at trace level concentrations;
2. Formation of toxic or harmful by-products can be avoided;
3. Minimal production of waste (sludge); and
4. Possibility to utilise sunlight as energy source.

Hence, the research and development in the field of HP is growing to find improved photocatalysts and systems for various environmental applications. Fundamentals of HP for water treatment using TiO_2, including reactor engineering, the effect of operational parameters, and kinetics and applications of the photocatalytic reactions will be discussed in the following sections.

19.2 FUNDAMENTALS

The band gap (i.e. the gap between the conduction and valence band) of semiconductors can be simply calculated from the formula: E_G (Band gap in eV) = 1,240/λ (nm), where λ is the excitation wavelength of the semiconductor (Chen et al. 2000). In general, the photocatalytic properties of semiconductors depend on several factors: i) the position of the energetic level; ii) the mobility and mean lifetime of the photogenerated electron and holes; iii) the light absorption coefficient; and iv) the nature of the interface (Augugliaro et al. 2010).

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UV irradiation of TiO_2 promotes an electron (e^-) from the valence band to the conduction band, which leaves a positive charge carrier hole (h^+) in the valence band. The e^- and h^+ charges migrate in random directions to the bulk or the surface of the particles. Those elementary charges that reach the surface of the catalyst can react with electron-donor and electron-acceptor species present at the semiconductor/electrolyte interface. In contrast, those charge carriers that are trapped in the bulk material can only recombine with the release of heat (Linsebigler et al. 1995; Fujishima et al. 2008). The position of the valence band and conduction band edges, as well as the energetic levels of any redox couples, are essential factors to establish if thermodynamics allow the occurrence of oxidation and/or reduction of the species in solution (Chen et al. 2000).

The adsorption of photons by TiO_2 allows the direct transformation of light quanta into chemical energy (Figure 19.1). After illumination by a UV source the following sequence of events can occur on the surface of TiO_2 (Augugliaro et al. 2010):

$$TiO_2 + h\nu \rightarrow TiO_2(e^-_{(CB)} + h^+_{(VB)}) \qquad \text{(Eq. 19.1)}$$

$$OH^- + h^+_{(VB)} \rightarrow {}^{\bullet}OH \qquad \text{(Eq. 19.2)}$$

$$O_2 + e^-_{(CB)} \rightarrow {}^{\bullet}O_2^- \qquad \text{(Eq. 19.3)}$$

$${}^{\bullet}O_2^- + H^+ \rightarrow {}^{\bullet}HO_2 \qquad \text{(Eq. 19.4)}$$

$$2{}^{\bullet}HO_2 \rightarrow O_2 + H_2O_2 \qquad \text{(Eq. 19.5)}$$

$$H_2O_2 + {}^{\bullet}O_2^- \rightarrow OH^- + {}^{\bullet}OH + O_2 \qquad \text{(Eq. 19.6)}$$

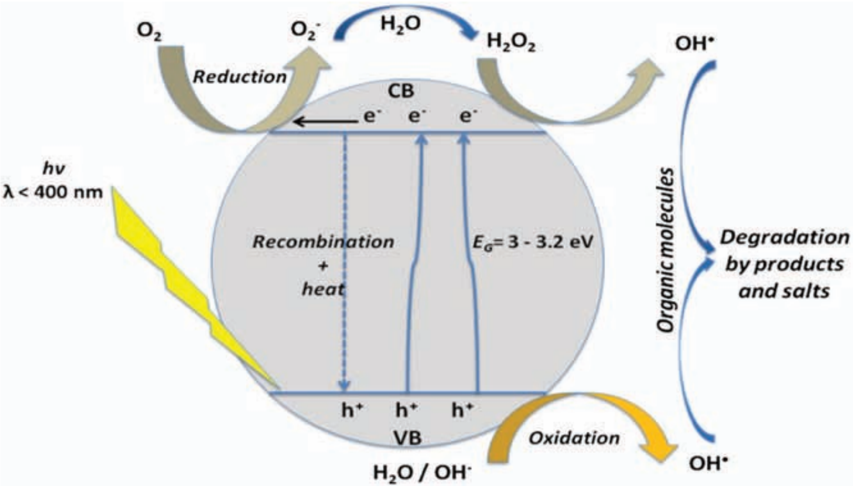

Figure 19.1. A scheme of photo-induced reactions occurring in the bulk and at the surface of a spherical TiO_2 particle

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At the solid-liquid interface and on different zones of the same particle, the redox reactions permit the degradation of many organic and inorganic pollutants by means of formation of very reactive radical species generated in the presence of O_2 and H_2O. The role of oxygen is crucial since it i) assists the charge separation in TiO_2 by capturing electrons; ii) participates in reactions as an oxidiser; and iii) also required for the generation of active species such as H_2O_2, $^{\bullet}O_2^-$.

19.3 PHOTOCATALYTIC REACTORS

There are many factors which have to be considered when designing photoreactors for water or wastewater treatment. The geometry of the photoreactor, the photocatalysis mode, and the energy source (UV lamps or solar light) are the main parameters that impact the final design (McCullagh et al. 2011). Based on the geometry, photoreactors could be divided into:i) immersion well; ii) annular; iii) elliptical; iv) multi-lamp; v) film; and vi) fluidised bed classes. According to the photocatalysis mode, photocatalytic reactors are generally classified into: i) slurry photoreactors (Figure 19.2); and ii) fixed-bed photoreactors (Mozia 2010).

For slurry reactors, an aqueous suspension of the photocatalyst is mixed with the polluted stream to ensure maximum contact. Even though the efficiency of these systems is relatively high, the separation of the photocatalysts after treatment for reuse increases process complexity and costs. For fixed-bed

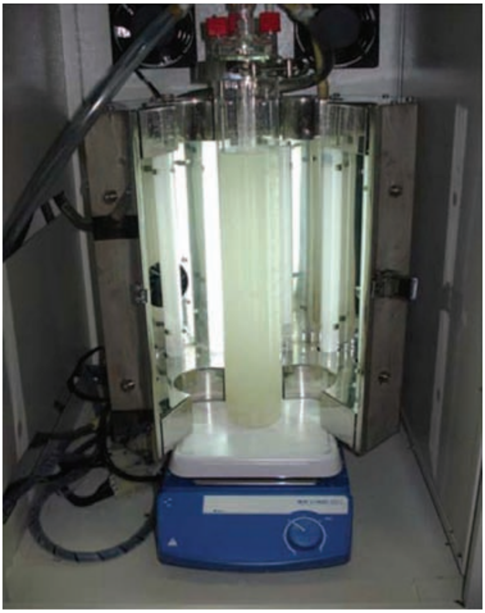

Figure 19.2. A slurry-type annular photoreactor

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photoreactors, the photocatalyst is immobilised on a solid non-reactive support, such as glass or quartz, to avoid the problem of particle separation. Unfortunately, the photocatalytic performance of such systems is typically lacking due to the reduced exposure and activation of photocatalytic surfaces (McCullagh et al. 2011).

The type of energy source affects the feasibility of photocatalytic systems. The traditional use of UV lamps is effective but requires electrical energy, which can negatively affect the cost of the treatment system. In contrast, up to 5% of the solar light spectra is in the UV range that can be used to activate TiO_2. Solar reactors are divided into concentrated and non-concentrated reactors. Various types have been used for heterogeneous photocatalysis, including i) parabolic trough reactor, ii) compound parabolic collecting reactor, iii) double skin sheet reactor, and iv) thin film fixed bed reactor (McCullagh et al. 2011).

In the last decade, the photocatalytic degradation of organics was accomplished in hybrid photoreactors such as the photocatalytic membrane reactor (Molinari et al. 2000; Choi et al. 2007; Zhang et al. 2009) and the submerged membrane photocatalysis reactor (Ryu et al. 2005; Fu et al. 2006; Chen et al. 2009). Such hybrid membrane-photocatalytic systems combine the more effective slurry type photoreactors with membrane modules to ensure the effective separation of suspended photocatalysts' particles.

In a recent publication, McCullagh et al. (2011) discussed the latest photoreactor configurations used in environmental remediation. They concluded that the future of photoreactor technology depended on the engineering and design of photoreactors, as well as on the development of more effective photocatalysts, especially in rate-limited systems. For industrial applications, photoreactors need to meet the challenges of capacity, ruggedness, reliability, and ease of operation. In the view of those authors, currently only suspension (slurry) type reactors are capable of (with some limitations) meeting such expectations.

19.4 OPERATIONAL PARAMETERS

There are several factors (including operational or process parameters) that directly influence the overall photocatalytic process efficiency in a given photoreactor system. The most significant factors include photocatalyst loading, composition and characteristics of the catalyst, contaminant composition and concentration, light intensity, pH of the solution, oxygen supply, and the temperature of reaction. Process engineering parameters such as the type of reactor, retention time, and reactor hydraulics are case-specific and will not be discussed hereafter.

19.4.1 Photocatalyst Loading

The increase of TiO_2 loading generally increases the rate of the photocatalytic reaction up to some limit, which is due to the increase in the surface area of the

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photocatalyst available for adsorption and degradation (Mozia 2010). Since the photocatalytic activity is also dependent on the surface absorption of photons by TiO_2 particles, the further increase of TiO_2 loading above the optimum level leads to light screening (shading effect) that results in a decrease in photoefficiency (Chong et al. 2010). Moreover, increased particle collision and agglomeration at high loadings also results in loss of the active surface area (Kaneco et al. 2004). Therefore, the optimum photocatalyst loading for a particular application only can be established experimentally (Gaya and Abdullah 2008).

19.4.2 Composition and Characteristics of Photocatalysts

While photocatalysis is sometimes described as being non-selective to various pollutants, this is only an appearance and is due to the extreme reactivity of hydroxyl radicals that readily attack many compounds. However, reaction rates are still strongly dependent on the physicochemical properties of both the photocatalyst (Figure 19.3) and pollutants. Rutile, anatase, mixed photocatalysts (i.e. the industry "standard" Evonik P25), as well as doped photocatalysts show significant differences in photocatalytic performance. The main physical factors affecting photodegradation of certain pollutants are the particle size, surface area, porosity and surface charge. For metal doped TiO_2, the presence of impurities and non-metal compounds also can significantly affect the rate of photocatalytic reaction. Therefore, there is no single "best" photocatalyst that offers a universally high performance for every application.

19.4.3 Concentration of Pollutant

In HP, organic contaminants can be divided into many and various groups according to their chemical compositions, molecular structure, functional groups, solubility, and their pathways of decomposition. In general, the dark adsorption of organics onto TiO_2 surface precedes the photo-oxidation process that occurs during UV irradiation. However, at high pollutant loadings surface saturation may become a 'shading' barrier to the absorption of photons by TiO_2 leading to performance degradation by photocatalyst deactivation (Saquib and Muneer 2003; Arana et al. 2004). The determination of an optimal organic loading for a given photoreactor is essential to ensure effective operational conditions. Palmisano et al. (2007) have reported that organic molecules with electron withdrawing group adsorb better than molecules with electron donating groups. It was also shown that organics with complex molecular formulae (4-chlorophenol, humic acid, etc.) break down to various intermediate products before final mineralisation that have different adsorption affinities toward the photocatalyst than the original pollutant (Palmisano et al. 2007). In contrast, simple compounds such as oxalic acid have been reported to undergo direct mineralisation to CO_2 and H_2O (Bahnemann 2004). Therefore, the degradation of complex material is best monitored by COD/DOC and/or salt concentration measurements, while HPLC and UV-vis spectroscopy (for measuring a single compound concentration) are quite satisfactory for monitoring the degradation of simple compounds to establish the kinetics of the photoreaction.

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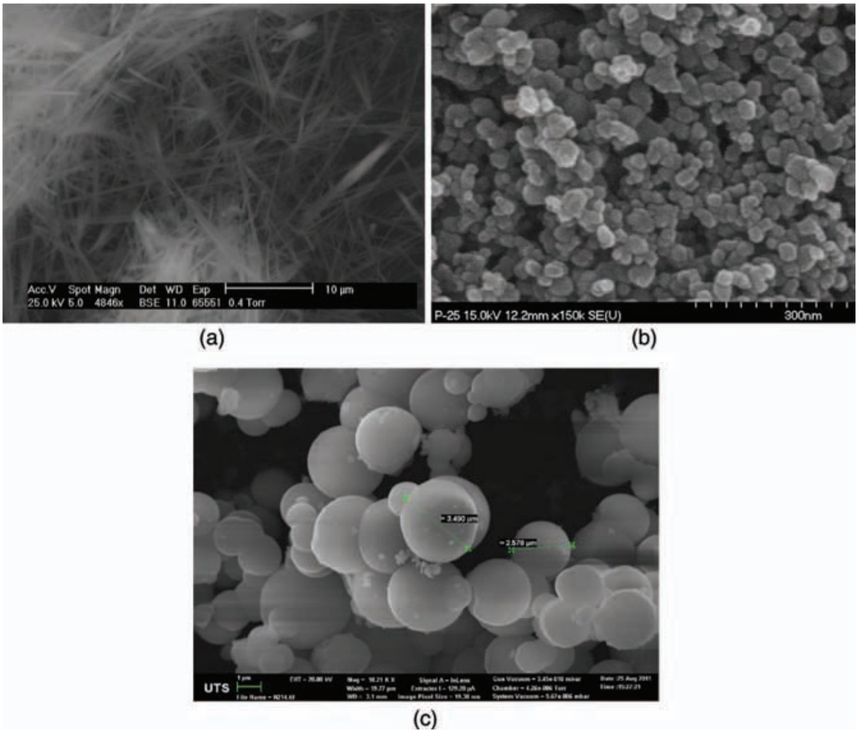

Figure 19.3. Photocatalysts with different physicochemical characteristics. ***(a)*** *H-titanate nanofibres;* ***(b)*** TiO_2 *nanoparticles;* ***(c)*** *nitrogen doped peroxotitanatemicropsheres*

19.4.4 Effect of pH

The variation of pH has a critical role in the photocatalytic treatment of aqueous organic contaminants. Konstantinou and Albanis (2004) described the effect of pH on the photocatalytic reaction over TiO_2 through: i) changing the ionisation state of TiO_2, ii) modifying the position of the conduction and valence bands, iii) assisting in the agglomeration or dissociation of TiO_2 particles, and iv) interfering in the formation of hydroxyl radicals.

Moreover, the process pH (by definition a measure of hydronium ion mol concentration in water) also directly affects the solubility of pollutants, and particle surface charges. In general, the isoelectric point or the point of zero charge (PZC) of Evonik P25 TiO_2 lies between pH 6 to 7. The increase of pH increases the negative surface charge, while a decrease will result in more positively charged photocatalyst surface, according to the following reactions (Gaya and Abdullah 2008; Chong et al. 2010):

$$\text{At pH} < \text{PZC: } \text{TiOH} + \text{H}^+ \leftrightarrow \text{TiOH}_2^+ \qquad \text{(Eq. 19.7)}$$

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$$\text{At pH} > \text{PZC: TiOH} + \text{OH}^- \leftrightarrow \text{TiO}^- + \text{H}_2\text{O} \qquad \text{(Eq. 19.8)}$$

Therefore, the adsorption of charged molecules or species onto TiO_2 is strongly influenced by the pH of the aqueous medium. Negatively charged contaminants are better adsorbed at lower pH (pH < PZC), while positively charged contaminants are better adsorbed at higher pH (pH > PZC) by electrostatic interaction.

Surface charge neutralisation (pH = PZC) promoted to the formation of larger particle clusters and easier sedimentation (Chong et al. 2010). However, the aggregation of particles also may be detrimental by reducing the photocatalytic efficiency through the reduction of the exposed surface area, and the shading effect. The size of agglomerates was found to be highly dependent on the pH difference relative to the PZC (Malato et al. 2009).

The reaction between a hydroxide ion and a positive hole generates a hydroxyl radical (Eq. 19.2). This reaction is favoured under alkaline conditions since there is more OH^- available at the TiO_2 surface. The reaction between H^+ ions and e^- also generates reactive radical species (Eq. 19.4), and under acidic conditions, the positive holes might be the major oxidation species (Konstantinou and Albanis 2004). Moreover, hydroxyl radicals also can form through Eq. 19.6. Therefore, it can be seen that the process pH has multiple effects on the photocatalytic reactions; and thus, it is essential to determine the optimal process pH for specific applications.

19.4.5 Light Intensity

The excitation of TiO_2 surface by a radiant photonic flux ($\lambda < 400$ nm) occurs at very low light intensity. Fujishima et al. (2000) indicated that few photons of energy (as low as 1 $\mu W/cm^2$) are sufficient for the initiation of the photocatalytic reaction. However, the increase in light intensity is essential to ensure that the photocatalyst surface is being appropriately irradiated. The photocatalytic activity of TiO_2 is related to the incident light intensity, and the relationship can be summarised as follows (Ollis et al. 1991; Qamar et al. 2006; Mozia 2010): i) at low light intensities (0–20 mW/cm^2) the photocatalytic reaction rate is proportional to the radiant flux; ii) at intermediate light intensities (approx. 25 mW/cm^2) the effect is proportional to the square root of radiant flux; and iii) at high light intensities the activity becomes constant.

The increase of reaction rate at low irradiation intensities is due to the formation of electron-hole pairs, with a negligible recombination rate. Above a certain radiant flux, the rate of recombination becomes significant that affects the photocatalytic reaction rate. At very high radiant flux intensities, the saturated surface coverage results in mass transfer limitations (adsorption and desorption), coupled with another limiting step of the electron transfer from the photocatalyst to the oxygen (Doll and Frimmel 2005).

19.4.6 Dissolved Oxygen

The role of oxygen in the photocatalytic reaction was presented in Equations 19.3 and 19.6 that describe the pertinent reactions occurring on TiO_2 surface. Dissolved

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oxygen (DO) has a primary role in the formation of reactive species and the stabilisation of intermediates. It was also reported that DO induced the cleavage mechanism for aromatic rings that are present in many organic pollutants (Chong et al. 2010). Previous work found that the concentration of DO can be a limiting factor that sometimes significantly hinders the photo-mineralisation process (Wang and Hong 2000). However, increased photocatalytic activity also can occur in the absence of oxygen, due to the reduced absorption of UV photon by dissolved oxygen molecules at $\lambda < 254$ nm. The DO molecules act as an inner filter and reduce the effective photonic flux on the surface of the photocatalyst (Shirayama et al. 2001).

19.4.7 Temperature

The photocatalytic decomposition of organics usually can proceed without a need for increasing the ambient water temperature. However, an increase in degradation rates was observed with an increase in the temperature range between 20°C and 80°C (Malato et al. 2009). Operating the photocatalytic process at low temperatures (near 0°C) hindered the desorption of the final product from the photocatalyst surface, which caused an increase in the apparent activation energy. In contrast, temperatures above 80°C disfavoured the adsorption of pollutants and also enhanced the recombination of charge carriers, which were considered the main limiting steps (Gaya and Abdullah 2008; Mozia 2010; Chong et al. 2010).

19.5 OPTIMISATION METHODOLOGY

The optimisation of photoreactor systems is usually undertaken by the conventional one-parameter-at-a-time approach. In other words, the optimisation is achieved by varying one parameter while all the others are kept constant. After determining the optimal condition for a given variable, based on the decomposition rate of a target pollutant, other parameters are subsequently tested until all parameters have been optimised. This method is widely accepted and has been used to optimise many operating systems. However, the limitation of this procedure is that the interaction of parameters at different levels cannot be tested. The multivariable optimisation approach is becoming increasingly popular because the optimisation process is more effective, and the interaction among different parameters can be interpreted using the analysis of variance, statistical regression, and response surface analysis (Chong et al. 2010).

19.6 PROCESS EFFICIENCY

The optimisation of a photocatalytic process for a specific reaction (single contaminant) is crucial for the determination of a sound photoreactor/operation parameter configuration. The process efficiency of the system should be assessed based on a

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standardised method to allow comparisons between different processes. The quantum yield "Φ" (Φ = rate of reaction/adsorption rate of radiation) was suggested to evaluate the process efficiency in photocatalytic processes (Calvert and Pitts 1966). However, it's very difficult to determine Φ by experimental investigation in many photocatalytic reactors. This is mainly due to the refraction, scattering, transmission and adsorption of light by the suspended particles (Chen et al. 2000).

A relative photonic efficiency "ζ_r" (ζ_r = initial disappearance rate of substrate/initial disappearance rate of phenol) has been proposed to overcome the difficulties encountered by the measurement of Φ (Serpone 1997). The method consisted of measuring the initial disappearance reaction rate of phenol using Evonik P25 as a "standard" photocatalyst, and then measuring the initial disappearance rate of the target substrate under identical experimental conditions. The ζ_r can be used to calculate the quantum yield of the substrate ($\Phi_{\text{substrate}}$) relatively to the quantum yield of phenol on Evonik P25 (Φ_{phenol}) by $\Phi_{\text{substrate}} = \zeta_r \Phi_{\text{phenol}}$. The relative photonic efficiency allows the comparison of results of studies performed in different laboratories. Nevertheless, experimental conditions must be identical, besides that the initial rate does not consider the formation of intermediate compounds, and how those might affect the degradation of their parental products. It follows that the evaluation of photocatalytic processes using a universal reference or indicator is still not possible, since many factors and parameters have interrelated influences on the reaction rate.

19.7 KINETICS OF THE PHOTOCATALYTIC REACTION

The kinetics of mineralisation in heterogeneous photocatalysis is often described in the literature with the Langmuir-Hinshelwood (L-H) model. Although this model was originally proposed for gaseous–solid reactions (Satterfield 1970) it also can describe solid–liquid reactions (Ollis 1985). In the L-M model the r rate of reaction is proportional to the ϑ fraction of surface covered by the substrate (pollutant):

$$r = -\frac{dC}{dt} = k\Theta \qquad \text{(Eq. 19.9)}$$

Θ is obtained from Langmuir's equation

$$\Theta = \frac{K \cdot C}{1 + K \cdot C} \qquad \text{(Eq. 19.10)}$$

Hence

$$r = k \cdot \frac{K \cdot C}{1 + K \cdot C} \qquad \text{(Eq. 19.11)}$$

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with k = reaction rate; K = constant of adsorption equilibrium; and C = substrate concentration at t time. The integration of Eq. 19.11 between zero and t times yields

$$\ln\left(\frac{C_0}{C_t}\right) + K \cdot (C_0 - C_t) = k \cdot K \cdot t \qquad \text{(Eq. 19.12)}$$

with C_0 and C_t = substrate concentration at zero and t irradiation times, respectively. Solving Eq. 19.12 for k requires the knowledge of K. For that, the ϑ surface coverage fraction can also be expressed from the number of adsorbed molecules at a given final (equilibrium) concentration as

$$\Theta = \frac{n_{ads}}{n_0} = \frac{K \cdot C}{1 + K \cdot C} \qquad \text{(Eq. 19.13)}$$

that can be re-arranged as

$$\frac{1}{n_{ads}} = \frac{1}{n_0} + \frac{1}{n_0 K} \cdot \frac{1}{C} \qquad \text{(Eq. 19.14)}$$

with n_{ads} and n_0 = covered and total number of available adsorption sites, respectively. Noting that Eq. 19.14 is linear, both K and n_0 can be determined from plotting $1/n_{ads}$ versus $1/C$. It also can be seen from Eq. 19.11 that the reaction will be of zero orderfor relatively high substrate concentrations (and/or K values) ($KC \gg 1$), and offirst orderfor relatively low substrate concentrations and/or K values ($KC \ll 1$).

In the photocatalytic degradation of Methylene Blue, a widely used model pollutant, Herrmann (1999) reported zero and first order reactions for 5 mmol and 1 mmol initial concentrations, respectively. For the latter case, which is typical in most applications of photocatalysis, the denominator in Eq. 19.11 approaches 1 (one), and thus

$$r = k \cdot \Theta = k \cdot K \cdot C = k_a \cdot C \qquad \text{(Eq. 19.15)}$$

with k_a apparent (pseudo) rate constant. The integral form of Eq. 19.15 is

$$C_t = C_0 \cdot e^{-k_a \cdot t} \qquad \text{(Eq. 19.16)}$$

The linearised form of Eq. 19.16 is often used to obtain the k_a apparent reaction rate. However, data linearisation also transforms the random (Gaussian) distribution of the error term, which is contrary to the fundamental assumption of random errors used in the derivation of linear regression. Therefore, it is advisable to obtain reaction rates from Eq. 19.17 using nonlinear regression/fitting techniques that are provided by many modern statistical software packages.

$$\ln\left(\frac{C_0}{C_t}\right) = k_a \cdot t \qquad \text{(Eq. 19.17)}$$

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It is also emphasised that both the k reaction rate constant used in the L-M model and the k_a apparent reaction rate constant used in the first order model are lumped (bulk) parameters. Those parameters take into account a number of factors, such as hydraulic conditions and photonic conditions. It follows that the obtained rate values are only valid for the given experimental conditions, cannot be used for the up-scaling of equipment, nor to compare catalyst performances reported elsewhere. Their utility is in quantifying and comparing relative performances when assessing the effects of various experimental factors.

19.8 APPLICATIONS IN WATER TREATMENT

Nowadays, most water remediation technologies generate a significant amount of wastewater that requires costly retreatment or discharge to evaporation ponds, rivers and oceans. Therefore, the development of zero-wastewater discharge technologies will help alleviate these problems. TiO_2 photocatalysis is considered a viable alternative to conventional water treatment systems with the added benefit of being a clean and environmentally friendly technology. Moreover, it can be used to degrade recalcitrant pollutants that are normally difficult to treat using conventional water treatment. HP applications in water treatment are numerous and embrace organic pollutants degradation, heavy metal removal, bacteria deactivation and nitrate reduction.

19.8.1 Degradation of Organic Pollutants

Organic pollutants are diverse and complex organic molecules that occur in natural waters, rainwater, and storm water as well as in wastewater. The majority of these organic pollutants could be immobilised, separated and removed from water using conventional methods such as flocculation, bioreactors and membrane filtration. However, some classified as recalcitrant micro-pollutants (antibiotics, toxins, PPCPs, dyes and herbicides,etc.) are difficult to separate, filter and resist biological wastewater treatment processes. The degradation of these pollutants could be achieved by heterogeneous photocatalysis using TiO_2, few examples are shown in Table 19.1.

Fluoroquinolone antibiotics such as moxifloxacin are increasingly used to treat microbial infections in humans and animals. As a result, antibiotic residues and by-products have been constantly detected in most of wastewater effluents across Europe (Speltini et al. 2010). The photocatalytic degradation of moxifloxacin in a batch slurry photoreactor over P25-TiO_2 resulted in fourteen degradation products (Van Doorslaer et al. 2013). However, the most important finding was that no residual antibacterial activity could be observed after 12 min of degradation time. Accordingly, effluent pre-treatment by heterogeneous photocatalysis was recommended to reduce theantibacterial activity of moxifloxacin in wastewater effluents.

Other micro-pollutants such as herbicides are easily transported from the site of application to surrounding ecosystems including rivers and groundwater.

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Table 19.1. Few recalcitrant micro-pollutant photocatalytic degradation systems over TiO_2

Photocatalysts	*Organic pollutants*	*Photocatalytic systems*	*Irradiation sources*	*References*
• $dTiO_2$ anatase • 20-MWCNT-TiO_2 • Commercial anatase	Ketoprofen	Batch slurry photoreactor	Heraeus TQ 150 medium-pressure Hg-vapor lamp and TNN 15/32 low-pressure Hg-vapor lamp	Martinez et al. (2013)
P25-TiO_2	2,4-dichlorophenol	Recirculating slurry photoreactor	Xenon lamp (PHILIPS XOP-15-OF, 1500 W)	Bayarri et al. (2013)
P25-TiO_2	Moxifloxacin	Batch slurry photoreactor	UV-A pen ray (300–440 nm with main peak at 365 nm)	Van Doorslaer et al. (2013)
P25-TiO_2	[D-Leu]-Microcystin-LR	Flat plate glass reactor coated with TiO_2	Natural solar light	Vilela et al. (2012)
P25-TiO_2	3-chloropyridine	• Batch slurry photoreactor • Compound parabolic collector solar photoreactor	• UV Spotlight Source LightningcureTM L8022 • Natural solar light	Ortega-Liebana et al. (2012)
Commercial TiO_2 (Riedel-de Haen, Germany)	Perfluoro-carboxylic acids	Batch slurry photoreactor	Low-pressure mercury UV-lamp (16 W, 254 nm, Phillips)	Panchangam et al. (2009)

(Continued)

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Table 19.1. Few recalcitrant micro-pollutant photocatalytic degradation systems over TiO_2 (Continued)

Photocatalysts	*Organic pollutants*	*Photocatalytic systems*	*Irradiation sources*	*References*
P25-TiO_2	Clomazone	Batch slurry photoreactor	• Natural solar light • 125 W high-pressure mercury lamp (Philips, HPL-N) • 50 W halogen lamp (Philips) and a 400 nm cut-off filter	Abramović et al. (2013)
Hybrid BiOBR-TiO_2	Rhodamine B	Batch slurry photoreactor	300 W Xe lamp with a 400 nm cut-off filter	Wei et al. (2013)

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This is mainly due to their high solubility, persistence in the environment and long half-life dissipation. For instance, clomazone herbicide has a half-life ranging from 24–82 days which permit its mobilisation to the groundwater (Abramović et al. 2013). Contaminated groundwater was efficiently treated with a suspension of P25-TiO_2 under different light sources (Table 1). A UV/TiO_2 treatment system eliminated clomazone from water with an optimum loading of TiO_2 equal to 0.5 mg/ml at the pH 10.3.

19.8.2 Heavy Metal Removal

Heterogeneous photocatalysis has been also used for the reduction of aqueous heavy metals, their immobilisation and removal. To achieve successful photoreduction, the bottom level of the conduction band of the photocatalyst should be more negative than the reduction potential of the heavy metal (Litter 2009). In this way, heavy metals are reduced to less toxic forms, precipitated/immobilised than filtered using membrane. The conventional chemical reduction processes involve the use of large quantities of expensive reducing agents such as $FeSO_4$, $FeCl_2$, $NaHSO_3$ or SO_2, which creates secondary pollution (Barrera-Diaz et al. 2012). Photocatalytic reduction of heavy metals is a promising technology to clean heavy metal contaminated waters and wastewaters.

Mercury(II) is a frequent component of industrial wastewaters and is found in pesticides, fungicides, herbicides, insecticides and bactericides. The photocatalytic transformation of Hg(II) metal ion was achieved to species of lower toxicity and easier to separate from the aqueous phase (De La Fourniere et al. 2007). P25-TiO_2 photocatalysed the reduction in a recirculating photoreactor set up under UV light irradiation. The absence of oxygen favoured Hg(II) removal at pH 11, where HgO was formed together with Hg(0). Photoreduction reactions were also proposed for two different phenylmercury salts (PMA ($C_6H_5HgCH_3CO_2$) and PMC (C_6H_5HgCl)) used as mercury source:

$$C_6H_5Hg^+(Cl^- \text{ or } CH3COO^-) + (HO^\bullet) + H^+ \rightarrow C_6H_5OH + Hg^{2+}(Cl^- \text{ or } CH_3COO^-) \quad \text{(Eq. 19.18)}$$

$$Hg^{2+} + e^-_{cb} \rightarrow Hg(I) \quad \text{(Eq. 19.19)}$$

$$Hg(I) + e^-_{cb} \rightarrow Hg(0) \quad \text{(Eq. 19.20)}$$

$$C_6H_5OH + h^+_{vb}(HO^\bullet) \rightarrow \ldots \rightarrow CO_2 + H_2O \quad \text{(Eq. 19.21)}$$

$$CH_3COO^- + h^+_{vb}(HO^\bullet) \rightarrow \ldots \rightarrow CO_2 + H_2O \quad \text{(Eq. 19.22)}$$

Later on, Lopez-Munoz et al. (2011) studied the influence of pH and the addition of methanol, formic acid and oxalic acid as sacrificial additives on the extent of Hg(II) photocatalytic reduction. The photoreaction was carried out using P25-TiO_2 in a cylindrical Pyrex batch reactor illuminated by 150 W medium pressure mercury lamp (Heraeus TQ-150). It was found that the addition of organic additives enhanced the photocatalytic reduction to Hg(0) in acidic medium while no effect was observed at high solution pH (10).

The photoreduction of Cr(VI), a common toxic pollutant of wastewater, to Cr(III) was achieved by a new class of visible-light active titania photocatalyst (Zhang et al. 2013). The photocatalyst was synthesised by a one-step low-temperaturesolvothermal route using HNO_3 as a nitrogen precursor to acquire visible activity. Cr(VI) aqueous solutions were exposed to both visible and UV light and treated with different types of TiO_2photocatalysts. It was shown that the new photocatalyst performed better than others for the reduction of Cr(VI) to Cr (III) in water under both UV and visible light ($\lambda > 420$ nm) irradiation. The conversion of Cr(VI) into more environmentally benign oxidation states was also investigated by Gherbi et al. (2013) using $CuAl_2O_4/TiO_2$ hetero-junction photocatalyst (spinel-titania bi-functional system). The photoreduction was carried out at 25°C in a double walled sealed tank reactor with infrared cut-offfilter and a 200 W tungsten lamp. Results revealed that the chromate reduction rate increased as light flux increased, and it was also enhanced by the presence of salicylic acid in a solution which favoured the separation of ($e^-/h+$) pairs.

A new generation of titanate materials has been also developed as effective adsorbent of toxic heavy metals. A family of peroxo-titanate was synthesised for the optimal sorption of strontium and actinide (Nyman and Hobbs 2006). The new materials were better adsorbent than the conventional sodium titanate materials and exhibited improved performance in highly alkaline and high-ionic-strength solutions. Also, the adsorption of As(III) was carried out using TiO_2 nanofibers with different phases such as amorphous, anatase, mixed anatase-rutile and rutile (Vu et al. 2013). The highest adsorption capacity was recorded for the amorphous nanofibers and was attributed to their high surface area and porous volume.

19.8.3 Bacteria Deactivation

The deactivation of pathogenic microorganisms over TiO_2 has been investigated as a means to treat contaminated water (Table 19.2), and the deactivation process could be summarised in the following:

- Adhesion of bacteria to the photocatalyst (immobilised or slurry type);
- Generation of hydroxyl radicals on TiO_2 during irradiation; and
- Deactivation of bacteria by creating irreversible damage (through hydroxyl radicals attack) to the cell wall leading to dissociation of the microorganism.

Pablos et al. (2013) reported that the bacterial adhesion onto immobilised TiO_2 was mainly due to hydrophobicity (under electrostatically favourable conditions) and aquatic chemistry (under unfavourable conditions). Two bacterial strains with differences in their membrane structure (*Escherichia coli* and *Enterococcus faecalis*) were studied. It was found that bacterial adhesion was not due to

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Table 19.2. Inactivation of bacteria in aqueous photocatalytic systems

Bacteria	*Photocatalyst*	*Irradiation source*	*Inactivation^/time**	*References*
Escherichia coli O157:H7	• TiO_2 ceramic • TiO_2 coated carbon nanotubes	Fluorescent light (30 mW/cm^2)	• 5×10^{-2} min^{-1} • 2.23×10^{-2} min^{-1}	Oza et al. (2013)
• *Escherichia coli* • *Pseudomonas aeruginosa*	TiO_2 nanoparticles	Philips TL 8 W, black light lamp	• 99.9%/120 min • 99%/120 min	Wang et al. (2013)
Escherichia coli ATCC 700891	Immobilised TiO_2	UVA/LED lamp 3 W	100%/90 min light 240 min dark cycle	Xiong and Hu (2013)
• *Salmonella typhimurium* • *Listeria monocytogenes*	P25-TiO_2	Philips LEA-180B, 8 W, black light lamp	• 100%/180 min • <100%/180 min	Long et al. (2014)
• *Escherichia coli* ATCC 10536 (Gram-negative) • *Lactobacillus rhamnosus* S25 (Gram-positive)	TiO_2 xerogels	Halogen lamp (50 W)	• 100%/48 h • 100%/24 h	Tasseroul et al. (2013)
Bacillus amyloliquifacience NCIM 2829	N-doped TiO_2 mesoporous thin films	Tungsten lamp 30 mW/m^2	100%/3 h	Soni et al. (2013)
• *Enterococcus faecalis* MTCC 439 • *Klebsiella pneumoniae* MTCC 4030	Reactive plasma processed nanocrystalline TiO_2	UVA lamp (365 nm, 125 W)	• 95%/60 min • 60%/60 min	Vijay et al. (2013)

^(%) percentage or rate constant in min^{-1}

*Minutes or hours

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differences between both bacteria. In contrast, the configuration of the catalyst and the composition of the suspension (affecting electrostatic forces) affected the extent of bacterial adhesion. The highest level of adhesion was recorded in solutions containing organic matter in combination with divalent ions such as Ca^{2+} which can bridge between bacteria and catalyst or bacteria and organic matter. The bivalent cations neutralise the repulsion forces between similarly charged surfaces of bacteria and TiO_2 leading to more effective deactivation.

The deactivation of bacteria is not considered complete before the point of irreversible damage (Wang et al. 2013; Xiong and Hu 2013). Microorganisms are complex, compared to organic molecules by having complex structures and capability of repairing and re-growing after damages are done. A residual disinfecting effect was reached using a UVA/LED/TiO_2 photocatalytic system that treats antibiotic-resistant bacterium (*E. coli* ATCC 700891). The system significantly inactivated the bacterium at higher light intensities, and residual disinfecting effect could kill almost all bacteria after 90 min UV periodic illumination within the following 240 min dark period (Xiong and Hu 2013). In a different setup, the inactivation of gram-negative bacteria was complete after 120 min of UVA irradiation over TiO_2 and reached 99.9% for *Escherichia coli* and 99% for *Pseudomonas aeruginosa*. Under similar conditions, the inactivation efficiency against bacteria by nano-TiO_2 varied, and it was attributed to a higher self-defence property or self-repair ability of *P. aeruginosa* than *E. coli* (Wang et al. 2013).

19.8.4 Nitrate Reduction

The overuse of fertilisers worldwide had a negative impact on groundwater quality. Water contamination with nitrate has been recorded due to runoff and leaching of nitrogen fertilisers into water aquifers. In addition, the discharge of untreated industrial wastewater into natural waters has played a significant role in algae blooming which threatened the health and sustainability of aquatic fauna. In water, nitrate (NO^{3-}) is considered a potentially hazardous material that is converted to nitrite by microbes which causes harmful effects on the human body, such as liver damage, cancers and blue baby syndrome (Garron et al. 2005).

The photocatalytic reduction systems designed for nitrate reduction are not different from the systems used for organic, bacteria and heavy metal removal. Therefore, the concurrent treatment of various contaminants is always possible which significantly reduce the installation and operation costs.

The catalytic reduction of nitrate is well investigated using metallic doped titania such as Pd-Cu/TiO_2 (Bae et al. 2013; Kim et al. 2013), Pd-Cu/titania nanotubes (Chen et al. 2013) and Pd-Cu/(Mg-Nb)-TiO_2 (Bou-Orm et al. 2013). However, the photoreduction of nitrate over TiO_2 was also reported using organic acids as a hole scavenger (Kominami et al. 2001; Li et al. 2010; Yang et al. 2013). Kominami et al. (2001) examined the photocatalytic reduction of nitrate ion (NO_3^-) in an aqueous suspension of metal-loaded TiO_2 in the presence of oxalic acid (OA) as a hole scavenger. The photoreduction increased with the following order of loaded metals, (Pt, Pd, Co) < (Ni, Au) < (Ag, Cu). It was concluded that

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TiO_2 powder loaded with Cu showed both high nitrate reduction and OA consumption. Li et al. (2010) used benzene as a hole scavenger and Pt-Cu/TiO_2 photocatalyst in his nitrate photoreduction investigations. N_2 was the final product of the photocatalytic nitrate reduction over the bimetallic photocatalyst. N_2 production was strongly dependent on TiO_2 calcination temperature, the Pt/Cu ratio and the metal loading amount. A 300°C calcination temperature, a Pt loading amount of 5 wt.% and the Pt/Cu ratio of 4/1 were reported as optimums. Recently, the photoreduction of nitrate in synthetic and real brines was carried out in the presence of formic acid and TiO_2 (Evonik P90) (Yang et al. 2013). This system converted most of the reduced nitrate to volatile N species and a small portion to ammonium.

19.9 COMBINED PROCESSES: HP + CHEMICAL/PHYSICAL TREATMENT

Coupling HP systems with other technologies in order to increase the efficiency of water treatment processes has been described (Table 19.3). Augugliaro et al. (2006) reviewed the combination of heterogeneous photocatalysis with chemical and physical operations. Operations were divided into two different categories based on the type of activities coupled:

- Processes that affect the photocatalytic mechanism thus improving the efficiency of the photocatalytic process such as ultrasonic irradiation, photo-Fenton reaction, ozonation and electrochemical treatment; and
- Processes that do not affect the photocatalytic mechanisms but improve the efficiency of the overall process such as biological treatment, membrane reactor, membrane photoreactor, or physical adsorption.

Combining different operations with HP provides an excellent way to achieve better quality product water than single process treatment systems. In conventional systems, the main drawback of water chlorination in drinking water treatment plants is the formation trihalomethanes precursors, which are considered carcinogenic compounds. An Activated Carbon Bed (ACB), an Ozonation Reactor (OR) and a Submerged Membrane Photocatalytic Reactor (SMPR) with TiO_2/UV were compared in terms of reduction efficiency of trihalomethanes precursors after chlorination (Reguero et al. 2013). OR showed low removal percentages of 40–50% while SMPR and ACB were more efficient technologies achieving 87% and 86%, respectively. The SMPR process can run continuously with a minor loss of efficiency and with almost no-waste products and doesn't need frequent regeneration. Bai et al. (2013) studied the performance of a concurrent photocatalytic membrane water purification system using hierarchical 3D dendritic TiO_2 nanospheres built with ultra-long 1D nanoribbon/wires. Hierarchical TiO_2 nanoribbon/wire spheres showed better photodegradation of acid orange 7 and Rhodamine B pollutants and less ability to fouling the membrane compared to TiO_2-P25 under the same conditions. The porous

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Table 19.3. A list of recently combined photocatalysis/physical chemical operations for water treatment

HP combined processes	*Target pollutant(s)*	*References*
Hydrodynamic cavitation	Diclofenac sodium	Bagal and Gogate (2014)
Photo-Fenton reaction	3-chloropyridine	Ortega-Liebana et al. (2012)
	Oxalic acid	Quici et al. (2005)
Dielectric Plasma discharge	Toluene	Ban et al. (2006)
Ozonation	Benzenesulfonate	Zsilák et al. (2014)
HP process intensification with static mixer	Phenol, Cr(VI) and acid orange 7	Li et al. (2011)
Photocatalytic membrane reactor	Trihalomethanes	Reguero et al. (2013)
	Synthetic wastewater	Erdei et al. (2008)
	Benzene	Molinari et al. (2009)
Non-woven membrane filtration	4-chlorophenol	Horng et al. (2009)

functional layer that was formed on the membrane surface resulted in high water flux, in comparison to the dense layer formed by TiO_2-P25. This strategy has mitigated the disadvantages usually encountered when using nanoparticles in hybrid photocatalytic-membrane treatment systems for water purification.

The degradation of diclofenac sodium using combined processes based on hydrodynamic cavitation and heterogeneous photocatalysis was investigated (Bagal and Gogate 2014). The efficiency of the system was dependent on the cavitational effects (intense turbulence with liquid circulation currents) which created local hot spots resulting ingeneration of hydroxyl radicals. Hydroxyl radicals were then expected to intensify the efficacy of the heterogeneous photocatalysis operation. Intense turbulences were formed by a slit venturi (cavitating device) in the hydrodynamic cavitation reactor which was described in details by Bagal and Gogate (2014). Different operating parameters and photocatalytic systems were tested. Under optimised conditions, a hydrodynamic cavitation in conjunction with $UV/TiO_2/H_2O_2$ was reported for high degradation of diclofenac sodium (95% removal) with 76% reduction in total organic carbon.

19.10 CONCLUSIONS AND FUTURE PROSPECTS

Heterogeneous photocatalysis processes that decompose aqueous contaminants are highly dependent on the reaction conditions and the setup of photocatalytic

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reactors. The adoption of a "standardised" reactor system only allows the partial comparison of different classes and types of photocatalysts, since the "quantum yield" itself depends on the experimental conditions used. Therefore, the evaluation and assessment of photocatalytic treatment systems requires substantial experimental work.

Visible-light responsive photocatalysts promise a moreeffective utilisation of solar energy, and thus stimulate significant research. Doping and co-doping of titania is a practical approach to obtain improved visible-light active photocatalysts. However, many of the reported doping processes require expensive equipment and/or complicated procedures that are expensive, and often unfeasible for industrial-scale production. The research and production of engineered nanomaterials that are both highly photoactive and easily separated from water are of great interest for water purification and pollution control.

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CHAPTER 20

Disposal and Recycling of Sewage Sludge

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20.1 INTRODUCTION

Sewage sludge is regarded as the residue produced in the largest volumes in the wastewater treatment process. The two principal types of sludge (primary and secondary sludge) constitute the material collected from the primary settling tanks and the sludge generated from the biological treatment process, respectively (Ren 2004). Sewage sludge contains various toxic compounds, such as pathogens, surfactants, hydrocarbons, heavy metals, and residues derived from plastics (Schmidt et al. 2006). Recently, the amount of sewage sludge produced by wastewater treatment plants has been increased rapidly due to industrialization, urbanization and movement in water/wastewater treatment and reuse (Méndez et al. 2005).

At present, the common disposal methods of sewage sludge include ocean disposal, landfill, incineration, compost, and land application, with incineration and landfill being the primary ways (Koenig et al. 1996; Fang et al. 1997; Khalili et al. 2000; Cotxarrera et al. 2002; Hejazi et al. 2003). However, the above disposal methods are hampered by their poor public image due to the common problems such as high disposal costs, gigantic energy consumption and secondary pollution to the environment (Lundin et al. 2004). Because of the low porosity and high water content, the compost of sewage sludge is more difficult to operate using ordinary aeration methods compared with the routine domestic garbage. Although a large amount of sewage sludge can be reduced through incineration, the process is high-cost and fuel demand. Landfill, on the other hand, is being commonly used nowadays, but can induce the hazardous substances in sewage sludge to be transmitted to plants, livestock and humans, and this will obviously lead to long-term risks for public health (Spinosa and Veslind 2001). Therefore,

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searching for an economical and effective way to reuse the sludge has become one of the increasingly concerned issues.

Usually, sewage sludge is composed of offensive, pathogenic and toxic substances, contains complex components, including inorganic and organic matter, nitrogen, phosphorus as well as other nutrients (Méndez et al. 2005; Wang et al. 2005a), and thus, is recognized as a potential resource. Thus, nowadays people view the practice of using conventional treatment methods to treat sewage sludge as wasting the resources (Khwairakpam and Bhargava 2009). Recently, the concept of sustainable development has been emphasized increasingly, which calls for sustainable treatment and disposal of sewage sludge (Fytili and Zabaniotou 2008). Considerable research has been conducted on more cost effective and environmentally benign alternatives for treatment and disposal of sewage sludge, including composting (Schmidt et al. 2006), energy generation (such as producing hydrogen and methane through fermentation, wet oxidation or pyrolysis) (Shen and Zhang 2003; Szwaja et al. 2013), making building materials (Fytili and Zabaniotou 2008; Tian et al. 2011; Cusidó and Cremades 2012; Lin et al. 2012) and adsorbents (Otero et al. 2003; Méndez et al. 2005; Monsalvo et al. 2012). Among these aforementioned options, the one that may reap extremely significant benefit, due to the potential to valorize the sludge, is the conversion of the sludge into water treatment materials, such as activated carbon that can be used as adsorbents and ceramic particles as filter medium materials. This chapter mainly introduces techniques in these areas.

20.2 CHARACTERISTICS OF SEWAGE SLUDGE

The sources of solids in a treatment plant vary according to the type of the plant and its operating method. Thus, the disposal and recycling of sewage sludge should be based on the characteristics of sludge. The main constituents of sewage sludge are proteins, fats (soap, oil, grease), urea, cellulose, silica, nitrogen, phosphoric acid, iron, calcium oxide, alumina, magnesium oxide and potash (Turovskiy and Mathai 2006). Table 20.1 shows the typical chemical composition and properties of untreated and digested sludge (Fytili and Zabaniotou 2008). Compared with primary sludge, secondary sludge, which is largely composed of microbes, is poor in grease, fats and cellulose but rich in nitrogen, phosphorus and protein. Because of the physical-chemical processes involved in wastewater treatment, heavy metals are also present in sewage sludge. Through the food chain in nature, the potential accumulation of heavy metals (such as Zn, Cu, Ni, Cd, Pb, Hg and Cr) in human tissues and biomagnifications can induce serious human health problems and environmental concerns. Therefore, the potential toxicity of sewage sludge should be considered during its disposal and recycling processes. The concentrations of heavy metals also vary widely depending on the sludge origins, and the typical values are shown in Table 20.2 (Hsiau and Lo 1998; Fytili and Zabaniotou 2008).

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Table 20.1. Typical composition and properties of sewage sludge

	Untreated primary		*Digested primary*		
Item/sludge	*Range*	*Typical*	*Range*	*Typical*	*Activated range*
Total dry solids (TS), %	2.0–8.0	5.0	6.0–12.0	10.0	0.83–1.16
Volatile solids (% of TS)	60–80	65	30–60	40	59–88
Grease and fats (% of TS)					
Ether soluble	6–30	—	5–20	18	—
Ether extract	7–35	—	—	—	5–12
Protein (% of TS)	20–30	25	15–20	18	32–41
Nitrogen (N, % of TS)	1.5–4	2.5	1.6–6.0	3.0	2.4–5.0
Phosphorous (P_2O_5, % of TS)	0.8–2.8	1.6	1.5–4.0	2.5	2.8–11.0
Potash (K_2O, % of TS)	0–1	0.4	0.0–3.0	1.0	0.5–0.7
Cellulose (% of TS)	8.0–15.0	10.0	8.0–15.0	10.0	—
Iron (not as sulfide)	2.0–4.0	2.5	3.0–8.0	4.0	—
Silica (SiO_2, % of TS)	15.0–20.0	—	10.0–20.0	—	—
Alkalinity (mg/l as $CaCO_3$)	500–1500	600	2500–3500		580–1100
Organic acids (mg/l as HAC)	200–2000	500	100–600	3000	1100–1700
Energy content	10,000–12,500	11,000	4000–6000	200	8000–10,000
pH	5.0–8.0	6.0	6.5–7.5	7.0	6.5–8.0

Source: Fytili and Zabaniotou (2008); reproduced with permission from Elsevier

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Table 20.2. Typical metal content in dry sewage sludge (mg/kg)

Metal	*Range*	*Median*	*Metal*	*Range*	*Median*
As	1.1–230	10	Mn	32–9870	260
Cd	1–3.410	10	Mo	0.1–214	4
Cr	10–990,000	500	Ni	2–5300	80
Co	11.3–2490	30	Pb	13–26,000	500
Cu	84–17,000	800	Se	1.7–17.2	5
Fe	1000–154,000	17,000	Sn	2.6–329	14
Hg	0.6–56	6	Zn	101–49,000	1700

Sources: Hsiau and Lo (1998); Fytili and Zabaniotou (2008)

Table 20.3. A typical composition of inorganic matters in dry sewage sludge

Composition	SiO_2	Fe_2O_3	K_2O	*CuO*	Al_2O_3	*CaO*	SO_x	Na_2O	*MgO*	*Other*
Mass ratio (%)	29.28	16.35	1.71	1.48	13.92	21.08	8.32	2.78	4.22	3.64

Note: based on empirical date

In sewage sludge, inorganic matters are mainly composed of Si, Al, Fe and Ca as shown in Table 20.3. Due to the similar composition compared with construction material, sewage sludge is a potential alternative raw material in the production of brick, glass, cement and ceramics. In addition, the organic matters may play the role of gas producer in high-temperature activation processes. Therefore, it is useful for producing function material with a high degree of porosity and particulate surface area (Smith et al. 2009).

20.3 CERAMIC PARTICLE PRODUCTION FROM SLUDGE

20.3.1 Preparation and Characterization of Sludge-Based Ceramic Particles (SBCP)

Commercial ceramic particles (CCP) are generally used as materials in building industries and the filter media in water treatment units (Yang et al. 2005). Clay is applied as the main raw materials. The production process of CCP has a huge demand for clay exploited from farmland mostly, which will lower the quality of the cultivated field and threaten food production in the long run (Han et al. 2009b). Therefore, it is very significant to find an appropriate substitute for clay. Currently, some waste materials such as grain-slag, waste ceramics and polyethylene plastic have been successfully utilized as filter media for the biological

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aerobic filter (Osorio and Hontoria 2002; Yu et al. 2008), which provides us a new "win-win" approach to dispose of the sludge, that is, treating wastes with wastes.

According to their roles in the producing process, chemical compositions in raw material of ceramic particles can generally be classified as three sorts (Cusidó et al. 2003; Mun 2007): (1) glassy materials, such as SiO_2 and Al_2O_3, which were major components of ceramics, forming the ceramic framework; (2) gasogenic constituents, which generated gaseous bubbles bloating the body of ceramics, include carbon, ferric oxide, ferrous oxide and magnetic iron; and (3) flux oxides, including CaO, MgO, Na_2O, Fe_2O_3 and MnO, lowered the melting point of the glassy phase. Due to similar mineral contents, dewatered sludge can be applied to replace a part of clay in the production of novel sludge-based ceramic particles (SBCP) as being proposed first by Nakouzi et al. (1998). Rich in organics, sewage sludge can produce tiny aperture inside the ceramic particles after being sintered. In addition, some other industrial wastes also have similar mineral contents with clay, such as fly ash, and they can be used as a cementing agent.

For instance, Han et al. (2009b) produced a novel sludge-fly ash ceramic particles (SFCP) following this manufacturing process. First, raw materials were mixed with powdery dewatered sludge, fly ash and clay at a mass ratio of 1:1:1; shaking in a rotational disk with water input. The powdered materials were conglutinated to particles with diameters of 2–8 mm. Then the particles were diverted to a rotary kiln and sintered at a high temperature of 1100°C for 45 minutes. At the end of the rotary kiln, products were separated by a screen and particles with diameters of 3–5 mm were chosen finally. Table 20.4 lists the characteristics of CCP and SFCP, in which CCP was produced in the same process using clay as the sole material. It can be noticed that SFCP have higher total porosity, larger total surface area and lower bulk and apparent density compared to CCP.

To inspect the safety of SFCP for water treatment, heavy metal elements in lixivium of SFCP should be considered. Han et al. determined the leaching toxicity of SFCP using a sulphuric acid and nitric acid extraction method (State Environmental Protection Administration of China 2007a). The concentrations of heavy metal elements as well as the thresholds are shown in Table 20.5. It can be seen that all heavy metal contents in lixivium were much lower than thresholds determined by the national standard (State Environmental Protection Administration of China 2007b). Because of the high sintering temperature,

Table 20.4. Characteristics of SFCP and CCP

Filter material	*Total porosity (%)*	*Pore size distribution (μm)*	*Bulk density ($g\ cm^{-3}$)*	*Apparent density (g/cm^3)*	*Total surface area (m^2/g)*
SFCP	37.7	0.5–1.0	1.32	2.11	8.99
CCP	24.7	0.5–1.0	1.89	2.51	3.05

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Table 20.5. Concentrations of heavy metal elements in the leachate of SFCP

Heavy metal	*Cu*	*Zn*	*Cd*	*Pb*	*Cr*	*Hg*	*Ba*	*Ni*	*As*
Concentrations	0.042	0.017	0.001	0.073	0.006	0	0.019	0	0.011
Thresholds	100	100	1	5	15	0.1	100	5	5

Note: Leachate test was done according to solid waste-extraction procedure for leaching toxicity–sulphuric acid & nitric acid method (State Environmental Protection Administration of China 2007a) as follows: 150 g SFCP was extracted with 1.5 L sulphuric acid & nitric acid solution (solid: $\text{liquid} = 1{:}10$, $\text{pH} = 3.20$) shaking at $30\ \text{r}/\text{min}$ for 18 h. Thresholds were determined according to Hazardous Wastes Distinction Standard-Leaching Toxicity Distinction (State Environmental Protection Administration of China 2007b)

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pathogens existing in the sewage sludge can be destroyed, and organics can be decomposed and gasified. Thus, the products do not generate odors. In addition, the heavy metal elements with low boiling points (e.g. Hg) can volatilize in the sintering process with exhausted air (Cusidó et al. 2003). Other heavy metal, such as Cd, Cr, Cu, Mn and Pb, may exist mostly in the form of ion crystal after high-temperature sintering, and be solidified stably in the ceramic particles (Xu et al. 2008). Thus, discharge of heavy metals from SFCP into the environment become difficult, and the secondary pollution is avoided effectively.

Figure 20.1 illustrates the surface morphology of SFCP and CCP with SEM at the visual pore diameter of 150 and 30 μm. It can be seen that the rougher surface of SFCP distributed with large pores was represented clearly compared with that of CCP. The inside morphology of SFCP and CCP are shown in Figure 20.2, and a similar result was presented. These phenomena indicate that SFCP would be more beneficial to the immobilization of microorganisms if they are utilized as filter media, since the essences of feasibility for filter materials refer to higher porosity and larger surface area (Kent et al. 1996).

20.3.2 Application of SBCP as Water Treatment Material in Biological Filters

Biological aerated filter (BAF), a novel, flexible and effective bioreactor based on the immobilization of microorganisms on a support, was developed in Europe during the late-1970s. This type of reactor has been widely applied all over the world due to the following benefits: BAFs can maintain high hydraulic and organic loadings, and retain a much higher biomass concentration than conventional suspended growth activated sludge systems and tricking filters, which make possible less sludge formation, stronger environmental shock resistance and a smaller size of reactor. In addition, suspended solids in raw water can be filtered directly by the submerged support media so that the requirement for separate secondary sedimentation is negligible (Umaña et al. 2008).

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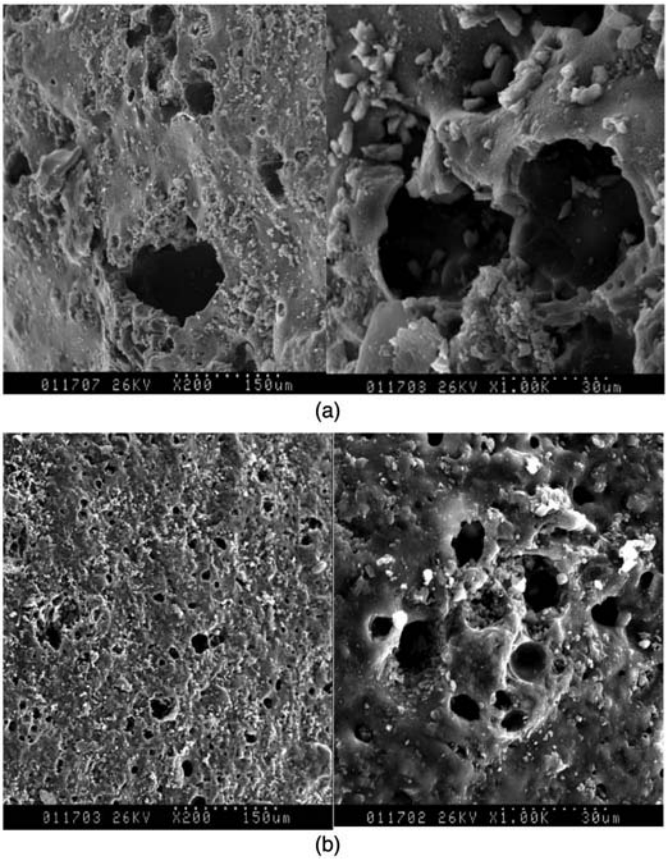

Figure 20.1. SEM photographs of the surface of SFCP (a) and CCP (b)
Source: Han et al. (2009a); reproduced with permission from Elsevier

In a BAF system, filter media play a significant role in wastewater treatment. The characteristics of media are not only related to the initial capital outlay, process design and operation mode of BAF, but also affect daily operation cost such as backwashing, air influx. Many materials such as refractory brick, special ceramic, polyurethane foam, PVC, zeolite, glass, carbon filter, rock wool, loofah sponge and others have been employed for the attachment and growth of biomass (Yang et al. 2004). Characteristics of the bed materials for immobilization have shown a significant influence on the reactor performance in all cases. For example, the reactor packed with high medium porosity obtained better organics removal efficiency compared with that using non-porous supports (Show and Tay 1999). Therefore, it can be speculated that SBCP may perform well as a filter medium material due to its higher porosity and larger surface area. Some examples of the application of SFCP in BAF for water treatment are listed as follows:

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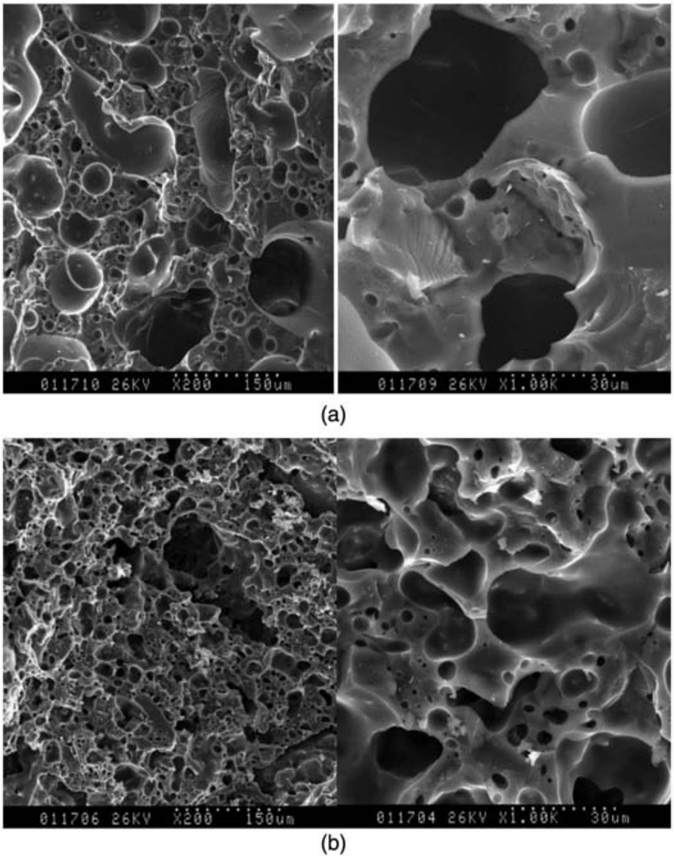

Figure 20.2. SEM photographs of the cross section of SFCP (a) and CCP (b) (Note: based on individual experimental data)

Example 1: Comparison of SBCP and CCP for wastewater treatment in BAF

Zhao et al. (2009) investigated the availability of SFCP as biofilm support compared with CCP. In this research, SFCP and CCP were employed in two lab-scale up-flow BAFs. The experimental system is shown in Figure 20.3. The effect of hydraulic retention time (HRT) and medium height on the removals of chemical oxygen demand (COD_{Cr}) and ammonium nitrogen (NH_4^+-N) as well as the the capabilities responding to loading shock and recovery after short intermittence were investigated in the two reactors comparatively. To start up the two BAF reactors, an acclimatization period lasted for 20 days were taken until both reactors reached steady state. At the end of the start-up period, SFCP column had larger removal efficiencies than CCP column, presumably because the microorganisms adapted to the environment in SFCP better than that in CCP.

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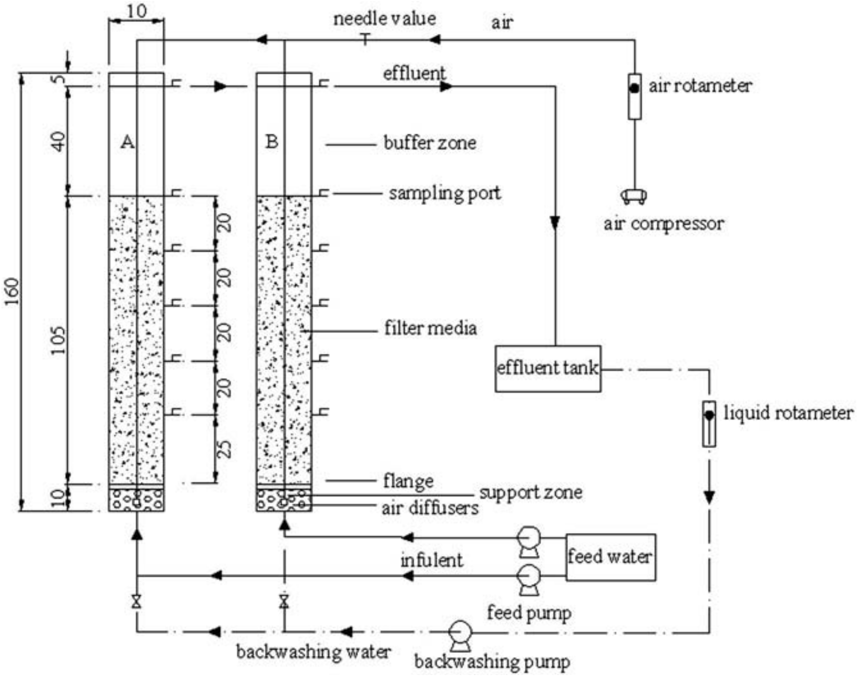

Figure 20.3. Schematic diagram of the experimental system for comparison of SFCP and CCP for wastewater treatment in BAF (dimensioning unit: cm). A: column filled with CCP; B: column filled with SFCP

Source: Zhao et al. (2009); reproduced with permission from Elsevier

Figure 20.4 shows the influence of HRT on COD_{Cr} and NH_4^+-N removal in two reactors treating synthetic wastewater. The effluent quality from SFCP column was better than that from CCP column. Because more surface area was supplied to microorganisms for contacting and digesting pollutants by SFCP than CCP, the SFCP reactor had higher removal efficiencies than the CCP reactor. In addition, the microorganisms adapted to the environment in SFCP faster than that in CCP, as SFCP had a larger total porosity. The influence of hydraulic retention time (HRT) on synthetic wastewater treatment in the SFCP column was smaller than that in the CCP column.

In order to simulate some accidents occurred in the practical operation such as power failure, water and air were resupplied to both columns after a one-day stop. COD_{Cr} and NH_4^+-N removals in the following 10 days after short intermittence are shown in Figure 20.5 (a and b), from which it can be seen that concentrations of COD_{Cr} and NH_4^+-N in the effluent from SFCP column were higher than those from CCP column in the first 2 days, but since the 3rd day, the SFCP reactor behaved better than the CCP reactor. Because nitrifying bacteria which oxidized NH_4^+-N in the reactors were aerobic, they were sensitive to the lack of dissolved oxygen; while heterotrophic bacteria which degraded COD_{Cr} were

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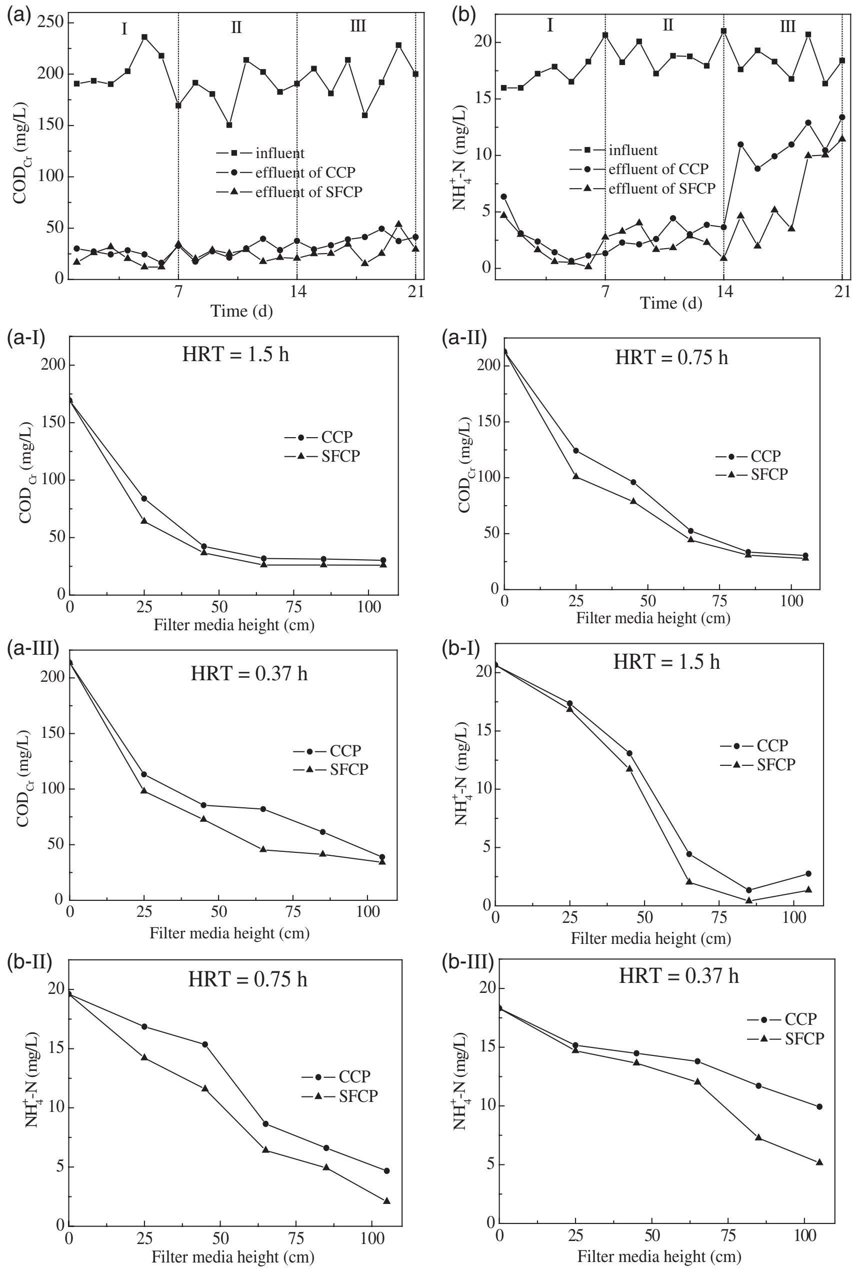

Figure 20.4. Influence of HRT on COD_{Cr} (a) and NH_4^+-N (b) removals (HRT: I - 1.5 h; II - 0.75 h; III - 0.37 h) and variation of concentrations of COD_{Cr} (a-I; a-II; a-III) and NH_4^+-N (b-I; b-II; b-III) with the filter media height in two reactors
Source: Zhao et al. (2009); reproduced with permission from Elsevier

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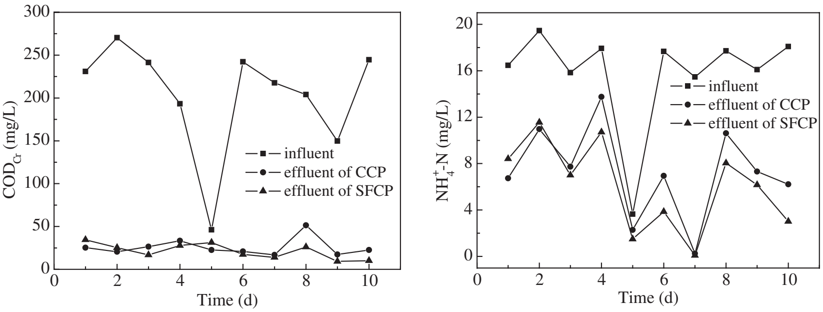

(a) (b)

Figure 20.5. COD_{Cr} (a) and NH_4^+-N (b) removals after short intermittence in two reactors

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facultative aerobic and some were even anaerobic. In order to recover the removal efficiency of NH_4^+-N, low organic loads were adopted on the 5th day. It could be concluded that it took more time for the removal of NH_4^+-N to recover in the CCP reactor than in the SFCP reactor. In other words, the SFCP reactor performed better capabilities responding to loading shock and a faster recovery after short intermittence than the CCP reactor did.

Example 2: Application of SBCP in A/O Combined BAF

SFCP is also suitable for wastewater treatment in A/O combined BAF. In the research of Han et al. (2009b), SFCP were employed in an upflow lab-scale A/O BAF to determine its performance for synthetic wastewater treatment. The effect of HRT, air-liquid ratio (A/L), media height, and recirculation on the removal of ammonium (NH_4^+-N), total nitrogen (TN) and COD_{Cr} in the experimental system were investigated, and the result was as follows: the optimum operation conditions were obtained as HRT of 2.0 h and A/L of 15:1 and 200% recirculation. Under the optimal conditions, 90% COD_{Cr}, more than 98% NH_4^+-N and approximately 70% TN were removed. The functional zones of the reactor affected the removal of COD_{Cr}, NH_4^+-N and TN significantly, which resulted in some different but regular variations. The characteristics of SFCP such as higher total porosity and larger total surface area accounted for a strong buffer capacity of the BAF system.

Example 3: Application of SBCP in Anaerobic Bio-filter

The anaerobic bio-filter (AF) is a special biological filter without aerating. Due to the simple operation, easily restarting, large biomass attachment, high organic loadings and long sludge retention time, this type of reactor has been widely used for the treatment of concentrated municipal and industrial wastewater. Especially for treatment of high-strength organic wastes (del Pozo et al. 2000), anaerobic systems are superior to conventional aerobic systems in saving capacity and operational costs, reducing production of sludge and producing of biogas

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(Manariotis and Grigoropoulos 2008). There are some studies on the application of SBCP in AF (Han et al. 2009a; Yue et al. 2009).

Yue et al. (2009) did a research on two lab-scale upflow AF packed with SFCP and CCP, to investigate the potential advantage and substitutability of the former for wastewater treatment. The results showed that the SFCP reactor had an advantage over the CCP reactor in terms of TN removal at the optimum C/N ratio of 4.03 when different volumetric loading rates were applied. During the restart period, nitrate was removed entirely at the C/N ratio of 3.5; SFCP represented a relatively weak performance in nitrate removal compared with CCP, but this difference would disappear gradually with an increase in the C/N ratio. At lower C/N ratios, nitrite accumulation (NA) was obvious and was affected significantly by HRT; while the process of dissimilatory nitrate reduction to ammonia (DNRA) had some negative influence on nitrate removal only when the C/N ratio was very low (Han et al. 2009a). Lower NA was observed in the SFCP column, especially when the C/N ratio was more than 3.5. NA disappeared when the C/N ratio was more than 5.0, corresponding to the maximum TN removal; TN could not be removed completely due to the process of DNRA; Orthophosphate uptake also took place in the restart performance; P removal increased with the increase of the C/N ratios, especially when the C/N ratio was beyond 3.5. The maximum value (about 55%) was achieved at the C/N ratio of 5.0, which agreed well with the TN removal. The SFCP reactor indicated a better performance in TN and P removal compared with the CCP reactor. In addition, the microorganism group presented layered characteristics with the column height, and the zonation of P removal was clearer than that of TN removal. Biofilm was mainly distributed at the height of 25 cm from the column bottom, which suggested that bacteria structure during the restart period did not change obviously compared with that during the start-up period. When the C/N ratio of 2.60 was applied, a linear correlation between HRT and nitrite accumulation ratio was observed, which was more obvious in the CCP column. Due to incomplete nitrate conversion, the linear correlation between HRT and TN removal was relatively weak. Under different HRTs, the SFCP reactor kept a stronger inhibition of NA. When no external nitrogen resource was spiked, the structure of the bacterial group varied. P-uptake bacteria were replaced by heterotrophic anaerobes. The process of DNRA became stronger and stronger with the increase in the C/N ratios; when the C/N ratio was more than 30, a line correlation between C/N and DNRA was found. During the start-up and restart period of AF, SFCP represented a higher performance in TN and P removal. Therefore, it could be concluded that SFCP had a potential advantage and substitutability for CCP, which was a very promising filter medium.

Example 4: Application of SBCP for Pharmaceutical Advanced Wastewater Treatment

Treating pharmaceutical wastewater effectively was a significant challenge, since the condition and composition of pharmaceutical wastewater was often changeful. Generally, most of the wastes from pharmaceutical industry were characterized by a low BOD_5/COD ratio (Badawy et al. 2009), high salinity (Li and Jin 2009), a

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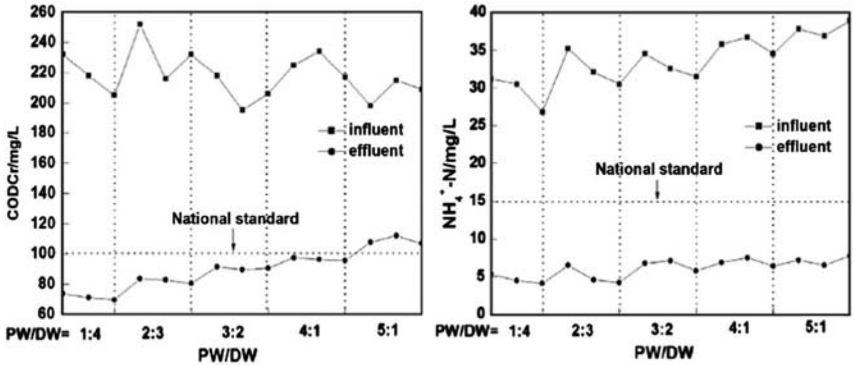

Figure 20.6. Influence of the volume ratio of pharmaceutical wastewater to domestic wastewater (PW/DW) on COD_{Cr} and NH_4^+-N removals in the ULSC reactor
Source: Wu et al. (2011b); reproduced with permission from Elsevier

variety of organic and inorganic constituents including spent solvents, catalysts, reactants and small amounts of intermediate or product (Chen et al. 2008; Oktem et al. 2008). In order to achieve advanced treatment efficiency, Wu et al. (2011b) prepared a novel SBCP named media-ultra-lightweight sludge ceramics (ULSC) to investigate its possibility for pharmaceutical wastewater treatment. In their research, an upflow lab-scale BAF was designed. Because the BOD_5/COD ratio in pharmaceutical wastewater was lower than the typical demand of the biological wastewater treatment process, domestic wastewater was added for microorganism growing. The influences of some operating factors (including the volume ratio of pharmaceutical wastewater to domestic wastewater (PW/DW), HRT and A/L) on COD_{Cr} and NH_4^+-N removal were investigated. The influence of PW/DW, for example, was shown in Figure 20.6. The research indicated that at the PW/DW of 4:1, HRT of 6 h and A/L of 5:1, both the requirement of better effluent water quality and lower running cost could be achieved in the ULSC reactor.

20.3.3 Application of SBCP as Water Treatment Material in Electrobath Reactor

Micro-electrolysis technology is a new water treatment techniques based on electrochemistry. It performs well on breaking the construction of refractory organics in wastewater, which can increase the value of BOD_5/COD and facilitate biological treatment (Fan et al. 2009; Yin et al. 2009). The mechanism of micro-electrolysis is that the electrons are supplied by the galvanic corrosion of many micro-scale sacrificial anodes instead of external power. Thus, a hypothesis is put forward: if sludge and scrap iron are utilized as additives to produce ceramic particles, numerous microscopic galvanic cells could be formed between the particles of carbon and iron. When the ceramics are applied for wastewater treatment, C in sludge plays the role of cathode, Fe in scrap iron does anode and

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wastewater is electrolyte solution. The half-cell reactions can be represented as follows (Cheng et al. 2007):

$$\text{Anode (oxidation)}: 2\text{Fe} \rightarrow 2\text{Fe}^{2+} + 4\text{e}^{-}, \text{E}(\text{Fe}^{2+}/\text{Fe}) = -0.44\ \text{V}$$

$$\text{Cathode (reduction)}: 2\ \text{H}^{+} + 2\text{e}^{-} \rightarrow \text{H}_2 \uparrow, \text{E}(\text{H}^{+}/\text{H}_2) = 0\ \text{V}$$

$$\text{Or O}_2 + 4\ \text{H}^{+} + 4\text{e}^{-} \rightarrow 2\text{H}_2\text{O}, \text{E}(\text{O}_2/\text{H}_2\text{O}) = +1.23\ \text{V}$$

$$\text{Or O}_2 + 2\text{H}_2\text{O} + 4\text{e}^{-} \rightarrow 4\text{OH}^{-}, \text{E}(\text{O}_2/\text{OH}^{-}) = +0.40\ \text{V}$$

On the basis of the hypothesis above, new filter medium named as ceramic-corrosion-cell fillers was produced by Wu et al. (2011a). The new filler included two ceramic particles: a) cathode ceramic-corrosion-cell fillers (CCF) and b) anode ceramic-corrosion-cell fillers (ACF). CCF is a sludge-based ceramic particle which was prepared using 60.0 wt% of dried sewage sludge and 40.0 wt% of clay through sintering at 400°C for 20 min in anoxic condition. For ACF, the raw materials were mixed with 40.0 wt% of scrap iron and 60.0 wt% of clay, and the preparation process was similar as CCF. The two particles were employed in an electro-bath reactor for cyclohexanone industry wastewater treatment. A 90% removal efficiency of COD_{Cr} and cyclohexanone could be achieved according to their research results at the optimum conditions of pH of 3–4, HRT of 6 h and the medium height of 60 cm. Thanks to the comparatively lower bulk density and grain density of CCF and ACF, the backwash process in the reactor were more easily operated compared with the common electrobath reactor, and the service life of the reactor could be extended to a certain extent as a result.

20.3.4 Application of SBCP in Building Material

Sewage sludge can be applied for the production of building material, such as bricks, tiles and cement-based materials (Cheeseman and Virdi 2005; Wang et al. 2005b; Cusidó and Cremades 2012; Lin et al. 2012; Zhou et al. 2013). For example, Qi et al. manufactured an SBCP named ultra-lightweight ceramic (ULWC), which was suitable for cement production, due to its distinctive characteristics of low density as well as high strength, heat insulation and quakeproof property (Qi et al. 2010). The optimum ULWC was produced with the sewage sludge addition of 20–30 wt.%, preheated at 400°C for 20 min and sintered at 1150°C for 10 min (Qi et al. 2010). Property tests showed that bulk density and water absorption of ULWC was 330.80 kg/m^3 and 5.30 wt.%, respectively, which could meet the requirement of ordinary lightweight aggregate. They also did some research on its application for cement production: using a water-to-cement mass ratio of 0.50 and ULWC-to-water volume ratio of 2, compressive strength of 41.40 MPa and rupture strength of 5.50 MPa could be achieved after 28 d age of concrete.

The example above shows the application of SBCP in traditional building materials, and some studies have also been done on the novel building material,

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such as phase change material (PCM). PCM is an energy storage material, which can retain heat energy in a latent form by phase change (usually solid-liquid phase change), resulting in high energy storage density and little temperature fluctuation (Sarı and Kaygusuz 2001; Zhu et al. 2009; Sun et al. 2013). Therefore, it is a potential building material in consideration of energy conservation. In practical works, encapsulation of solid-liquid PCM is critical. The combination of PCM with porous materials is a new encapsulation method: storing PCM in the small pores, the porous materials can not only improve the thermal conductivity but also stabilize the shape of PCM in the phase change process (Zhang et al. 2006). Therefore, SBCP with high porosity may be a suitable porous material of composite PCM, and the relevant research has been done by He et al. (2013).

According to He et al. (2013), polynary fatty acid eutectic mixture (a PCM they prepared) can be retained by 46 wt.% into the pores of SBCP without seepage. The melting temperature of composite PCM was 26.66°C, and the corresponding melting enthalpy was 47.1 J/g, suitable to regulate building room temperature. The preparation of composite PCM was just a physical combination, and its chemical structures can remain stable in the application process. In addition, the model experiment showed that the prepared composite PCM can significantly reduce indoor temperature fluctuation, implying its applicability for building energy conservation.

20.4 ACTIVATED CARBON PRODUCTION FROM SLUDGE

Activated carbon is a carbonaceous material with a high degree of porosity and extended particulate surface area (Byrne and Marsh 1995; Bansal and Goyal 2005). Granular activated carbon (GAC) is often utilized in biological treatment processes, to act as a support for microorganisms and to adsorb organics (Zhang et al. 1991). While for powdered activated carbon (PAC), it is added to activated sludge in order to achieve similar effects (Sublette et al. 1982; Aktas and Cecen 2007). Because of the high content of organic matters, sewage sludge is a suitable feedstock for the production of activated carbon (Rozada et al. 2005a).

According to numerous studies on the production of sludge-based activated carbon (SBAC), the methods can be grouped into two categories: physical activation and chemical activation (Martin et al. 2003; Yu and Zhong 2006; Rozada et al. 2007; Fan and Zhang 2008). Physical activation entails the selective burn-off (oxidation) of atoms from the carbon structure by means of controlled gasification. The sewage sludge was exposed to an oxidizing gas at high temperature (around 700–1100°C) to burn-off, and then pore-blocking tarry substances are removed to form carbon structure (Byrne and Marsh 1995). Chemical activation entails mixing sewage sludge with an activation reagent and then heating in an inert atmosphere at a relevant temperature. Thus, the carbonization and activation steps proceed simultaneously (Hayashi et al. 2002). The mechanism

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by which the reagent reacts with sewage sludge depends on the activant employed. Through the activation process, sewage sludge turns into useful carbonaceous adsorbent for wastewater treatment.

20.4.1 SBAC Produced by Physical Activation

Generally, the adsorption capacity of an adsorbent is determined by the quantity of pollutant it can physically contain within its porosity (according to the pollutant adsorbed by a unit mass of the adsorbent). Brunauer, Emmett and Teller (BET) surface area is the most commonly used measure to evaluate the utility of an adsorbent, which is typically calculated from its nitrogen gas uptake (Brunauer et al. 1938). Many researchers have prepared SBAC using the physical activation method, which proceeds by the progressive burn-off of the carbon fraction. However, since sewage sludge still contains a certain amount of inorganic content which is substantially non-porous, SBACs that have been produced by physical activation typically exhibit relatively low surface areas. The properties of SBAC produced by physical activation in some studies are shown in Table 20.6 (Smith et al. 2009).

As shown in Table 20.6, the highest BET surface area of 226 m^2/g was attained by Rio et al. (2006a, b), implying that steam is an excellent physical activation reagent. Rio et al. employed a two-stage preparation procedure, that is, carbonization followed by activation. They determined that 1 h and 600°C was the optimum carbonization condition. In the following activation process, the BET surface area was maximised at an activation temperature of 763°C and a dwell time of 39 min (Rio et al. 2006a, b). As the BET surface area of an activated carbon, 226 m^2/g is relatively low. However, the maximum BET surface area attainable as well as the optimum activation conditions would be likely to be influenced by the choice of sewage sludge. For example, Ros et al. (2006b) produced SBACs with different surface areas from three different sludge types.

According to Rio et al. (2006b) activation by CO_2 tends to yield higher BET surface areas than steam if activation temperatures in excess of 800°C are employed. The larger molecular size of CO_2 impedes its diffusion through the porous network, which results in its lower reactivity than steam and the more endothermic nature reaction with carbon (159 kJ/mol for CO_2 and 117 kJ/mol for steam) (Byrne and Marsh 1995). Thus, activation by CO_2 requires higher temperatures. The more competitive property of CO_2 than steam attributed to the greater degree of control over the activation process afforded by its slow reaction rate, which partly arises from 'production-inhibition.' Therefore, the reaction products may be adsorbed on the carbon's active sites. However, the carbon-steam reaction products and especially H_2 may also be adsorbed, again retarding the activation rate (Smith et al. 2009).

The inorganic content of a carbonaceous material can be lowered through partial dissolution in acid. Thus, HCl washing can be applied as a useful tool. Investigations on the effect of HCl washing on physically activated sludge have been done by some researchers, and the results showed that an improvement in the BET surface could be achieved. For example, the BET surface area of SBAC

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Table 20.6. Properties of SBACs produced by physical activation

	Carbonisation cond.		*Activation conditions*					
Sludge type	*Temp. (°C)*	*Dwell time (h)*	*Gasifying gas*	*Temp. (°C)*	*Dwell time (h)*	*Pre-treatment*	*Post-treatment*	*BET surface area (m^2/g)*
WWTP	Not carbonised		Steam	700	NA	NA	None	55[a]
D M WWTP	Not carbonised		Not specified	NA	NA	D-NA-NA	None	30–50[b]
2°WWTP WBS	700	NA	H_2O	800	NA	D-105°C-16 h	None	200[c]
M WWTP C	700	1	Steam	800	0.75	D-air-10 days, PL	HCl, H_2O	123[d]
D M	850	1	CO_2	550	0.5	D-108°C-24-36hrs	None	88[e]
D M	Not carbonised		Air	350	3	D-108°C-24-3 6 h	None	80[e]
M WWTP	Not carbonised		CO_2	750	0.5	D-air-NA	None	61[f]
M WWTP	Not carbonised		CO_2	550	60	NA	None	70[g]
M WWTP	Not carbonised		Steam	550	60	NA	None	97[g]
A WWTP	450	1	O_2:N_2 (1:29 by vol)	275	4	D-air-NA	None	102[h]
AN WWTP	450	1	O_2:N_2 (1:29 by vol)	275	4	D-air-NA	None	105[h]
WWTP	650-850	NA	Steam	800	NA	NA	None	49[i]
D 2° M WWTP	Not carbonised		Air	700	3	None	None	18[j]
D 1°M WWTP	Not carbonised		Air	700	3	None	None	11[j]
M WWTP,VL	600	1	Steam	760	0.5	D-NA-NA	None	226[k]
D M A Ad WWTP	700	0.5	CO_2	800	2-4	D-105°C-48 h	None	7[l]
D M A Ad WWTP	700	0.5	CO_2	800	2-4	D-105°C-48 h, HCl-C	None	269[l]

(Continued)

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Table 20.6. Properties of SBACs produced by physical activation (Continued)

	Carbonisation cond.		*Activation conditions*					
Sludge type	*Temp. (°C)*	*Dwell time (h)*	*Gasifying gas*	*Temp. (°C)*	*Dwell time (h)*	*Pre-treatment*	*Post-treatment*	*BET surface area* (m^2/g)
D Ax M WWTP	Not carbonised		Air:N_2 (1:5 by vol)	700	0.5	D-105°C-48 h	None	55[m]
D A M WWTP	Not carbonised		Air:N_2 (1:5 by vol)	700	0.5	D-105°C-48 h	None	45[m]
D Ax L M WWTP	Not carbonised		Air:N_2 (1:5 by vol)	700	0.5	D-105°C-48 h	None	12[m]

Abbreviations: Temp.—Temperature; Cond.—Conditions; 1°— primary sludge; 2°—secondary sludge; A—aerobically digested; Ad—activated sludge; AN—anaerobically digested; Ax—extended aeration sludge; C—sludge cake; D—dewatered; D-X °C-Y h—dried at a temperature of X°C for Y h (Air = air dried) (CM = dried to constant mass); HCl—washed in Hydrochloric acid; HCl–C—washed in HCl after carbonisation; L—sludge treated with lime; M—municipal/urban; NA—not known (information not given in paper); PL—pelletised; WWTP—wastewater treatment plant; and WBS—sludge without biological stabilisation. Major references: [a]Bilitewski (1979); [b]Bojner (1973); [c]Bosch et al. (1976); [d]Fitzmorris et al. (2006a, b); [e]Jeyaseelan and Lu (1996); [f]Jindarom et al. (2007); [g]Kojima et al. (2002); [h]Mendez et al. (2005); [i]Mitchell et al. (1978); [j]Pan et al. (2003); [k]Rio et al. (2006a, b); [l]Ros et al. (2006a); [m]Ros et al. (2006b)

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employing HCl washing prior to its activation with CO_2 was 269 m^2/g (Ros et al. 2006a). Without the HCl washing step, the BET surface area of SBAC exhibited was only 7 m^2/g. According to Ros et al. (2006a), it was calculated that the BET surface area of 897 m^2/g could be achieved for the carbonaceous fraction alone of the HCl washed. Therefore, further improvements can be attained by improving the efficiency of washing procedure in removing the inorganic fraction. In addition, the comparison between SBACs obtained by Fitzmorris et al. (2006b) and Ros et al. (2006a) shows that HCl washing prior to activation is more effective than post-activation washing, which might be due to the fact that activation increases the stability of inorganic fraction. Since high temperatures can convert the inorganic fraction into mineral-like compounds and induce the encapsulation of some metals by the carbon phase (Bagreev et al. 2001), activation lowers the propensity of inorganic fraction towards leaching.

20.4.2 SBAC Produced by Chemical Activation

Many reagents can be applied for chemical activation of SBAC, which often include acid, alkali and inorganic salt. Table 20.7 lists the properties of some SBACs produced by chemical activation using different activation reagents.

Activation of Acid. As shown in Table 20.7, the highest BET surface area of SBAC activated with phosphoric acid and H_2SO_4 was 289 m^2/g and 408 m^2/g, respectively (Zhang et al. 2005). These two acids are widely used for activation due to their relatively low activation temperature (Guo and Rockstraw 2007) and the ease of the post-activation extraction process (Molina-Sabio et al. 1995). For H_2SO_4, an activation temperature of 300°C was sufficient to affect the activation process.

Activation of Alkali. It can be seen apparently from Table 20.7 that SBACs activated with KOH attained the highest BET surface areas among these literatures, and NaOH was the second most effective activation reagent following KOH. The large surface areas of these SBACs may be caused by the two-stage producing method: carbonization-activation procedure, because the pores formed during the carbonisation step could further aid pore development during activation (Hu and Vansant 1995). In addition, the way how alkaline reagent reacts with sewage sludge might also impact on the phenomenon. In comparison with acidic reagents, which principally react with oxygen functional groups to develop porosity, KOH and NaOH react directly with carbon atoms (Ahmadpour and Do 1997; Hsu and Teng 2000). During the carbonization process, dehydration occurs and increases the concentration of carbon, which leads to a rise in the C:H and C:O ratios, making the carbon atoms more accessible to the impregnated reagent.

In the research shown in Table 20.7, the difference in the highest surface areas may stem from differences in the way KOH employed. Ros et al. (2006a) determined that dry, physical mixing using ground KOH was more effective than wet impregnation. In addition, this may also be influenced by the difference in sludge characteristics. For example, Lillo-Rodenas et al. (2008) compared the response to KOH activation of a sludge produced from synthetic wastewater

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Table 20.7. Properties of SBACs produced by chemical activation

		Carbonisation conditions		*Activation conditions*						
Sludge type	*Ash content (wt.%)*	*Temp. (°C)*	*Dwell time (h)*	*Reagent*	*Reagent: sludge ratio (by mass)*	*Temp. (°C)*	*Dwell time (min)*	*Pre-treatment*	*Post-treatment*	*BET surface area (m^2/g)*
T	35	Not carbonised		H_2SO_4	46:75	300	30	None	None	26^a
M	35	950	1	H_2SO_4	46:75	300	30	Act	None	205^a
M	23	Not carbonised		H_2SO_4	100 g in 250 ml 3 M H_2SO_4	650	60	D-105°C -24 h	NaOH_W	408^b
M	23	Not carbonised		H_3PO_4	100 g in 250 ml 3 M H_3PO_4	650	60	D-105°C -24 h	NaOH	289^b
D M A Ad WWTP	31	700	0.5	H_3PO_4	2 ml 50 wt.% H_3PO_4:1 g sludge	450	240	D-105°C -48 h	HCl	17^c
D M A Ad WWTP	31	700	0.5	NaOH	3:01	700	60	D-105 30-48 h	HCl	1224^c
PaM WWTP	NA	400	1	KOH	1:01	700	90	D-110°C -24 h, HCl-C	4%NaOH_W, H_2O	900^d
Syn	47	700	30	KOH	1:01	700	60	D-105 °C -48 h	HCl	1882^e
A Ad WWTP M	31	700	30	KOH	1:01	700	60	D-105°C -48 h	HCl	1058^e
D M A Ad WWTP	31	700	0.5	KOH	3:01	700	60	D-105°C -48 h	HCl	1686^f
D Ax L M WWTP	53	700	0.5	KOH	1:01	700	60	D-105 30-48 h	HCl	130^g
M	59	400	NA	KOH	1:01	850	60	NA	HNO_3, H_2O	658^h

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D M 2° Ad WWTP	NA	Not carbonised	KOH and steam	Soaked in 3 M KOH	600	60	D-105°C -CM	H_2O	382[i]
T	35	Not carbonised	$ZnCl_2$	1:0.31	600	60	None	HCl	397[j]
AN D M	NA	Not carbonised	$ZnCl_2$	10 g in 25 ml 5 M $ZnCl_2$	500	2	D-103°C-6 h	HCl	647[k]
A M	41	Not carbonised	$ZnCl_2$	200 g in 500 ml 0.5-7M $ZnCl_2$	550	60	D-105°C-24 h	HCl	585[l]
AN M	45	Not carbonised	$ZnCl_2$	200 g in 500 ml 0.5-7M $ZnCl_2$	550	60	D-105°C-24 h	HCl	455[l]
D M	NA	Not carbonised	$ZnCl_2$	Soaked in 3 M $ZnCl_2$	650	120	D-108°C-24h-36 h	NA	247[m]
R PaM	NA	Not carbonised	$ZnCl_2$	2.5:1	800	120	D-110°C -24 h	HCl, H_2O, Act C	1249[n]
R PaM	NA	Not carbonised	$ZnCl_2$	3:01	750	120	D-110°C -24 h	HCl, H_2O	996[o]
R PaM	20	Not carbonised	$ZnCl_2$	3.5:1	800	120	D-110°C -24 h	HCl, HF, H_2O	1092[p]
AN D	37	Not carbonised	$ZnCl_2$	Soaked in 5 M $ZnCl_2$	650	120	D-108 °C -24 h	NA	309[q]
AN M WWTP	47	Not carbonised	$ZnCl_2$	1: 1	650	5	D-NA-NA	HCl	472[r]
R PaM	NA	Not carbonised	$ZnCl_2$	3.5:1	800	120	D-110°C -24 h	HCl, Act C	1059[s]
R PaM	NA	Not carbonised	$ZnCl_2$	3.5:1	800	120	D-110°C -24 h	HCl, Act C, 2 [HCl&HF]	1705[s]
R M	30	Not carbonised	$ZnCl_2$	10 g in 25 ml 5 M $ZnCl_2$	650	120	D-103°C -24-36 h	HCl	542[t]

(Continued)

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Table 20.7. Properties of SBACs produced by chemical activation (Continued)

		Carbonisation conditions		*Activation conditions*						
Sludge type	*Ash content (wt.%)*	*Temp. (°C)*	*Dwell time (h)*	*Reagent*	*Reagent: sludge ratio (by mass)*	*Temp. (°C)*	*Dwell time (min)*	*Pre-treatment*	*Post-treatment*	*BET surface area* (m^2/g)
D AN M	35	Not carbonised		$ZnCl_2$	10 g in 25 ml 5 M $ZnCl_2$	650	120	D-103°C-24-36 h	HCl	463[t]
66 wt.% D AN M, 33 wt.% CH	NA	Not carbonised		$ZnCl_2$	10 g in 25 ml 5 M $ZnCl_2$	500	120	D-103°C -NA	HCl	868[u]
R PaM	NA	Not carbonised		$ZnCl_2$ and $FeNO_3$	3:1 (Zn-Fe ratio is 2:1)	750	120	D-NA-NA	HCl	310[v]
Su WWTP	51	550	2	$ZnCl_2$ and H_2SO_4	2:1 ratio of $ZnCl_2$- H_2SO_4	550	120	D-103°C -24 h	HCl	145[w]
PWW	NA	Not carbonised		$ZnCl_2$	1:1	500	60	D-NA-NA	HCl	1080[x]
PWW	NA	Not carbonised		K_2S	1:1	700	60	D-NA-NA	HCl	1160[x]

Abbreviations: 2[HCl&HF]—washed in HCl and hydrofluoric acid (HF) twice; 4%NaOH_W—washed in 4% NaOH solution; Act—activated prior to being carbonised; ActC—activated at 800°C for 2 h in a 75% CO, 25% CO_2 gas mixture; CH—coconut husk; HF—washed in HF; HNO_3—washed in nitric acid; NaOH_W—washed in 1 M NaOH solution; PaM—paper mill sludge; PWW—pulp mill wastewater sludge; R—raw sludge; Su—surplus sludge; Syn—biological sludge from synthetic wastewater; and T—fertilizer derived from municipal sludge. For all other abbreviations please refer to the previous table

Major references: [q]Lu and Lau (1996); [r]Rozada et al. (2005a, b, 2007); [s]Sandi et al. (2003); [t]Tay et al. (2001a); [u]Tay et al. (2001b); [v]Khalili et al. (2000a); [w]Yu and Zhong (2006); [x]Cho and Suzuki (1980)

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with the two sludges previously tested by Ros et al. (2006a, 2007). The synthetic sludge, which contained the most carbon and the least ash, yielded the SBAC with the highest BET surface area. However, they also reported the decrease of char's ash content by water washing reduced the BET surface area obtained by its activation, implying the inorganic fraction dose a positive contribution.

Activation of Inorganic Salt. Table 20.7 shows that $ZnCl_2$ was the third most effective chemical activation reagent. Utilizing a typical sewage sludge, the highest BET surface area of 647 m^2/g was achieved by Chen et al. (2002), while the utilization of paper mill/pulp mill derived sludge (which contains lower inorganic matters) represents higher BET surface areas (Cho and Suzuki 1980; Khalili et al. 2000a, b, 2002; Sandi et al. 2003). In the activation of paper mill sludge, K_2S was found to be more effective than $ZnCl_2$, and the optimum activation temperature was higher due to the different boiling points of the reagents (Cho and Suzuki 1980).

When $ZnCl_2$ was applied for activation, some factor should be considered, including the activation temperature and the heating rate. It have been reported that the optimum temperatures for activation using $ZnCl_2$ ranged from 550°C to 650°C in different studies, and dwell times were 1 or 2 hour (Smith et al. 2009). The variety of reported optimum activation conditions depended on the variety of mechanisms by which $ZnCl_2$ could develop porosity, which was generally believed to act as dehydrating reagent and tar formation suppressant (Caturla et al. 1991; Balci et al. 1994). The essence of the mechanism for $ZnCl_2$ activation is that it promotes the aromatization of the carbon skeleton with the concomitant generation of a pore structure (Yue et al. 2002).

20.4.3 Application of SBAC for Water Treatment

SBAC can be widely used for the capture of pollutants in liquid phase, including heavy metal ions, dyes, phenol and phenolic compounds, benzoic acid, phosphates, COD, etc. (Smith et al. 2009), and a lot of research have been conducted in this area. This section mainly describes the preparation of two forms of SBAC (powdered and granular SBAC) from paper mill sewage sludge and their application in water treatment via the examples.

Example 1: Application of Powdered SBAC in Water Treatment

Li et al. employed paper mill sewage sludge as the raw material for producing powdered SBAC by physical activation with steam (Li et al. 2011a, b, c). The producing process was as follows: firstly, dewatered sludge was carbonized at 300°C in a muffle furnace for 60 min; secondly, the carbonization product was activated at different temperatures (from 650°C to 950°C) for a certain time (10–100 min) in steam atmosphere; after the product was dried again at 105°C for 24 h to constant weight, crushed and sieved into a uniform size of ~0.15 mm, SBAC was obtained finally. The dye removal performance of SBAC was investigated in comparison with the carbonized sludge (CS, which was obtained by carbonizing sludge directly without steam activation and sieving the products into

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a uniform size of 0.15 mm approximately). The important parameters which greatly affect the characteristics of SBAC, such as the carbonization temperature, carbonization time, activation temperature and activation time, were investigated through batch experiment.

Li et al. (2011b) indicated that the effective SBAC for dye removal was obtained at a carbonization temperature of 300°C, carbonization time of 60 min, activation temperature of 850°C and activation time of 40 min. SBAC prepared under the optimum conditions had remarkable adsorptive properties and notable treatment effect for Methylene Blue compared to CS. In addition, the toxicity of SBAC was much lower than the thresholds and was safe to be applied in wastewater treatment.

In another research (Li et al. 2011a), SBAC was applied to remove cationic methylene blue (MB) and anionic reactive red 24 (RR 24) from aqueous solutions. The removal efficiency was found to vary with particle size, SBAC dosage, pH, salt concentration, contact time and initial dye concentration. The isothermal data fitted Langmuir model much better than the Freundlich model, confirming the monolayer adsorption capacity of dyes onto SBAC. Through the desorption experiment, it was found that little dyes would be desorbed from SBAC in deionized water within a pH range from 1.0 to 13.0 (with the desorption ratio of less than 6%), and the lower desorption rate of MB than of RR 24 demonstrated that cationic dye was more stable on SBAC. In addition, the thermal treatment at 300°C for 30 min can effectively regenerate the adsorption capacities of dye-exhausted SBAC. The maximum adsorption capacity (263.16 mg/g for MB and 34.36 mg/g for RR 24), high regeneration efficiency and low cost (365 US $/t) of SBAC provided strong evidence of the potential of SBAC for removing dyes from aqueous solutions.

In the column study conducted afterward (Li et al. 2011c), SBAC was applied in a fixed-bed adsorption column for MB and RR 24. Desorption of dyes on SBAC was repeated for several cycles using HCl, NaOH solution and deionized water. The results showed that breakthrough time and exhaustion time increased with the decrease in inlet dye concentration, particle size, flow rate and increasing adsorbent mass. The column adsorption capacities of SBAC were 103.58 mg/g for MB and 15.68 mg/g for RR 24, which were lower than the maximum adsorption capacities obtained in equilibrium studies, indicating that the capacity of activated carbon was not fully utilized in the fixed-bed column. However, the adsorption capacity of SBAC was much higher than that of commercial activated carbon in both equilibrium and column adsorption, implying the high potential of it for dye wastewater treatment.

Example 2: Application of Granular SBAC in Water Treatment

Li et al. (2012) prepared granular SBAC through stream activation and utilized it in a fluidized-bed bioreactor (FBBR). In their research, solution with 0.5 wt% of polyvinyl alcohol and 1.5 wt% of carboxymethylcellulose sodium (NaCMC) was used as the adhesive for granulation, and the grain size of the granular SBAC

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was $\varphi = 1-5$ mm. The optimum SBAC was obtained via carbonizing at 450°C for 50 min and activating at 800°C for 60 min. The characteristics of this SBAC, such as iodine adsorption value, the specific surface area and grain density, were 137.6 mg/g, 130 m^2/g and 1.34×10^3 kg/m^3, respectively. Then, the granular SBAC was used as FBBR filters to investigate its property for wastewater treatment. The results showed that, under the influent conditions of COD 800 mg/L and HRT of 2 h, a steady removal efficiency of above 90% could be achieved for COD after 40 days of running, implying that the SBAC filler was feasible for the FBBR system.

In addition, the property of granular SBAC was further improved through the method of bentonite adding and acid washing by Li et al. (2011d). Hereon, powdered bentonite (Na contained) was mixed in the raw materials in order to enhance the abrasion resistance strength of the fillers. With a bentonite adding of 8 wt%, granular SBAC was more easily formed and the abrasion resistance strength increased by 15% compared with the above none-bentonite-added one. Experiment on different acid washing treatments was conducted to produce FBBR fillers with optimum performance. The results showed that acid washing prior to activation had a better effect on the removal of inorganic matter (Fe), and the optimum treatment condition was soaking with 2 M HCl for 6 h. Through the improvement method, SBAC fillers with smaller grain density (1170 kg/m^3) and higher specific surface area (176 m^2/g) were obtained.

20.5 SUMMARY

Sewage sludge is an inevitable by-product in the process of wastewater treatment. Its increasingly huge quantity and persistently environmental contamination makes the disposal and recycling of it remain an issue of great importance. Therefore, it is imperative to search for an economical and effective way to solve the problems.

On the basis of research on the potential techniques for converting sewage sludge into environmentally benign materials, this chapter mainly describes the application of sewage sludge in the production of SBCP and SBAC. For wastewater treatment, SBCP as filter medium material perform better than commercial ceramic particles due to the higher porosity and larger surface area. In addition, SBCP also combined well with phase change material, exhibiting an excellent possibility for building energy conservation. SBAC can be widely used as an adsorbent for the removal of various pollutants in the liquid phase, and the property varies with both the production method and the character of the sludge itself.

In conclusion, sewage sludge is a highly promising feedstock for the production of water treatment materials as well as some novel materials. Through appropriate conversion methods, it will represent an attractive alternative for the disposal and reuse of sewage sludge.

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CHAPTER 21

Adapting to Climate Change: Water Management Strategy

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21.1 INTRODUCTION

“Climate Change” in Intergovernmental Panel on Climate Change (IPCC) parlance refers to a change in the state of the climate that can be identified (e.g. using statistical tests) by changes in the mean and/or the variability of its properties and that persists for an extended period, typically decades or longer. Climate change can be caused due to both natural processes and human activities, although it is attributed that human activities are the major factor contributing to this.

For the past many years, human activities like agricultural, industrial, deforestation, exploitation of land resources, etc. have greatly influenced the composition of the earth’s atmosphere. These result in the increase of the emission of what is known as the ‘greenhouse gases’ (GHGs) like the Carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O). They create holes in the ozone layer which is responsible for preventing the ultraviolet rays from entering the earth’s atmosphere. As a result, the temperature of the atmosphere increases. The global mean annual temperature at the end of the 20th century as a result of this has increased by 0.4–0.7°C above that recorded at the end of the 19th century (Pathak et al. 2012). IPCC has projected the temperature rise to be between 1.1°C and 6.4°C by the end of the 21st century (IPCC 2007). This global warming affects other parameters of climate such as the extreme events of precipitation, mean sea level, melting of the glaciers, etc.

In several regions across the globe, variability in climatic conditions is already resulting in broad-ranging impacts, especially on water resources and agriculture. Climate change studies inherently have to consider the significance of uncertainty. Some sources of uncertainty, namely (1) natural variability, (2) future emissions,

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and (3) downscaling methodology, currently limit the detail of the regional projects. Overall, climate change has the potential to erode the gains in development made over centuries in several parts of the world and increase the susceptibility of humankind to climatic events for earning a sustainable livelihood across the world. Hence, efforts must be taken for mitigation and adaptation to these changes so that its adverse effects on water resources and agriculture can be dealt with. The adaptive capacity of the farmers in India to these climate changes is limited due to subsistence agriculture and lack of education. Hence, such adaptive strategies must be incorporated which are economically and socially effective and can be integrated with the existing resources of farmers.

21.2 CLIMATE CHANGE IMPACT ON WATER RESOURCES AND AGRICULTURE SECTOR

Nelson (2009) stated that “agriculture is part of the climate change problem, contributing about 13.5 percent of annual GHG emissions (with forestry contributing an additional 19 percent), compared with 13.1 percent from transportation.” Climate change threatens water management through changes in precipitation patterns (variability in terms of intensity and frequency) and agricultural production through variable temperatures, and increased occurrences of extreme events like droughts and floods. (Figure 21.1)

21.2.1 Emission of Greenhouse Gases

There are three major GHGs namely carbon dioxide, methane and nitrous oxide and a brief description about these GHGs is given below.

Carbon dioxide (CO_2). Deforestation, industrial emissions, decay and decomposition of organic matter, volcanic eruptions, burning of fossil fuels, forest fires, etc. are the major contributors to the emission of CO_2. Agricultural activities also result in the emission of CO_2 although they are not considered to be a major contributor. The major sinks of CO_2 are plants, oceans and atmospheric reactions. CO_2 is a major GHG and responsible for the increase of the atmospheric temperature.

Methane (CH_4). Wetlands, decay and decomposition of organic matter, termites, biomass burning, natural gas and oil extraction, etc. are the main sources of methane emission. Animal digestive processes, rice cultivation, manure, etc. also contribute towards the methane production in the agricultural sector. In ruminating animals, methane is produced as a result of the digestion in the rumen under anaerobic conditions. Methane is also produced in the soil through the metabolic activities of a bacterial group known as ‘methanogens’. The main sinks of methane are the removal in the stratosphere and soil. Methane is about 25 times more effective as a heat-trapping gas than CO_2 (Pathak et al. 2012).

Nitrous Oxide (N_2O). Nitrogenous fertilizers, burning of biomass and fossil fuels, forests, large water bodies like oceans, soil, etc. are the typical sources of Nitrous oxide, in which soil is the main contributor. Production of nitrous oxide

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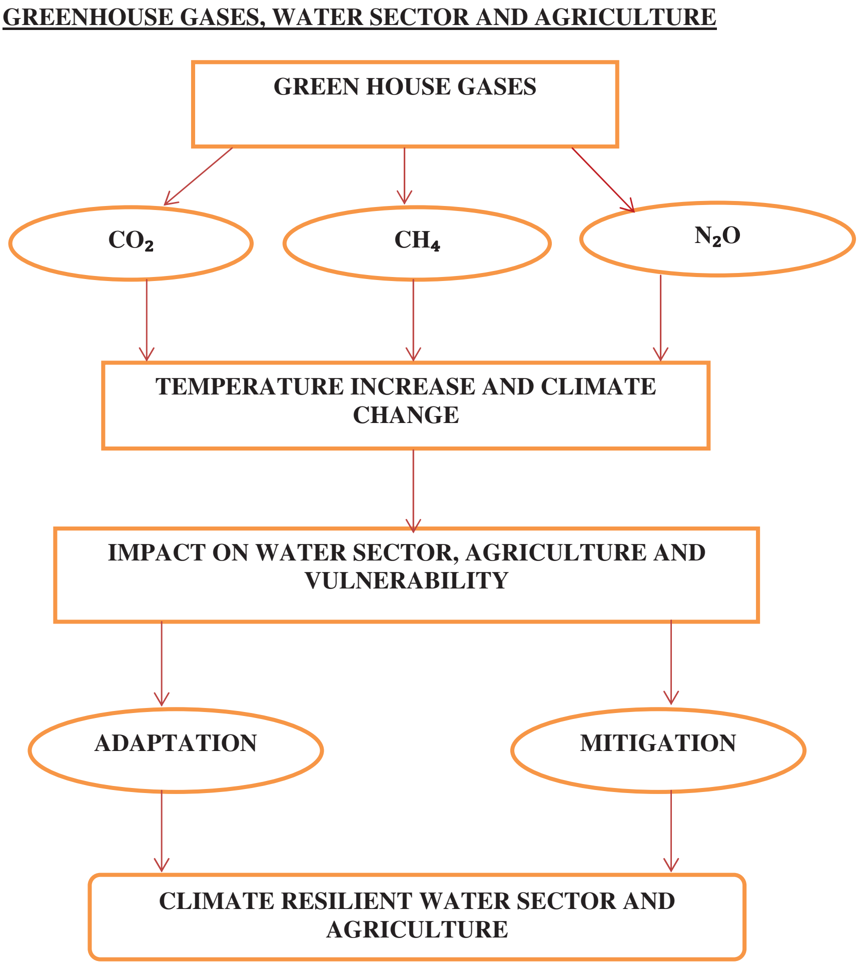

Figure 21.1. Outline of climate change impact, mitigation and adaptation

from soil results in the decrease of nitrogen in the soil, resulting in adverse effects in agricultural owing to less efficiency in nitrogen use. Nitrous oxide is around 298 times more effective as a heat-trapping gas than CO_2.

21.2.2 Impacts of Climate Change and Water Resources for Agriculture

Water is vital to human life and many activities such as agriculture, electricity generation, industry applications, waste management, etc. Therefore, it is necessary to evaluate the extent and degree of the impacts.

Irregularities in the Arrival of Monsoon, Droughts and Flood. Agriculture in India depends a lot on the monsoon season and the amount of precipitation

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taking place during this season. IPCC documents and various climate modelers have depicted a rising irregularity in the Asian Monsoon circulation in a warmer world. Climate change in India has resulted in inadequate and irregular rainfall (i.e. changes in intensity and frequency of precipitation), which causes untimely droughts, henceforth, which adversely affects the agricultural yield in several regions across India. Climate change has also resulted in untimely floods which destroy the irrigation field, thereby damaging the agricultural yield of the country.

Shortage of water. The increased temperature results in the shortage of water, which affects agriculture, consequently increasing the demands of irrigation water supply. Atmospheric temperature increase results in the rise of evapotranspiration in the areas south of 40 °N. Also, shortage of water would result in the net decline of rice yield in India by about 20%.

Crop Yield. The increase in the atmospheric carbon dioxide results in a fertilization effect on crops with C_3 photosynthetic pathway, thereby increasing their growth as well as productivity. But also an increase in the temperature, depending on the present ambient temperature, can result in the reduction of crop duration, increase in the crop respiration, alter photosynthate partitioning to economic products, affect the pest population thereby disturbing the existing equilibrium and creating a new equilibrium between crops and pests, hasten nutrients' mineralization process in soil, reduce the efficiency of fertilizers and increase in the evapotranspiration (Pathak et al. 2012). Change in the minimum temperature has more effects than the change in the maximum temperature. For example, the grain yield of rice reduced by 10% for each 1°C rise in the minimum temperature during the growing season above 32°C (Pathak et al. 2003). The climate change impact on the production of rice in the state of Punjab in India has showed that with all other climatic conditions remaining the same, temperature increase of 1°C, 2°C and 3°C would decrease the grain yield of rice by 5.4%, 7.4% and 25.1%, respectively (Aggarwal et al. 2009a, b).

Productivity of Soil. Soil temperature affects the rates at which the decay and decomposition of the organic matter, release and taking up of nutrients, plant metabolism, etc. take place. The accelerated decomposition of the organic matter may result in the release of nutrients but will affect the fertility of the soil later on. The increase in the CO_2 results in the increase of plant biomass production, efficiency of soil water use by plants, and also the C/N ratio of plants, which influences the soil microbial processes. A change in the precipitation due to the climate change affects the surface moisture content, which influences the germination and the crop establishment in the rainfed regions.

Pests, Insects and Diseases. Pests and insects significantly damage the yield as well as the quality of the crops. The increase in temperature results in the increase of the abundance of pests and insects due to numerous reasons like phonological processes, growth of population, migration, etc. The increase in the winter temperature may lead to the reduction of the hibernation time of the pests and insects, thereby increasing their damaging activities. The areas, which are at present not suitable for the pests due to low temperature, may become appropriate if the temperature increases, thereby resulting the growth of their population. The

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nature and epidemiology of the diseases in plants will be altered, making it hard in the prediction and diagnosis during a disease outbreak.

Loss of Biodiversity. Due to the drastic changes in climatic conditions, many species of animals and plants are becoming extinct because of the lack of their necessary environment or loss of habitat caused by the climate change.

21.3 METHODOLOGY FOR STUDY: CASE STUDY OF PICHOLA LAKE BASIN

To understand the impact of climate change, a time series of surface climatic variables such as maximum and minimum temperatures, precipitation for future climate scenarios is required. The objective of this case study is to assess the impact of climate change on lake basin in an arid region in India for the various IPCC SRES scenarios (A1B, A2, B1 and COMMIT) on predictands.

21.3.1 Study Area and Data Used

The Lake Pichola catchment is chosen as study area for this purpose, located in Udaipur district, Rajasthan, India. This region receives an average annual precipitation 597 mm. The NCEP reanalysis data was extracted for a period of January 1948 to December 2000 for the monthly mean atmospheric variables (Kalnay et al. 1996). The atmospheric variables are extracted for nine grid points whose latitude ranges from 22.5 to 27.5°N, and longitude ranges from 72.5 to 77.5°E at a spatial resolution of 2.5°. For precipitation data, records are available at monthly time scale in Udaipur for the period January 1990 to December 2000 (Khobragade 2009). For GCM data, the Canadian Center for Climate Modeling and Analysis (CCCma) (http://www.cccma.bc.ec.gc.ca) provides GCM data for a number of surface and atmospheric variables for the CGCM3 T47 version which has a horizontal resolution of roughly 3.75° latitude by 3.75° longitude and a vertical resolution of 31 levels. The atmospheric variables such as air temperature, zonal wind, meridional wind and geopotential height are extracted for nine grid points whose latitude ranges from 22.5 to 27.5°N, and longitude ranges from 72.5 to 77.5°E at a spatial resolution of 2.5° (Goyal and Ojha 2012).

21.3.2 Downscaling Approach

With the relatively recent emergence of machine learning methods, kernel methods have become well-known and used frequently in several applications including r pattern detection, discrimination problems and many other engineering applications (Yee and Haykin 1993). Kernel regression is a non-parametric modeling tool which belongs to the family of smoothing methods (Hardle 1990). Kernel regression does not assume any underlying distribution to estimate the regression function. Kernel regression is a modeling tool which belongs to the family of smoothing methods. The characteristics of Kernel Regression depend on

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the use of a kernel function, bandwidth and polynomial degree. Several kernel functions such as Gaussian, Uniform, Triangle, Epanechnikov, Quartic and Cosine are used. Out of existing various kernel functions, Gaussian kernel is very popular for practical use (Nabil et al. 2002; Keerthi and Lin 2003). Gaussian Kernel is defined as follows (Nabil et al. 2002):

$$K(x, X) = \exp\left(-\frac{(x-X)^2}{2\sigma^2}\right) \tag{1}$$

where σ is bandwidth of Gaussian Kernel, giving an idea about the smoothness of the derived function.

Polynomial degree may vary from 0 to 2. In the case where the polynomial degree is 0 (constant polynomial), the Nadaraya-Watson formula (Nadaraya 1964) is used to compute the i'th prediction:

$$Y_j = \frac{\sum_{i=1}^{N} w_i(K(x_j, X_i)}{\sum_{i=1}^{N}(K(x_j, X_i)} \tag{2}$$

For the constant polynomial, the explanatory variables are only taken into account for computing of the weight of the observations in the learning sample. For higher polynomial degrees, the variables are used in calculating a polynomial model. Once the model has been fitted, it is applied to the validation or prediction sample in order to estimate the values of the dependent variable. Once the parameters of the model have been estimated, the prediction value is calculated using the following formulas:

$$\text{Degree 1: } Y_i = a_0 + \sum_{l=1}^{K} a_l\, x_{il} \tag{3}$$

$$\text{Degree 2: } Y_i = a_0 + \sum_{l=1}^{K} a_l\, x_{il} + \sum_{l=1}^{K}\sum_{m=1}^{K} b_{lm} x_{il} x_{im} \tag{4}$$

21.3.3 Potential Predictor Selection

The most relevant probable predictor variables necessary for developing the downscaling model are identified by using the correlation coefficient. In general, the predictor variables are realistically simulated by the GCM. It is noted that air temperature at 925 mb (Ta 925) is the most realistically simulated variable with a CC greater than 0.8, while meridional wind at 200 mb (Va 200) is the least correlated variable between NCEP and GCM datasets ($CC = -0.17$). It is found that air temperature at 925 mb (Ta 925), meridional wind at 925 mb (Va 925), zonal wind at 925 mb (Ua 925) are better correlated than air temperature at 200 mb (Ta 200) meridional wind at 200 mb (Va 200), zonal wind at 200 mb (Ua 200) and zeo-potential height at 500 mb (Zg 500).

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21.3.4 Downscaling of GCM Models

Three predictor variables namely air temperature (925 mb), zonal wind (925 mb) and meridoinal wind (925 mb) at 9 NCEP grid points with a dimensionality of 27, are used which are highly correlated with each other. The different statistical parameters of each model are calculated during calibration to get the best statistical agreement between observed and simulated meteorological variables. These measures are defined below.

1. **Coefficient of Correlation:** The Coefficient of Correlation (CC) can be defined as:

$$CC = \frac{\sum_{i=1}^{N}(Y_o - \bar{Y}_o)(Y_c - \bar{Y}_c)}{[\sum_{i=1}^{N}(Y_o - \bar{Y}_o)^2 \cdot \sum_{i=1}^{N}(Y_c - \bar{Y}_c)^2]^{1/2}} \tag{5}$$

2. **Sum of Squared Errors:** The Sum of Squared Errors (SSE) can be defined as:

$$SSE = \sum_{i=1}^{N}(Y_o - Y_c)^2 \tag{6}$$

3. **Mean Square Error:** The Mean Square Error (MSE) between observed and computed outputs can be defined as

$$MSE = \frac{\sum_{i=1}^{N}(Y_c - Y_o)^2}{N} \tag{7}$$

4. **Root Mean Square Error:** The Root Mean Square Error (RMSE) between observed and computed outputs can be defined as

$$RMSE = \sqrt{\frac{\sum_{i=1}^{N}(Y_c - Y_o)^2}{N}} \tag{8}$$

5. **Normalized Mean Square Error (NMSE)**: The Normalized Mean Square Error (MSE) between observed and computed outputs can be defined as (Zhang and Govindaraju 2000).

$$NMSE = \frac{\frac{1}{N}\sum_{i=1}^{N}(Y_c - Y_o)^2}{\sigma_{obs}^2} \tag{9}$$

6. **Nash–Sutcliffe efficiency index:** The Nash–Sutcliffe efficiency index (η_1) can be defined as (Nash and Sutcliffe 1970):

$$\eta = 1 - \frac{\sum_{i=1}^{N}(Y_c - Y_o)^2}{\sum_{i=1}^{N}(Y_o - \bar{Y}_o)^2} \tag{10}$$

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7. Mean absolute error (MAE): Mean absolute error (MAE) can be defined as follows (Johnson et al. 2003):

$$MAE = 1 - \frac{\sum_{i=1}^{N} |Y_c - Y_o|}{\sum_{i=1}^{N} |Y_o - \bar{Y}_o|} \tag{11}$$

where N represents the number of feature vectors prepared from the NCEP record, Y_o and Y_c denote the observed and the simulated values of predictand respectively, Y_o and σ_{obs} are the mean and the standard deviation of the observed predictand.

Kernel regression (KR) is performed on this dataset with Gaussian kernel and standard deviation is used as bandwidth (Nabil et al. 2002; Keerthi and Lin 2003). Various polynomial degrees (viz. 0 to 2) were used to fit the model to the observations of the learning sample for each predictand. Results of the different models (*KRM1* to *KRM3*) as discussed in Table 21.1 are tabulated in Table 21.2. For predictand precipitation, Coefficient of Correlation (CC) was in the range of 0.52-0.83, RMSE was in the range of 47.27-105.84, N-S Index was in the range of- 0.39-0.67 and MAE was in the range of 0.10-0.60 for kernel regression based models for training and validation. A comparison of mean monthly observed precipitation with precipitation simulated using kernel regression has been shown in Figure 21.2 for calibration and validation period. Calibration period is from 1990 to 1995, and the rest is validation period.

The GCM simulations are run through the calibrated and validated KNNM1 downscaling models to obtain future simulations of predictand. The predictand

Table 21.1. Different downscaling model variants used in the study for obtaining projections of predictand at monthly time scale

Predictand	*Period of downscaling*	*Length of the record*	*Approach*	*Model/ Specification*
Precipitation	1990–2100	1990–2000	Kernel Regression	KRM1 Gaussian Kernel, Polynomial Degree 0
Precipitation	1990–2100	1990–2000	Kernel Regression	KRM2 Gaussian Kernel, Polynomial Degree 1
Precipitation	1990–2100	1990–2000	Kernel Regression	KRM3 Gaussian Kernel, Polynomial Degree 2

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Table 21.2. Various performance statistics of model using Kernel regression

Model		*KRM1*	*KRM2*	*KRM3*
CR	Training	0.83	0.62	0.52
	Validation	0.78	0.66	0.63
SSE	Training	189333.30	574703.23	806622.38
	Validation	134085.71	374353.62	352607.86
MSE	Training	2629.63	7981.99	11203.09
	Validation	2234.76	6239.23	5876.80
RMSE	Training	51.28	89.34	105.84
	Validation	47.27	78.99	76.66

NMSE		*N-S Index*		*MAE*	
Training	*Validation*	*Training*	*Validation*	*Training*	*Validation*
0.32	0.49	0.67	0.50	0.60	0.49
0.98	1.38	0.01	−0.40	0.26	0.07
1.37	1.30	−0.39	−0.32	0.20	0.10

(viz. precipitation) patterns are analyzed with box plots for 20 year time slices. Typical results of downscaled predictand (precipitation) obtained from the predictors are presented in Figure 21.3. The projected precipitation for 2001–2020, 2021–2040, 2041–2060, 2061–2080 and 2081–2100, for the four scenarios A1B, A2, B1 and COMMIT are shown in (ii), (iii), (iv) and (v) respectively. It can be inferred that for A1B, A2 and B1 scenarios, precipitation is projected to increase in future. This is because among the scenarios considered, the scenario A1B and A2 have the highest concentration of atmospheric carbon dioxide (CO2) equal to 720 ppm and 850 ppm, while the same for B1 and COMMIT scenarios are 550 ppm and ≈370 ppm respectively (Anandhi, et al. 2009). In the COMMIT scenario, where the emissions are held the same as in the year 2000, no significant trend in the pattern of projected future precipitation could be discerned. The overall results show that the projections obtained for precipitation are indeed robust.

21.4 STRATEGIES FOR FUTURE SUSTAINABLE WATER SUPPLIES: MITIGATION AND ADAPTATION

21.4.1 Introduction to Mitigation and Adaptation

The IPCC defines adaptation as the "adjustment in natural or human systems to a new or changing environment. Adaptation to climate change refers to adjustment in natural or human systems in response to actual or expected climatic stimuli or

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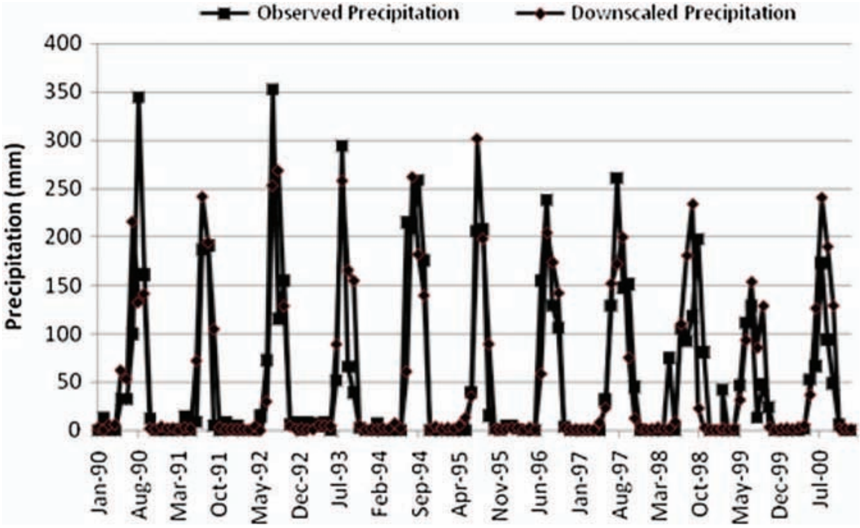

Figure 21.2. Typical results for comparison of the monthly observed precipitation with precipitation simulated using kernel regression downscaling model KRM1 for NCEP data. In the Figure, calibration period is from 1990 to 1995, and the rest is validation period

their effects, which moderates harm or exploits beneficial opportunities." It mainly refers to an ability to adjust and adapt to the climate change to cope up with the effects of the possible damages. Adaptation is basically an understanding of how human and natural systems can prepare for the respond to changes in climate or their environment, which is essential to lessen the vulnerability. Adaptation can be of different types such proactive, autonomous, planned, etc. Proactive adaptation is the one which is predictive and hence, measures are taken before changes are observed in the climatic conditions. Autonomous adaptation is the one that consists of measures taken, not because of the changes in the climatic stimuli but because of the changes in natural systems and by welfare changes in the human systems. Planned adaptation is the one based on awareness that conditions have changed or are about to change and hence, actions are required to adapt to it.

People whose livelihoods depend on agriculture have to develop ways to cope with the changes in climate and adapt accordingly. Today, the climate is changing at an alarming rate. As a result, if proper adaptation strategies are not planned now, they will be unable to handle the changes in the climatic conditions, and hence it would affect them significantly. Adaptation will lead to food security, which is one of the main criteria's for the effectiveness of adaptation at local as well as national levels. It should be specified in the adaptation of the agriculture, forestry and related sectors to changes in climate and its variability. Awareness should be raised by policy makers, and the most resilient food production systems should be promoted and made available to the people. For developing countries, good adaptation techniques should be available and it should be discussed at the

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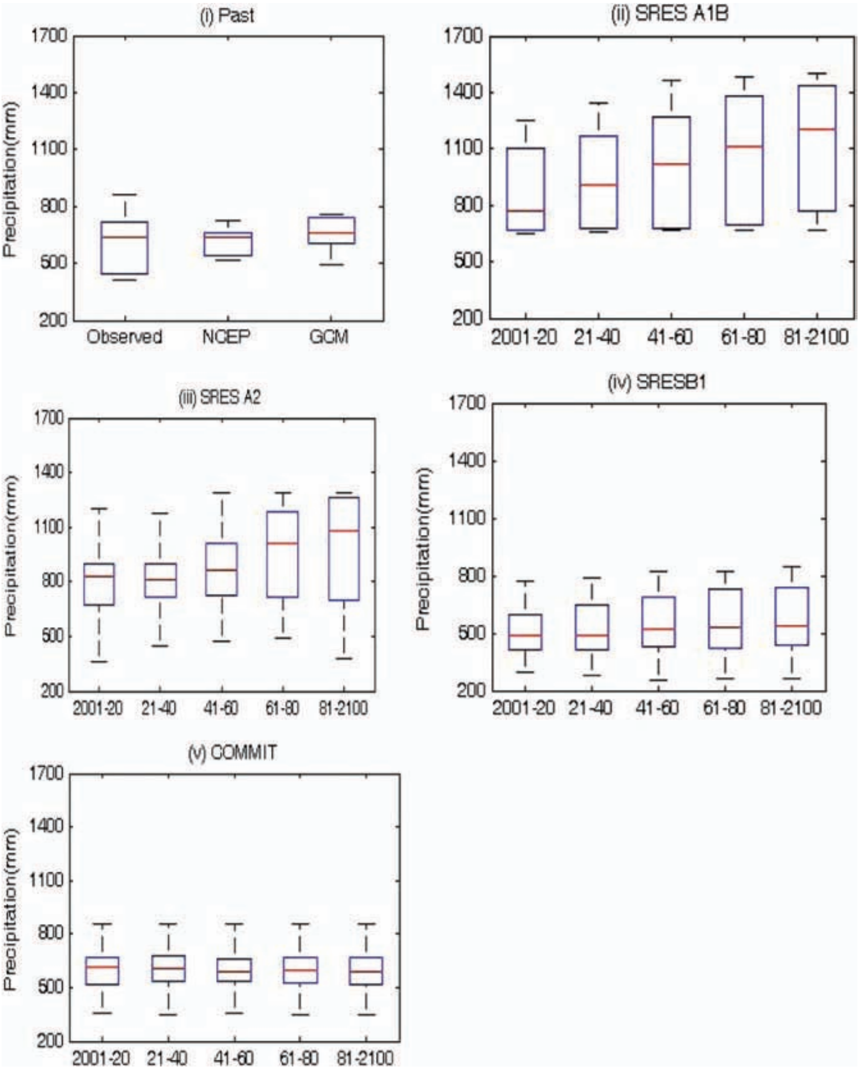

Figure 21.3. Box plots results from the KNNM1-based downscaling model for the predictand precipitaion

central level instead of regional level as in a country like India, the economy relies on agriculture which will in turn depend on the adaptation techniques undertaken to tackle the climate changes.

The IPCC defines mitigation as “an anthropogenic intervention to reduce the sources or enhance the sinks of greenhouse gases (GHG).” It is primarily referred to the steps taken up to permanently get rid of or decrease the long-term adverse effects of climate change to nature and society. This, like adaptation, should be analyzed and discussed at the local, as well as global level because the need of the

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hour is to neutralize the effects of climate change. Mitigation tackles the factors that cause climate change and hence a successful mitigation technique is very necessary. IPCC discussed mainly seven sectors of mitigation: energy supply, transportation and its infrastructure, residential and commercial buildings, industry, agriculture, forestry and waste management. The United Nations Framework Convention on Climate Change (UNFCCC) mentioned the conditions specifically while dealing with stabilization of Green House Gases in the atmosphere:

1. it should take place within a time frame which will be enough to allow ecosystems to adapt to climate change naturally;
2. the food production should not be threatened; and
3. the economic development should proceed in a sustainable manner.

Both adaptation and mitigation techniques are of immense importance to tackle and eliminate or reduce the adverse effects of climate change to life and property.

21.4.2 Drought Relief and Rainwater Harvesting

In some places, mainly western India, people face drought at times. These droughts are bound to increase with the recent climate change, reduction in rainfall and increase in temperature. At such times, the farmers in the drought affected regions become helpless. It is the duty of the state and the central government to take care of the situation. The concerned authorities should make arrangements for sending water tanks to the affected areas or opening up the water from dams and reservoirs in other nearby areas. This has got a political side, but it is up to the government to take care of the affected people at such times. The government should also implement drought relief funding and aid schemes to help out the people.

Nowadays with very much untimely rainfall, rainwater harvesting has become an important tool to make way for sufficient water in times of water crisis. At a domestic level, rainwater harvesting from roofs is an effective way of augmenting drinking water and watering gardens. Rainwater harvesting techniques can be installed on the roofs of houses, and the collected rainwater can be stored in huge tanks. This will ensure the additional recharge of the aquifer by making arrangements for the stored water to reach there and also reduce the run-off.

21.4.3 Desalination and Reduction of Leaks

Desalination deals with the conversion of the seawater into fresh water. Right now, this technique is not very much cost efficient, and it might make the cost of water out of reach of the municipal corporations, sometimes 3–4 times the cost of water from other conventional sources. In some countries like the ones in the Middle East, however, there is no other option. 95% of their drinking water comes from the sea (Makin 2005). This sea water if tapped and converted into fresh water

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economically can be used in agriculture, and this will almost solve all the water scarcity problems. However, studies are going on to make this technology cost-efficient.

Due to improper management, leaks in pipes and other water storage devices result in a lot of leakage of water causing a lot of wastage. For example, in South Africa, the level of unaccounted for water in urban distribution systems is between 15 and 20 % which is viewed as high by international standards (Goldblatt et al. 2002). This results not only in wastage of water but also in revenue as then extra budget is required for distribution and additional treatment. The measures such detection of leaks, repairing visible and reported leaks, pressure management, adequate and proper zoning of the distribution systems, and pipe replacement programme as should be recommended to water departments to cope up with the distribution leaks.

21.4.4 Water Education, Water Tariff Structures and Reuse of Grey Water

One of the most effective ways is to educate about the water and to encourage consumers to use water more efficiently through tariff mechanisms. Efforts should be made to influence their consumption behaviour. The goal of implementation of an education campaign is to make people aware of water saving practices. Grey water utilisation at a domestic level can be beneficial for irrigating lawns and small gardens. Such initiative will help in reducing the water demand and relieves the volume on the waste water treatment works.

21.4.5 Developing Climate-Ready Crops and Crop Diversification

The development of crops which have higher yield potential and resistance to drought, flood, cold, etc. will play an important role in tackling the effects of climate change in agriculture. Efforts should be taken so that there occurs an improvement in the germplasm of important crops in a way that they are more tolerant to heat stress, abiotic stress, oxidative stress, etc. Also, studies have been going on since long for better water-use and nitrogen-use techniques. They are important because, with climate change, the water quantity is sure to fall in the future. High temperature and heavy rainfall may also reduce the efficiency of nitrogen use causing loss by volatilization and leaching. Cultivators need to be provided with the modern technology of producing climate-ready crops so that they can stabilize their production system against climate change.

Crop diversification refers to the replacement of the existing crops and livestock with a new variety that is more tolerant to drought, heat, extreme climatic conditions, etc. This will result in a better productivity during the period of various stresses than the existing crops. Diversification of the genetic structure and composition of the seeds lead to better defence against various pests, insects and plant diseases as well as hazardous climatic conditions. However, there is a negative side to it because keeping in mind the economic condition of most of the farmers in India, crop diversification turns out to be a costly affair for them.

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21.4.6 Changes in Land-Use Management Practices and Adjusting Cropping Season

The change in the land-use from one form to another can result in reducing risks from the effects of climate changes in agriculture. There are six possible broad land-use categories according to the IPCC Good Practice guidance for Land Use, Land-Use Change and Forestry (LULUCF) such as forest land, cropland, grassland, wetland, settlements, etc. Change in the land-use, like the change in use of cropland to grassland, can lead to changes in the carbon stocks and other impacts on the water sector areas. Altering the intensity of the fertilisers, changing the labour quantity, shifting production from traditional areas, shifting production between crops and livestock, changing the location of crop production, etc. can lead to reducing risks of climate change in agriculture. In addition to this, more vegetative cover, reduced tillage, etc. may also help in preventing erosion and lead to better water and soil quality.

With climate change, it is suggested that the time of planting different types of crops also have to be changed. This includes adaptation measure incorporating changes in the crop planting calendar in order to reap benefits of the wet and rainy period and avoid the extreme climate period. According to the present weather and seasons, different types of crops are to be planted and cultivated. Farmers will thus have to adapt to the changing climatic conditions by changing crops accordingly.

21.4.7 Relocation of Crops in Alternative Areas

Production of crops is bound to be affected by climate change like increase in temperature, precipitation patterns, emission of GHGs, extreme events such as floods, droughts, etc. But these effects vary with different places. Another way of tackling the effects of climate change is to relocate the crops to a place where the adverse effects of climate change are much lesser than the present one. Hence, such alternative areas which are suitable for the growth of crops are needed to be identified for the relocation of crops.

21.4.8 Better Weather Forecasting and Crop Insurance Schemes

With an early weather forecasting, the farmers can be warned early about the imminent climatic conditions. Hence, they can be better prepared to tackle the climate change. Also, proper public and private insurance policies should be made available to these farmers to reduce the risk of crop failure during these hazards and encourage them to go ahead with their irrigation plans without any pause.

21.5 CONCLUSIONS

It is clear now that climatic changes and increasing climatic variability are expected to intensify the problems of future water and food security by exerting burden on agriculture and human life. Predictions from climate change models are

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plausible projections of climate and how these climatic scenarios could affect local and global water resources. It is therefore, important that policy makers, stakeholder and water managers take into account the possible consequences of climate change on the water resources and in so doing, adopt strategies that ensure the long-term sustainability of the water supplies and the local resources.

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CHAPTER 22

The Resource Economic Dimension of Wastewater Treatment vs. Green Technologies

Thomas Dockhorn[1]

22.1 INTRODUCTION

Regarding conventional wastewater treatment technologies, it has to be considered that these end-of-pipe technologies are mostly incompatible with the requirements of sustainable resource management. One main characteristic of existing systems is their extensive resource demand in order to eliminate resources such as nutrients and energy contained in municipal sewage. Therefore, based on the principle of materials flow management, concrete incentives should be identified to promote solutions in terms of sustainable resource management. In particular, the separation of highly concentrated partial streams (source separation) such as faeces and urine with subsequent recycling represents a suitable approach with high resource efficiency.

In this respect, Chapter 22 describes a resource-economic approach to the assessment of the economic value of wastewater-borne resources as well as a model to determine the pollution-dependant (conventional) treatment costs for single wastewater parameters, e.g., Chemical Oxygen Demand (COD), N and P. Such a model can be used as an economic steering instrument for strengthening the implementation of green technologies by identifying their resource economic potential (Dockhorn and Dichtl 2006).

22.2 WASTEWATER AS A RESOURCE

In the context of the present chapter, wastewater is seen primarily as a source of potentially usable resources rather than a compound of substances that require disposal. The basis of our motivation and approach is the critical appraisal of the appropriateness of the great technical and economic efforts made with regard to

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wastewater treatment, and how necessary they are to achieve the overriding objective of preventing water pollution. Considering wastewater as a source of resources plays a decisive part, because it introduces the aspect of economic usefulness in addition to the factor environmental protection – which is usually seen as a mere cost driver – thus opening up a completely new range of possible activities.

The relevant resources dealt with here are firstly the water itself, and secondly the recyclable materials contained in wastewater. The main focus is on organic compounds, nitrogen and phosphorus; all of these are relevant for sewage treatment, as their removal is one of the central objectives of wastewater purification. Potassium, being a plant nutrient, is also considered because of its significance as a fertilizer.

In principle, it is also possible to extend the scope of our consideration to include other resources such as sulphur, magnesium or calcium, as well as pollutants such as heavy metals or organic micropollutants. The choice of substances for consideration will be geared towards the relevance of the resource under scrutiny, the quantities present in the systems under review and the specific treatment costs generated by these substances during wastewater treatment. Although pollutants in domestic wastewater are certainly not a resource in the true sense of the word, they are still a relevant factor in the global overview in as far as their removal from wastewater also results in costs.

The significance of a given resource can generally be measured by whether it is essential or non-essential i.e. irreplaceable or capable of substitution by other resources, and whether it is renewable or non-renewable (= finite). In this context it is obvious that resources that are both essential *and* non-renewable (such as phosphorus, for example) are particularly precarious, as the uncontrolled use of these resources must become a system-limiting factor at some point in the future.

By contrast, the importance of a resource in our everyday perception is expressed mainly by its perceptible market price, although this in itself does not necessarily represent a distinction between, say, essential (e.g. phosphorus) and non-essential (e.g. crude oil), but merely reflects the current market interest and activity. On the other hand, it is safe to assume that a scarcity indicator in form of a rising market price will affect an adaptation of consumption behaviour – regardless of any distinction of the resource under scrutiny as mentioned above.

It is therefore only a matter of time before high demand for certain resources results in increased raw material prices, as developments on global markets have already shown in recent years. This is, of course, particularly true in the case of essential and non-substitutable resources.

We would now like to give a brief overview of individual resources relevant to the field of wastewater management and of their respective significance. In the interests of a better assessment of the relevance of these resources in the field of wastewater treatment with regard to materials-flow within the overall system, some examples of phosphorus and nitrogen materials-flow analyses within the boundaries of the German system will also be presented.

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22.2.1 Water

Water is not only essential for all vital processes, but also one of our most significant resources and our most important foodstuff. Terms such as "elixir of life" or "blue gold" serve to underline water's unique position as a vital resource on the one hand, and as a significant economic factor on the other.

Besides areas of life in which water is an indispensable foodstuff or production resource (in agriculture, for example), it is used much more widely and extensively as an operational resource e.g. as a coolant or transport medium – applications in which it could easily be replaced by other resources or processes. In this context, it is important to make clear distinctions in the role of water in wastewater management with regard to the requirements of resource conservation.

Although water is a renewable resource as far as its recyclability as a fluid goes, this is not always the case if one considers the freedom of natural bodies of water from, for example, non-degradable compounds. When water is mixed with man-made pollutants – heavy metals, xenobiotics, pharmaceutical residue or endocrine substances, to name but a few – this freedom no longer exists, at least not in cases where these substances pass through existing wastewater treatment technology and are released into the environment. The crucial point here is not so much the question if the substances under scrutiny are absolutely non-degradable or simply slow to degrade, but the fact that they are permanently present in the natural environment, albeit in a low concentration, and can, therefore, bring about changes of one kind or another. In other words, how water is used can also have a significantly detrimental effect on its quality as a resource, as well as on natural bodies of water or the environment as a whole, which may in turn restrict their subsequent usability. Only the thorough purification of wastewater with the object of eliminating all traces of these organic micropollutants would result in water also becoming a renewable resource in respect of this criterion. In order to achieve this, however, new standards would be required, as well as a set of technological procedures that, according to the current state of knowledge, would present (at the very least) an enormous challenge from an economic point of view.

The value of water as a resource, therefore, depends directly on its level of purity. The presence of organic compounds, nutrients, pollutants or (pathogenic) microorganisms further restricts the subsequent usability of the resource, with an unavoidable reduction in its value and/or usefulness. The objective of ensuring the continuing freedom of natural bodies of water from such undesirable compounds could be achieved much more efficiently if a source separation system was permanently in place to separate/decouple large quantities of unpolluted water from smaller water quantities with a higher pollutant concentration. This would allow the removal of problematic substances – inasmuch as they definitely need to be eliminated – with considerably less effort.

In principle, the same applies when the resources "water" and "nutrients" are mixed, which involves the same significant reduction of the usefulness of both the water itself and the resources contained in the wastewater. An exception here is the use for agricultural purposes of (partially treated) wastewater containing nutrients,

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although the scope for use is predetermined in this case. It is, therefore, important to differentiate between scenarios in which water really is an essential resource and those in which it can definitely be substituted. This defines the required quality of the resource and its subsequent usability.

The general rule regarding the other resources contained in wastewater (e.g. organic compounds and the nutrients nitrogen and phosphorus) is that the higher their respective concentration, the more effectively the resources can be utilized or recycled in an economically viable way. In most cases, any dilution of a resource results in the immediate deterioration of its subsequent usability. Consequently the conditions for effective recycling of the resource water on the one hand, and of the utilizable substances contained in wastewater on the other, are diametrically opposed. However, source separation at an early stage could create the necessary conditions for the optimum exploitation and recycling of the respective resources.

22.2.2 Phosphorus

From a resource conservation point of view, phosphorus is by far the most important resource occurring in (domestic) wastewater, as it is essential on the one hand – especially for agricultural production – but its natural availability finite on the other. Moreover, as increasing quantities of heavy metals and radioactive elements are causing a marked deterioration in the quality of phosphates from traditional mining, there is even more intensive interest in finding alternative sources of viable phosphates. 140 Mt/a rock phosphate is mined worldwide and processed industrially to ~40 Mt/a of phosphate fertiliser and 5 Mt/a of phosphate-based detergents (Gumbo et al. 2002). Conventional processing methods are extremely energy-intensive and/or consume large quantities of resources, varying between ~13 kWh/kg P for electro-thermal processing of white phosphorus (Falbe and Regitz 1995) and ~7.8 kWh/kg P, corresponding quantities of sulphuric acid for wet chemical processing and subsequent production of fertilizer. The removal of phosphorus in conventional wastewater treatment plants also requires the use of resources e.g. metal salts for chemical phosphate precipitation. According to Maurer et al. (2003), the consumption of primary energy equivalents for phosphorus precipitation is ~13.6 kWh/kg P.

Even if Wagner (2005) predicts a static life cycle of ~100–350 years for the resource phosphate in global terms, the search for possible recovery and efficient recycling is nevertheless gaining importance. We will now present a phosphorus balance based on German figures as a means of assessing the significance of the phosphate loads contained in wastewater in relation to the total German phosphate household. While Wagner (2005) considers the availability of raw phosphates, and Frede (2005) and Schnug et al. (2003) deal with the agricultural phosphorus balance, our aim is to collate these balances of partial systems with other relevant data from the literature to draw up a total phosphor balance within the framework of the German system as a whole. The objective is to identify the extent of the net inflows and outflows from the entire system and establish the proportional contribution of the wastewater treatment field to the removal of phosphates from the economic cycle and/or system as a whole. In order to

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harmonize the diverse sources of data used, all figures will refer to the year 2001 (or fiscal year 2000/2001).

According to the German Agriculture Industry Federation figures (IVA 2005), some 153,000 t of phosphorus in the form of fertilizer were sold in Germany in the fiscal year 2000/2001, of which only 87,320 t P were from German domestic production. Figures from the German Federal Statistical Office (2003) show a total number of inhabitants and population equivalents (IPE) for wastewater treatment of 126.2 million in 2001. This figure consists of 82 million inhabitants and ~44.2 million IPE of industrial origin. Given the German Association for Water Management, Wastewater and Waste Disposal assumption (ATV-DVWK 2000) of an inhabitant-specific load of 1.8 $\mathrm{g\,P/(I \cdot d)}$, calculations yield 53,900 t/a P attributable to the population and a further 29,000 t/a P attributable to industry, all of which are fed into wastewater treatment plants (WWTPs) via the wastewater path, resulting in a total of 82,900 t/a P. The phosphate load attributable to the population stems either from agriculture or from phosphate-based household detergents. According to figures from the German Industrial Association for Personal Hygiene and Detergents (IKW 2003), phosphate-based detergents, household cleaners and hygiene products accounted for an average of 5,275 t/a P between 1998 and 2003; so the proportion originating indirectly from agriculture amounts to 48,625 t/a P.

With an assumed mean phosphate concentration of 7.5 mg/L P for household sewage and a mean effluent concentration from WWTPs of 0.9 mg/L P (ATV-DVWK AK-1.1 2003), calculations for Germany yield – assuming connection of all households to the wastewater system – a direct discharge of 9,948 t/a P into the receiving waters and, therefore, a residual quantity of 72,952 t/a P in sewage sludge, of which there were 2,429,403 t total solids (TS) in Germany in 2001, according to the Federal Statistical Office (2003). The breakdown of the sludge by individual disposal routes has been undertaken according to the recent data of Durth and Schaum (2005), according to which a total of 56% of sewage sludge is recycled as secondary raw materials (30% in agriculture and 26% in landscaping) and 44% disposed of, with 38% being incinerated. 40,853 t/a P are therefore currently returned to the material cycle with wastewater sludge as secondary raw materials, while 32,099 t/a P (via dumping of incinerator ash) are disposed of, i.e. removed from the material cycle.

As Germany does not possess any natural phosphate deposits of its own, the entire net input (apart from secondary raw material fertilizers) in agriculture, put at around 304,000 t/a P by Frede (2005), must be supplied from external sources.

The physical outflow of phosphates beyond the boundaries of the German system occurs firstly via the removal of soluble phosphate residue from wastewater treatment plants (9,948 t/a P) and secondly via the export of vegetable and animal foodstuffs (calculated at 163,000 t/a P). Although the quantities of phosphate incinerated with sewage sludge, for example, are *de facto* removed from the materials cycle when incinerator ash is dumped in accordance with common practice, they are nevertheless still physically within the boundaries of the system under scrutiny.

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According to Schnug et al. (2003), field crops are grown on a total area of 10.7 million ha in Germany. In addition to this area, there are a further 4.5 million ha of meadows and pastures. If the accumulated quantity of phosphates on German farmland, some 900 kg/ha (Frede 2005), is assumed only for the 10.7 million ha of land under the plough, the result is a total soil-borne "phosphate pool" of around 9.63 million t P. The total yearly removal of phosphorus from the soil by agriculture is given by Schnug et al. (2003) as 560,000 t/a P, which is significantly higher than the system inflow stated by Frede (2005).

Bio-waste was not taken into consideration when compiling the present balance. According to figures from the Institute for Energy and Environmental Research IFEU (2005), it is true that more than 26,000 t/a of phosphate ore (the equivalent of ~3,500 t/a P) are currently already being saved through bio-waste recycling. However, as this quantity is in effect simply recycled within the boundaries of the system, it is not illustrated here. Gethke et al. (2005) give the total amount of phosphates provided by bio-waste as 11,520 t/a P. The sometimes extreme deviations between the figures amply demonstrate that the observations made can never do more than indicate rough orders of magnitude and identify material flows that are really relevant. The quantity of phosphates found in other residual waste fractions is not considered as significant in the context of the total balance, as the principal application fields for phosphates mean it is highly likely that, over and above the uses for phosphates as already described (for example surface phosphating in the metalworking industry) they account for only about 3% of the total input (EFMA 2000).

The surplus, given as 158,000 t/a P in Frede's (2005) balance, in livestock and field crop production is primarily nothing more than an expression of the discrepancy in the system resulting from the difference between land area balance and livestock balance. Amongst other factors, the reason for this is that the rule-of-thumb estimate of the phosphate contribution of animal excretions in the 1990s was too low, not least as a means of allowing farmers to continue the practice of spreading natural fertilizer (liquid manure) in areas that were already in part over-fertilized. At all events, almost the entire balance discrepancy can be attributed to livestock production, as the livestock balance sheet already contains a discrepancy of the same order of magnitude, whereas the discrepancy in the land area balance is practically zero.

A comparative balance of phosphate imports and exports via foodstuffs and animal feed – compiled from Federal Statistical Office figures (2003) and the respective specific P content of the goods considered – shows that the import and export of phosphates through these channels are more or less equal at ~130–140,000 t/a P, even if the imported phosphate is primarily in different products from those exported. This confirms that the P export quantity of 163,000 t/a P stated in the inventory balance is correct.

The outflow of phosphorus removed from the agricultural cycle via animal carcass meal and bone meal is a *de facto* livestock production surplus that is not taken into account in the other mass flows considered to date. The BSE crisis is not the least of the reasons for the steady increase in the proportion of carcass meal

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and bone meal that is ultimately disposed of. Calculations based on statistical sources (STN 2005) put phosphorus quantities for carcass meal and bone meal in Germany at 11,250 t/a P and 13,800 t/a P, of which 10,800 t/a are put to secondary use and 14,250 t/a disposed of by incineration.

For the sake of completeness, we would like to add that a phosphate quantity in the order of around 600 t/a P is removed from the economic cycle by deaths in the German population (mortality rate 10.44‰, 700 g P per person).

The most important relevant information given above is shown in the form of an inventory in Figure 22.1. Please note that some of the figures shown were obtained by calculation, so as to allow a cohesive balance of the entire system to be drawn up; consequently some of the figures do not necessarily tally with the frequently heterogeneous raw data stated in the text.

To sum up, the character of the balance framework for phosphorus material streams in Germany is such that, in principle, all the phosphorus required in the system must be imported from outside the system boundaries. Although some 148,000 t P are removed from the economic system again every year, there is no corresponding exportation of phosphorus on a level to match imports. The calculated 163,000 t/a P exported are matched by an equal quantity of imported food and animal feed. Although a quantity of ~46,000 t/a P disposed of in the form of sewage sludge and animal by-products is removed from the economic cycle, it ultimately remains within the system boundaries. Only the comparatively small quantity of ~10,000 t/a P lost through the effluent from wastewater treatment plants actually physically leaves the system. Germany is therefore not only a *de facto* net importer of phosphorus, but actually accumulates it at a net rate of ~180,000 t/a P (partly in unusable or unused form) within its system boundaries; amongst other things, the immense phosphate loads that have accumulated over the past few decades in the soil used for agricultural purposes are evidence of this fact.

22.2.3 Nitrogen

The industrial manufacture of ammonia using the steam reforming process consumes around 9.6 kWh of electric power per kg ammonia-nitrogen and according to the stoichiometry of the process ~570 g CH_4/kg NH_3-N. Patyk and Reinhardt (1997) put the total primary energy requirement for the production of an average nitrogen fertilizer at 14.9 kWh/kg N.

On the other hand, the wastewater treatment plant process to eliminate nitrogen consumes a significant amount of energy. According to the stoichiometry of the process and based on the customary energy parameters of wastewater treatment plants, the nitrification process requires 3.07 kWh/kg NH_3-N. Maurer et al. (2003) give a total primary energy requirement equivalent to 12.5 kWh/kg N for the entire nitrogen elimination process, consisting of nitrification and pre-denitrification. Based on this assumption, direct use of wastewater-borne nitrogen as a fertilizer results in a calculated total potential primary energy saving of 27.4 kWh/kg NH_3-N in comparison with the customary methods.

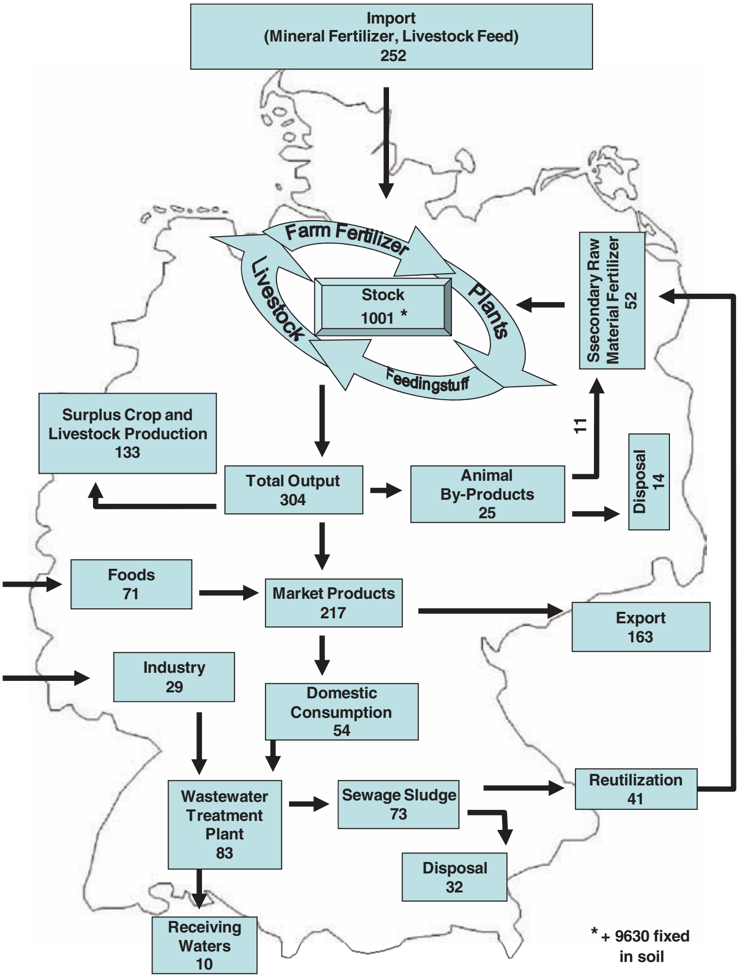

Figure 22.1. Inventory for the relevant material flows containing phosphorus within the boundaries of the German system (quantities in 1,000 t/a P; system stock in 1,000 t P; information based on figures from 2000–2005)

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Unlike phosphorus, it is much harder to compile a system balance for the resource nitrogen. One obvious reason is that there are – especially in industry – many more areas of application for nitrogen and nitrogenous compounds than for phosphorus, and therefore material flows to be analysed and evaluated. On the other hand, chemically bound nitrogen (e.g. nitrate) is easily converted into gaseous nitrogen by microbial activity, allowing it to cross the boundaries of the system under consideration more or less undetected. This creates a potentially

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high risk of balance discrepancies, the most significant of which occur in the fields of agriculture and wastewater management.

According to figures from the IVA (2005), nitrogen-based fertilizers accounted for sales of around 1,850,000 t N in Germany in the fiscal year 2000/2001. 1,200,000 t N of these nitrogen fertilizers were manufactured in Germany.

The agricultural nitrogen balance formulated by Frede (2003) was used as a basis for the balance. Initially the land area balance with a total area input of 3,398,000 t/a N and 2,157,000 t/a N in the harvested products shows a calculated so-called surplus in crop production of 1,241,000 t/a N. This represents the balance discrepancy and, provided that there are no significant deviations in none of the other parameters, could be assumed as the sum of all the nitrogen lost from the system through erosion, leaching into groundwater or via gaseous emissions (e.g. N_2 from denitrification or anammox processes). Of the 818,630 t/a N input of nitrogen into water in Germany (mean value for 1993–1997), about 51.4% or a calculated 420,776 t/a N can be attributed to the phenomena groundwater input or erosion (Behrendt et al. 1999, cited in Frede 2003). Lüttich et al. (2004) put the nitrogen load leached out of soil in Germany in 2002, which is ultimately a result of input from natural manure and mineral fertilizers, at 724,200 t/aN.

According to the information presented by Dämmgen et al. (2005), the total gaseous emissions of N_2, N_2O, NO, NO_2 and NH_3 from German agriculture in 2002 amount to ~928,000 t/a N. Of these, about 489,000 t/a N can be attributed to the growing of field crops and 439,000 t/a N to livestock farming. Together with system output via the wastewater path (although this includes an unspecified quantity that remains in the system, at least temporarily) it is possible to reconcile almost the entire discrepancy (surplus in production of crops and livestock) amounting to ~1.9 milliont/a N.

According to EFMA (2005) figures for Europe, the "nitrogen pool" present in farmland soil amounts to between 1,800–9,000 kg/ha N; however, since most of the nitrogen is bound up with organic material, it cannot act as a nutrient for growing plants in the short term. The calculated mean total mass present for an assumed arable land area of 10.7 million ha is, therefore, around 58 million t of soil-borne nitrogen.

The nitrogen mass in high-protein animal by-products (animal carcass meal and bonemeal) was calculated at a mean figure of 96,800 t/a N, based on ~605,000 t/a (STN 2005) and a nitrogen content of 16% in dry matter. Of these, ~57% (corresponding to 55,176 t/a N) are currently disposed of and 43% (corresponding to 41,624 t/a N) recycled.

The nitrogen input from wastewater is calculated analogue to Section 22.2.2, taking the total number of inhabitants and population equivalents and a specific nitrogen load of 11 $g/(I \cdot d)$ into consideration, to be 507,000 t/a N. Of these, around 86,000 t/a N would be found in sewage sludge and 204,000 t/a N dissolved in WWTP effluent, representing the total output of wastewater treatment plants. It would, therefore, follow that the difference – around 216,000 t/a N – was denitrified.

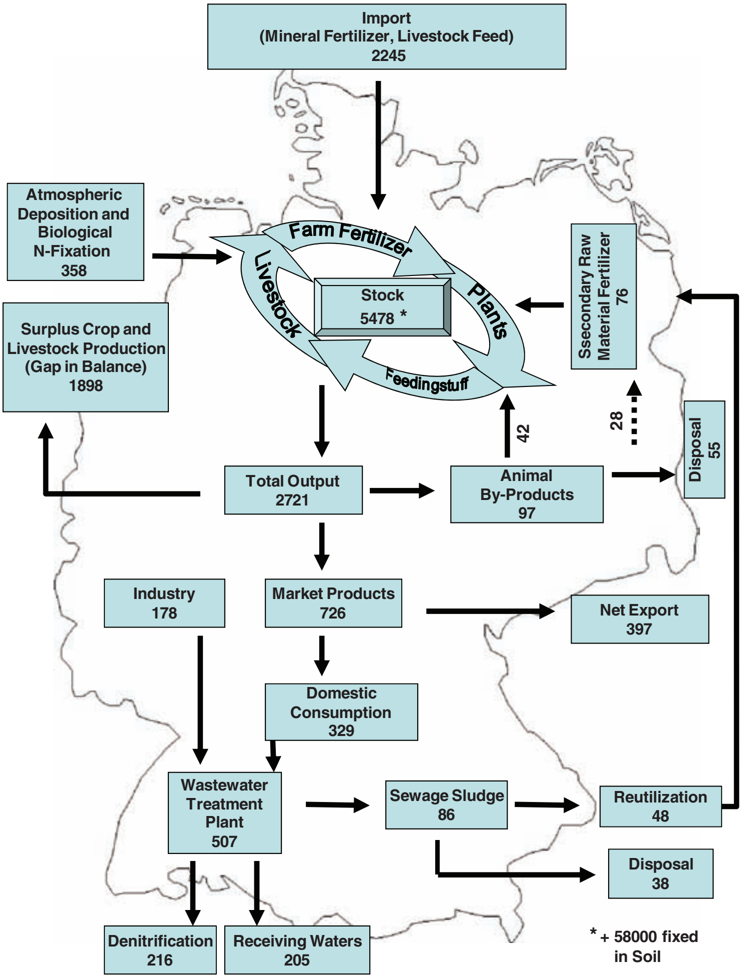

Figure 22.2. Inventory for the relevant material flows containing nitrogen within the boundaries of the German system (quantities in 1,000 t/a N; system stock in 1,000 t N; information based on figures from 2000–2005)

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Figure 22.2 gives a summary overview of the relevant material flows containing nitrogen in the German system. In this case it should also be noted that some of the figures shown were obtained by calculation, so as to allow a cohesive balance of the entire system to be drawn up; consequently some of the figures do not necessarily tally with the frequently heterogeneous raw data stated in the text. Unlike the phosphorus balance, where the innate low mobility of the substance ensures that virtually the entire input mass remains within the system boundaries, the nitrogen balance in Germany is characterized by an almost complete system

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throughput with correspondingly higher output rates. Whether deliberately (e.g. in WWTPs) or unintentionally (e.g. in the course of agricultural production), the "volatile" element nitrogen is subject not only to NH_3 stripping but also – in biological systems with alternating aerobic and anoxic environments – partly to conversion into nitrogen gas or other nitrogenous gases that can escape from the system. All in all, the system loses about the same amount of nitrogen in this way as it gains by the total input of mineral fertilizers. However, the greatest losses do not result from wastewater treatment but from agriculture.

22.2.4 Potassium

The element potassium is one of the principal nutrients of living cells, so it is essential for vegetable and animal organisms alike. Potassium is the seventh most common element in the earth's crust; it is extracted from mining mineral deposits and its main commercial use is in the production of fertilizer.

A virtually unchanged quantity of the original potassium input is found in an aqueous phase in the wastewater path; being highly soluble, it is only present in very small quantities in the accumulated biomass in sewage sludge. Therefore, further utilization of the potassium present in wastewater is closely linked to exploitation of the aqueous phase.

According to IVA (2005) figures, ~451,600 t of potassium in the form of fertilizers were sold in Germany in the fiscal year 2000/2001, although domestic fertilizer production was as high as 2,905,520 t K. Germany is therefore a net exporter of potassium fertilizers (in fourth place in the world ranking for potassium producers behind Canada, the Russian Federation and Belarus), but a net importer of nitrogen- and phosphate-based fertilizers as already shown above (Federal Statistical Office 2001).

In the context of wastewater treatment, potassium does not represent a wastewater-specific parameter, apart from in the analysis of sewage sludge used as an agricultural fertilizer. As far as the technical aspect of the balance goes, it can be assumed that the quantity of potassium used as fertilizer on agricultural land will, on account of its good solubility, ultimately find its way into the ocean, firstly after the crop has been harvested and subsequently via the wastewater path and direct leaching from the soil. In theory, the global potassium cycle is then complete with the formation of new marine mineral deposits (Johnston 2005).

22.2.5 Organic Compounds

Organic compounds in municipal wastewater are mainly degraded using aerobic processes that require energy for aeration, making them relatively energy intensive. On the other hand, anaerobic treatment of organic matter in wastewater can also be used to generate energy in the form of biogas. To increase the efficiency of this process, it is advantageous to ensure that there are high concentrations in the original substrate; this can, for example, be achieved by the separation of highly concentrated partial streams. While an estimated 0.35 $\mathrm{kWh/kg\,COD_{elim}}$ of electricity are required for the aerobic degradation of organic compounds in accordance with common practice in conventional WWTPs, anaerobic degradation can

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Table 22.1. Key figures for the aerobic and anaerobic treatment of organic substances

Aerobic Treatment	Ratio COD/BOD_5	2.3
	O_2 consumption aerobic degradation	1.2 kg O_2/kg BOD_5
	Specific O_2 yield	1.5 kg O_2/kWh
	Electricity costs conventional	0.065 €/kWh
Anaerobic Treatment	Degree of anaerobic COD degradation	80%
	Specific methane generation	0.25 kg CH_4/kg COD_{elim}
	Energy content CH_4	10 kWh/m^3
	Power input renewable	0.087 €/kWh
	Efficiency gas engine	32%

actually produce a calculated 0.9 kWh of electricity if the resultant biogas is used for generation purposes. A comparison of the anaerobic and aerobic processes, therefore, reveals a realizable total potential of ~1.25 kWh/kg COD_{elim}. If the primary energy requirements are also considered, there is an even higher potential of around 3.9 kWh/kg COD_{elim}. Table 22.1 contains a summary of the relevant key figures with respect to the aerobic and anaerobic degradation of organic compounds. Amongst other things, these were used to determine the economic resource potential of organic compounds in wastewater (cf. Section 22.5.5). The resource potential of organic compounds is calculated at 0.087 €/kg COD; the figure represents the compensation for electricity generated with the biogas resulting from the anaerobic treatment of organic compounds and then fed into the grid.

Although the anaerobic treatment of municipal wastewater with lower concentrations can also be successful, especially in warmer climates, and successful investigations of anaerobic wastewater treatment at low ambient temperatures have been carried out (Elmitwalli et al. 2002), it is more likely that large-scale technical implementation of anaerobic pre-treatment of sewage in temperate and cooler climates will continue to be restricted to highly-concentrated wastewater and mesophilic temperature zones. Where municipal material flow management is in place, anaerobic pre-treatment of partial streams is particularly suitable for the highly concentrated partial streams yellow and brown water, or a combination of both as black water, and possibly also for additional partial streams derived from industrial wastewater with high organic loads.

22.2.6 Other Resources

In the context of this chapter, other resources worthy of mention are other plant nutrients on the one hand and agricultural inputs such as sulphur, magnesium or calcium on the other. The focus can also be extended to include wastewater

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treatment, where – to name one instance – the iron and aluminium salts used for phosphate precipitation can also be taken into account.

In terms of resource economy and in the context of the topics under discussion here, there is particular interest in the resources with a “dual role”; on the one hand, they are used in production processes e.g. as a fertilizer in agriculture or a precipitation agent in a WWTP, but on the other hand they are in some way responsible for expenditure in the field of wastewater treatment. This increases their theoretically utilisable economic potential even further when a policy of “recycling is better than disposal” is adopted.

That said, a substance need not necessarily be wastewater-relevant for it to cause actual costs. For example, the element sulphur normally has little or no relevance as a wastewater parameter, but the release of H_2S in sewers can result in corrosion of concrete pipes and, in consequence, significant follow-on costs.

Even “pollutants” such as heavy metals or organic micro-pollutants, which are not commonly regarded as resources in the normal sense, can cause costs in the field of wastewater treatment. This is especially the case when their presence has an intolerably negative effect on quality, for example, when a cost-intensive disposal method must be used instead of the cheaper recycling alternative. Here, too, the separation of pollutants in partial streams with higher concentrations can result in an overall cost advantage, as the exclusion of pollutants means undiminished quality and a consequent increase in the value of other resources.

22.3 MATERIALS FLOW ANALYSIS

The objective of this section is to carry out a materials flow analysis for a concrete municipal case study. Section 22.5.5 below, the parameter-specific costs for treatment of individual partial streams within the municipal wastewater system will be compared with their resource economy potential; the purpose here is to identify the partial streams that offer a high resource potential on the one hand, but are the decisive material- and material flow-specific costs drivers in conventional wastewater treatment on the other. The overriding question is the extent to which, bearing resource conservation issues in mind, it could be sensible and economically feasible to gradually transform an existing system of conventional wastewater management into a system that recycles or reuses resources on the basis of partial stream separation and material flow management.

The case study selected deals with one municipality and one wastewater association with its municipal WWTP for 350,000 inhabitants and population equivalents (IPE), of which *de facto* 280,000 connected inhabitants are (I) and a further 70,000 IPEs result from industry. In the materials flow analysis carried out in the sections below, 350,000 inhabitants serve as the conceptual basis for the respective calculations. The technical equipment in place consists of a mechanical/biological sewage treatment plant with simultaneous nitrification/denitrification and simultaneous biological and chemical phosphate elimination. The resulting

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primary and surplus sludge are thermophilically digested, dewatered and then incinerated.

For the purposes of the case study described, the entire municipal wastewater with its real material-specific loads is theoretically separated into individual relevant partial streams. Subsequently (Section 22.5.5), the parameter-specific purification effort required for the respective partial streams is compared with the resource economy potential. This method permits the identification of the partial streams that, on the one hand, are cost drivers in terms of wastewater treatment and, on the other hand, contain a particularly high proportion of utilisable resources. The relevant individual partial streams in the present case are presented below.

22.3.1 Municipal Wastewater

In order to describe the initial situation, the operational data of the plant under consideration was evaluated, and the annual quantities and loads shown in Table 22.2 collated with the corresponding wastewater concentrations of the respective parameters. Whereas the figures given for the parameters Q, COD, TKN, P_{tot} and TS are measured operational data, inhabitant-specific loads according to Otterpohl and Oldenburg (2002) were assumed for the parameter potassium and extrapolated to the number of connected inhabitants, because on the one hand there were no measured values for potassium and on the other it is nevertheless a substance with resource economic relevance.

A conversion of the actual annual loads to inhabitant-specific loads displays a high level of conformity of almost all wastewater parameters with the assumed inhabitant-specific loads according to ATV-DVWK (2000). In addition, a connection figure of 350,000 inhabitants results if the inhabitant-specific loads according to ATV-DVWK (2000) are assumed for the parameters COD and TKN. An ~17% lower load results for the parameter phosphorus, while the dry solids load figure is about 36% below the standard assumptions. The water

Table 22.2. Annual loads and resultant concentrations in total wastewater of the case study for 350,000 inhabitants

Parameter	*Load (t/a)*	*Concentration (mg/L)*	*Calculated IPE*$^{(1)}$	*Inhabitant related load (g/(I · d))*$^{(2)}$
COD	15,695	689	358,333	122.9
TKN	1,409	61.9	350,934	11.0
P_{tot}	190	8.3	289,193	1.5
TS	5,694	250	222,857	44.6
K	630	27.7	350,000	4.9
Q	22,776,000 m^3/a	/	495,238	178.3$^{(3)}$ L/(l · d)

Note: $^{(1)}$assuming inhabitant-specific loads according to ATV-DVWK (2000) for K according to Otterpohl und Oldenburg (2002), $^{(2)}$for 350,000 inhabitants, $^{(3)}$mean daily *per capita* wastewater volume including rainwater and extraneous water

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quantity of 178.3 L/(I · d) lies considerably higher than the statistical estimate of 126 L/(I · d), but in this case rain and extraneous water are already included in the case study figures.

No further distinction was made between household wastewater and rainwater/extraneous water, as the calculation of the purification effort required and the resource potential of the total amount of wastewater is applicable to the respective concentrations measured in the WWTP inflow. If a further distinction were to be made here, it would firstly be necessary to apply a split scale of charges, and secondly to assume fictional concentrations for the more highly concentrated wastewater originating from households. In order to allow this approach to be linked appropriately with the costs for wastewater collection and treatment, the assumption here was not actually 1.83 €/m^3 of wastewater and 0.45 € per m^2 of sealed surface and year for rainwater, in accordance with the split scale of charges, but the real annual costs of wastewater treatment in relation to the total yearly volume of all wastewater. In the present case, the costs for specific treatment amount to 1.15 €/m^3.

In the following sections, the total volume of wastewater depicted in Table 22.2 is broken down into its respective relevant partial streams.

22.3.2 Yellow Water

Yellow water (urine) has by far the highest concentration of resources of all partial streams in household wastewater. With regard to the total incidence of the respective substances in all wastewater, Otterpohl and Oldenburg (2002) state that the yellow water partial stream accounts for 12% of COD, 87% of nitrogen, 50% of phosphorus and 54% of potassium in the total wastewater volume. The statistical annual yellow water volume is around 500 L/(I · a), which equates to ~1.4 L/(I · d).

So in terms of resource economy, it makes sense to ensure that this highly concentrated partial stream is not diluted any more before further treatment and/or recycling. In the present case study, therefore, it is assumed that the entire volume of yellow water is collected and remains undiluted.

An overview of the resulting calculated loads or concentrations for the partial stream yellow water in this case study can be seen in Table 22.3 below.

The above concentrations clearly demonstrate that the partial stream yellow water is of particular interest in relation to recovery and recycling of the plant nutrients phosphorus, nitrogen and potassium. However, the high COD concentration would also permit anaerobic treatment of yellow water and subsequent use of the resulting biogas as a source of energy.

At this point, we would like to draw the reader's attention to the "organic micro-pollutants" that are closely associated with yellow water. This is a group of substances that are inhomogeneous because of the variety of their origins and material composition (e.g. medicines and their residual products, plasticizers, various other household chemicals etc.) and only occur in low concentrations, but whose activity spectrum (e.g. endocrine disrupters) can have far-reaching ecotoxicological consequences, for example in aquatic environments. A significant proportion of, for instance, the pharmaceutical residues found in domestic

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Table 22.3. Annual loads and resultant concentrations in yellow water of the case study for 350,000 inhabitants

Parameter	*Load(t/a)*	*Proportional load (%)(1)*	*Concentration (mg/L)*
COD	1,883	12	10,762
TKN	1,226	87	7,005
P_{tot}	95	50	543
TS	0	0(3)	0
K	340	54	1,944
Q	175,000 m^3/a	0.8(2)	/

Note: (1)according to Otterpohl and Oldenburg (2002) with reference to all wastewater; (2)in the case study; (3)author's own assumption

wastewater is input via yellow water. Although the full dimensions of this problem have not yet been exactly quantified, increasing attention is now being paid to pharmaceutical residues and endocrine disrupters. However, experience to date shows that conventional wastewater treatment technology is almost or completely unsuitable for the satisfactory removal of these substances from wastewater. This would be another point in favour of partial stream separation, namely that it supports the retention and, where necessary, the separate treatment of partial streams containing pollutants – not least with the object of eliminating harmful substances.

22.3.3 Brown Water

Partial stream analysis has revealed that brown water (faeces) also plays a significant role in the treatment of household wastewater. Again, a further significant proportion of the phosphate contained in the entire municipal wastewater volume is found here. However, the predominant loads in brown water tend to be related to the parameters of COD and TS.

The conceptual assumption in the case study was the complete collection of brown water via vacuum separation toilets, with Otterpohl and Oldenburg (2002) assuming an annual volume of 50 $L/(I \cdot a)$ and 3 $L/(I \cdot d)$ of additional water for toilet flushing. In theory, it would be safe to assume an even lower consumption of flushing water and a corresponding reduction of brown water volume, given that modern vacuum toilets do not require more than about 500 mL/flush. The table below gives the calculated parameter-specific loads and wastewater concentrations for the partial stream brown water in the present case study.

Although the respective concentrations of nitrogen and phosphorus in brown water are much lower than in yellow water, the concept here is also to integrate the nutrients in a recycling scheme. However, since the predominant factor in brown water is its high organic matter load, the most sensible treatment or recycling alternative is (initially) anaerobic treatment for biogas production and energy generation.

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22.3.4 Grey Water

In the present case study, grey water represents the total volume of municipal wastewater minus the partial streams yellow water and brown water i.e. the relatively large but only lightly polluted volume of water used for food preparation, washing clothes and personal hygiene. It also includes any rainwater and extraneous water that is fed into the WWTP via municipal sewer systems. The method used to determine the substance-specific loads contained in grey water was to deduct the figures for yellow water (Table 22.3) and brown water (Table 22.4) from the loads and water quantities of the total wastewater volume (Table 22.2) and assign the remaining substance loads to the remainder of the wastewater stream. Table 22.5 shows the resulting partial-stream specific loads and concentrations.

After the deduction of yellow and brown water, the remaining concentrations of wastewater-relevant substances in the grey water are comparatively low, which suggests that the technical effort required for purification will also be significantly reduced by the same ratio. The low concentrations of nitrogen and phosphorus, in particular, indicate that they will no longer be necessary to eliminate nutrients

Table 22.4. Annual loads and resultant concentrations in brown water of the case study for 350,000 inhabitants

Parameter	*Load (t/a)*	*Proportional load (%)*(1)	*Concentration (mg/L)*
COD	7,377	47	18,407
TKN	141	10	352
P_{tot}	76	40	190
TS	2,847	50(3)	7,104
K	76	12	189
Q	400,750 m^3/a	1.6(2)	/

Note: (1)according to Otterpohl and Oldenburg (2002) with reference to all wastewater; (2)in the case study; (3)author's own assumption

Table 22.5. Annual loads and resultant concentrations in grey water of the case study for 350,000 inhabitants

Parameter	*Load (t/a)*	*Proportional load (%)*(1)	*Concentration (mg/L)*
COD	6,435	41	290
TKN	42.3	3	1.9
P_{tot}	19	10	0.9
TS	2,847	50(3)	128
K	214	34	9.6
Q	22,200,250 m^3/a	97.6(2)	

Note: (1)according to Otterpohl and Oldenburg (2002) with reference to all wastewater; (2)in the case study; (3)author's own assumption

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Table 22.6. Comparative overview of concentrations of the relevant substances contained in total volume of wastewater, yellow water, brown water and grey water in the case study for 350,000 inhabitants, assuming full selectivity

	Municipal wastewater	*Yellow water*	*Brown water*	*Grey water*
COD (mg/L)	689	10,762	18,407	290
TKN (mg/L)	61.9	7,005	352	1.9
P_{tot} (mg/L)	8.3	543	190	0.9
TS (mg/L)	250	0	7,104	128
K (mg/L)	27.7	1,944	189	9.6

when this wastewater is treated. Assuming the ratio $BOD_5:N:P$ of 100:5:1 to be necessary for the growth of a heterotrophic biomass, as is customary in municipal WWTPs, it is clear that in the scenario under consideration (assuming a $COD:BOD_5$ ratio of 2.3:1) the $BOD_5:N:P$ ratio is only 140:2.1:1, i.e. there is a theoretical nutrient limitation.

Table 22.6 presents a comparative overview of the concentrations of the relevant substances contained in wastewater in the partial streams considered in Table 22.2 to Table 22.5.

22.4 RESOURCES AND THEIR ECONOMIC VALUE

As the relevant plant nutrients are the principal raw materials or resources under consideration in the present study, this section will deal with the value of the corresponding resources, calculated in terms of the market prices of conventional fertilizers.

As fertilizers often consist of different fertilizing components, it is not always possible to establish the respective nutrient-specific prices of the individual components. On the other hand, it is obvious that the prices for the individual fertilizer components are directly linked to the prices of the individual raw materials or the required energy sources on the global market. In other words, the price of a multi-component fertilizer (or other raw material consisting of multiple elements) should be equal to the sum of the market prices for the corresponding quantities of its individual constituent elements.

The method we used here was to retrace this path “backwards” by first determining the material-specific prices of single-component fertilizers, and then using the findings to calculate the prices of multi-component products. Table 22.7 contains some examples of commercial fertilizers displayed with their calculated element-specific prices. In order to simplify their subsequent transferability to the wastewater treatment sector, all prices apply to an individual element (e.g. K) and not, as is usually the case for fertilizers, to an individual nutrient (e.g. K_2O).

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Table 22.7. Examples of commercial fertilizers, their specific elemental contents and specific prices with reference to the relevant active elements (cost status 2005)

		Elemental content (%)					*Specific price (€/kg element)*				
Product	*Price (€/t)*	*N*	*P*	*K*	*S*	*Mg*	*N*	*P*	*K*	*S*	*Mg*
CAN	164.50	27					0.61				
Urea	249.00	46					0.54				
Ammonium nitrate urea	146.00	28					0.52				
Triple phosphate	228.30		20					1.16			
Di-ammonium phosphate	251.50	18	20				0.54	0.78			
Ammonium sulphate	158.50	21			24		0.54			0.19	
40 K fertilizer	132.90			33					0.40		
K/mg fertilizer (40 K_2O + 6 mgO)	135.50			33		4			0.38		0.26
Potash magnesia	189.50			25		6			0.38		1.57
Magnesium oxides	406.00					60					0.67
Calculated values							0.54	0.78	0.38	0.19	0.67

The calculated values given in Table 22.7 will be used later to determine the economic resource potential of individual wastewater partial streams (cf. Section 22.5.5). In addition, these calculated values also serve as a basis for calculating possible revenue and/or realistic market prices for secondary raw materials and complementary products generated in the course of waste stream management. Sometimes this is necessary because the market prices paid for complementary products from WWTPs are often considerably lower than for products of identical composition and quality from other sources. The prices for fertilizers given by the Bavarian State Environmental Agency BayLfU (2004), that were also used for the economic evaluation of farmyard manure, corroborate the level of the values shown in Table 22.7, equating to 0.56 €/kg N, 1.26 €/kg P and 0.34 €/kg K, although the fertilizer value of phosphorus stated there is actually a lot higher.

One of the quintessential points – besides the determination of fertilizer prices – that goes further than the observations set out in Table 22.7 and elsewhere is that each individual component of a (chemical) compound has its own price, regardless of whether all or only some of these components can be used as a production resource, for instance. Up till now, not enough attention has been paid to this in the day-to-day practice of wastewater treatment, either when purchasing production resources or calculating the cost of secondary raw materials. For example, it often happens that when the specific treatment costs for phosphate recovery are calculated, the costs are only considered for the element phosphorus,

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even when the secondary raw material in question is actually magnesium ammonium phosphate (MAP). In this concrete example, magnesium and ammonium together represent no less than 52% of the calculated value of MAP, whereas phosphate accounts for only 48%.

22.5 COSTS OF WASTEWATER TREATMENT

In the following section, the fundamental conditions for a material-specific and partial-stream specific quantification of wastewater treatment costs are considered, as the starting point for the determination of degrees of economic freedom in respect of the future realisation of material flow separation concepts. The objective of this approach and the subsequent analysis is to quantify the *additional* costs incurred during the conventional treatment of wastewater for each partial stream considered, and separately for all relevant substances contained in wastewater.

In Germany it is customary to scale the costs of municipal wastewater treatment according to the volume of treated water, which results in specific treatment costs being shared more or less equally between all consumers in the respective catchment areas. The charges levied are decided by the measurability of the volume flows in accordance with the consumption of fresh water, and sometimes – where applicable – also for rainwater input according to the paved area ("splitting" method).

Despite this method being, in effect, a *de facto* levelling of all inhabitants in terms of fees charged for services, municipal wastewater disposal statutes often explicitly emphasize the underlying principle of calculating charges in proportion to use. In other words, charges should really be levied with due regard for the principle of causality: whoever uses the WWTP to excess should pay correspondingly higher fees. However, as practical implementation of this principle involves additional effort for administration and monitoring, local authorities who actually put the idea into practice are still in the minority. On the other hand, many municipal authorities have taken this idea into account when formulating their wastewater regulations and levy heavy pollution charges from industrial dischargers, for instance, as compensation for the additional effort their input causes.

Once a firm decision has been made to consider the idea of active materials-flow management as part of municipal wastewater management scheme, it is essential to assign the specific purification costs to the partial streams (described in terms of quality and quantity above) in the total volume of wastewater. Otherwise, it is extremely difficult to identify the relevant partial streams in terms of economic considerations.

The aim of the following study is to modify the existing instruments for determination of heavy pollution surcharges in such a way as to allow the additional costs for the treatment of individual wastewater partial streams to be established on a substance-specific level. The emphasis here is not so much on determining the extra effort required for input from industry sources, but rather

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quantifying the hidden costs involved in the treatment of individual partial streams originating in households, such as yellow water, brown water or grey water. Identification of the real treatment costs in relation to the resource potential contained in the individual partial streams ultimately constitutes a resource economic evaluation as a basis for the decision that must subsequently be made.

22.5.1 Heavy Pollution Surcharges

According to the working report of the German Wastewater Technology Association Specialized Group 7.4 (ATV 1990), heavy pollution surcharges are defined as surcharges on sewerage charges that can be levied for the additional effort required in WWTPs and collected from those responsible for the additional effort. This also includes additional effort for sludge processing and disposal, but not for sewage collection networks (drains).

A distinction must be made between parameters that affect the level of the heavy pollution surcharge and those which should not be included in the calculation. According to the ATV (1990), it is primarily BOD_5 that is used to determine charges, as this not only increases oxygen consumption in the WWTP (resulting in increased energy costs for aeration), but also involves the production of more surplus sludge (costs for sludge processing and disposal). Alternatively, COD could also be used as an indicator for the organic content of wastewater.

Other wastewater-relevant parameters, such as settleable solids, nitrogen and phosphorus compounds, lipophilic substances, hydrocarbons, heavy metals or organochlorides (AOX) can also be used for calculation of a heavy pollution surcharge as soon as it can be shown that they are a real and present additional cost factor in wastewater treatment. For instance, the nitrification of unduly high concentrations of nitrogen results in increased energy costs for aeration. Increased phosphate concentrations can lead to the consumption of more resources and additional sludge as a result of phosphate precipitation, but the removal of wastewater components such as AOX can also be more expensive because of the need for special treatment stages.

Wastewater charges are typically levied according to the principle of cost recovery (NKAG 2005). The running costs for public facilities (sewer system and WWTP) are correspondingly related to the total volume of wastewater, the aim being to avoid making a real loss or profit. As a rule, fresh water consumption is used as the reference value for invoicing.

In accordance with the principle of solidarity, a uniform wastewater charge must be levied from all fee-paying customers in the defined statistical territory (the solidarity-based community), the idea being to prevent inhabitants in comparatively remote areas from being charged more (as their wastewater has to be piped further for treatment) than fee-payers who live more centrally. Nonetheless, individual inhabitants can be made to contribute directly to connection costs in the form of an infrastructure charge (when roads to new housing estates are built, for example).

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Furthermore, in accordance with the equivalence principle, dischargers can be required to pay higher fees for a more frequent or extensive use of public facilities. In practice, this regulation is aimed primarily at (industrial) dischargers whose input contains a higher amount of pollutants than the wastewater from an average household, and are therefore responsible for higher costs and/or a greater proportion of effort or resource consumption in public facilities. In such cases, the level of the fee charged should always be appropriate and proportionate to the more intensive use of the facilities by the dischargers on the one hand, and to the services provided by the fee collector (wastewater collection and treatment) on the other.

In this context it is important to remember the principle of equality, which requires that fee-payers be treated equally and fairly and also states that an identical fee should be charged to everyone using the facilities in a similar way and a scale of differentiated fees should apply in the case of different kinds of use.

Whether and to what extent a discharger is actually required to pay a higher fee depends, amongst other things, on the effort resulting directly from the individual circumstances of a given case (e.g. performance of a series of measurements to determine the concentration of relevant substances in this particular discharger's wastewater). In accordance with the principle of proportionality, therefore, the above regulation is generally only implemented in cases where there is economic justification for it.

22.5.2 Relevant Parameters

The parameters given below illustrate the relevant properties of municipal wastewater that are also significant from a resource economic point of view. As mentioned above, the system can in principle be extended to include any additional desired parameter that can be proved to play a causal role in increased effort for wastewater treatment – or is theoretically responsible for more intensive use of the sewage network.

Organic substances in wastewater. The very nature of these organic substances, which are measured as BOD_5 or COD, means that they are extremely relevant wastewater pollution factors with a significant influence on the additional effort required for treatment. This is directly related to the increased reactor volume and machinery required for COD removal and treatment of the sludge. As the main volume of wastewater sludge requiring treatment and disposal results from the degradation of organic substances and precipitated solids, the organic load has a significant effect on all related running costs.

According to ATV-DVWK (2000) findings, surplus sludge production can be calculated with Eq. 22.1.

$$SP_{d,C} = B_{d,BOD} \cdot \left(0.75 + 0.6 \cdot \frac{X_{SS,IAT}}{C_{BODD,IAT}} - \frac{(1-0.2) \cdot 0.17 \cdot 0.75 \cdot t_{SS} \cdot F_T}{1 + 0.17 \cdot t_{SS} \cdot F_T} \right) \text{[kg/d]} \tag{Eq. 22.1}$$

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Nitrogen. The elimination of nitrogen from wastewater is a major cost driver. As the sludge age is longer than is necessary for simple carbon degradation, say, the sub-process of nitrification alone demands the reservation of corresponding increased reactor volumes. In turn, denitrification increases the necessary reactor volume again in accordance with the established value V_D/V_{AT} (ratio of reactor volume required for denitrification to total reactor volume). The indirect input of wastewater with an unfavourable TKN/BOD_5 ratio may involve a further displacement of the ratio V_D/V_{AT}. Moreover, 4.3 $g\,O_2/g\,NH_4$-N are required for nitrogen oxidation, which is directly reflected in increased energy costs.

On the other hand, making businesses that produce large quantities of easily degradable organic compounds (e.g. breweries) pay a heavy pollution surcharge can also induce these businesses to pre-treat their wastewater rather than paying the surcharge. In some cases, this can have an adverse effect on the TKN/BOD_5 ratio, which can subsequently even require the cost-intensive dosing of an external C source (Seyfried und Scheer 1993). The advantages and disadvantages above should be considered before implementation of any surcharges.

Phosphorus. In terms of construction requirements, the costs for phosphate removal are linked to the extra reactor volume for biological P elimination plus the special equipment required for chemical precipitation of phosphates. In addition, the parameter phosphorus influences the proportion of the running costs concerned with the treatment and disposal of sewage sludge, either in connection with costs for precipitation agents, increased uptake of P in the biomass or the increased incidence of sludge. According to ATV-DVWK (2000), the following formula (Eq. 22.2) can be used to determine the quantity of sludge resulting from phosphate elimination.

$$SP_{d,P} = Q_d \cdot (3 \cdot X_{P,BioP} + 6.8 \cdot X_{P,Prec,Fe} + 5{,}3 \cdot X_{P,Prec,Al})/1000[kg/d] \tag{Eq. 22.2}$$

22.5.3 Relevant Costs Centres and Cost Allocation

According to the principle of proportionality, only the so-called pollution-dependent cost factors should be considered when calculating heavy pollution surcharges. This cannot be done until a differentiated breakdown of the individual cost centres and a corresponding cost allocation has been carried out.

The main cost items in the wastewater budget are firstly the actual running costs e.g. expenditure on personnel, electricity, fuel etc. and secondly imputed costs such as interest and depreciation.

The ultimate aim is to carry out an assessment of the selected site that is as close a reflection as possible of the real allocation of costs to the individual cost centres and cost objects. In order to achieve this, it is basically desirable to perform a process cost calculation that is as comprehensive and consistent as possible and also integrates the detailed breakdown of all investments and running costs in the day-to-day accounting and invoicing system (Beier 2003). The main effort required when using this approach is allocating the imputed costs truly and fairly to the individual cost objects, given that it is customary to list entire blocks of costs under "overheads" or "miscellaneous". In contrast, the advantage of taking the trouble to make this extra effort only once at the outset is that it is then comparatively easy to make adjustments to the system when it is running, thus allowing optimum registration and continuous updating of the polluter-specific costs.

A cost evaluation with a breakdown of individual costs is always dependent on the specific existing boundary conditions at a given location. In view of this, the corresponding procedure is illustrated here using the case study for municipal materials flow management selected in Section 22.3 as an example. The WWTP in question consists of a mechanical pre-treatment unit, an activated sludge plant with simultaneous denitrification and a biological P elimination section with combined simultaneous P precipitation. In the sludge treatment facilities of the plant, the sludge is thickened, digested, dewatered and then incinerated.

The total annual wastewater treatment costs amount to 26,258,800 €, of which 12,100,000 € are spent on the sewer network and 14,158,800 € on the WWTP. In order to determine the actual pollution-related costs, it is necessary to first perform a breakdown of investment costs and running costs in as much detail as possible (cost-type accounting) – cf. Figure 22.3. These costs are then allocated

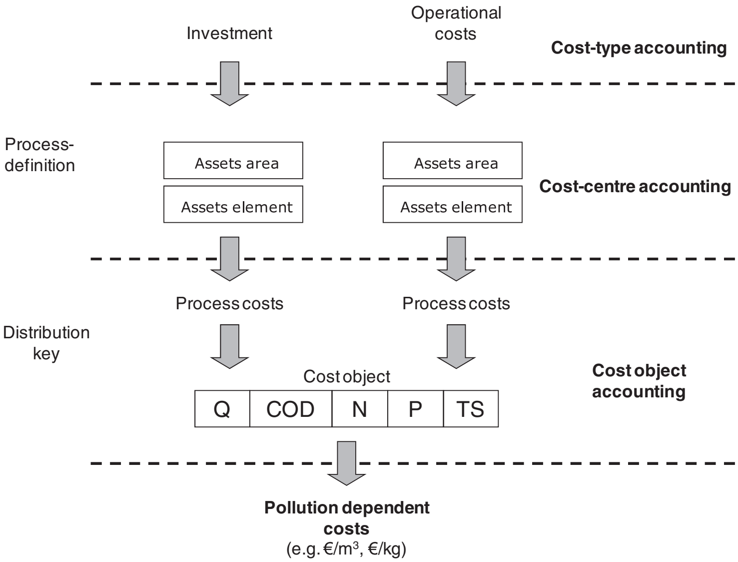

Figure 22.3. Procedure for determining parameter-specific costs for wastewater treatment

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via cost centre accounting to the individual sections of the plant (e.g. machinery, activated sludge system, sludge treatment). The last stage of the process is to use an appropriate distribution key to allocate the respective process costs to the corresponding cost objects i.e. the relevant parameters (e.g. water quantity Q, COD, N, P and TS) (cost object accounting).

The total cost for wastewater treatment is calculated by adding the costs for the sewer system to those of the WWTP. Of course, only the costs for the WWTP can be used to calculate the pollution-dependent proportion of the costs.

Breakdown of Imputed Costs. The imputed costs attributable to the existing plant and equipment (depreciation and interest) were allocated to the plant sections "Mechanical pre-treatment," "Activated sludge plant," "Sludge treatment" and the items "Buildings and miscellaneous." In this case, the respective imputed costs are also identical with the individual relevant costs for "Machinery," "Biology," "Sludge" and "Miscellaneous." If this allocation is not directly possible with the given imputed costs, the costs must be broken down proportionally into percentages of the original sums invested.

A breakdown of the imputed costs already shows that almost 40% of costs cannot be clearly allocated to any of the three cost centres proper, "Machinery," "Biology" or "Sludge." These costs, which are often not differentiated any further, are generally allocated to the cost object water volume as overheads; therefore, they are included in the calculation as pollution-independent costs. As a rule, this approach is a result of the fact that when most of the WWTPs in operation today were built, it was not customary to strictly distribute costs according to this procedure; consequently it is often extremely difficult or complicated to reconstruct the real factors leading to the costs. The inevitable result is that all the highly detailed calculations shown here nevertheless contain a relatively large number of imponderables, which is in practice also one of the main problems involved in the "exact" allocation of costs. One possible way of minimising such imponderables in future would be to ensure that there is a breakdown of costs right down to cost object level as a matter of course when new plants are built.

The next step in the cost breakdown process is the allocation of the imputed costs shown in Table 22.8 to the four cost objects water quantity, COD, N and P. While the costs "Machinery" can be directly allocated to the water quantity (Q), the costs "Miscellaneous" are also allocated to the water quantity as overheads, as explained above.

The costs for Biology are allocated to the cost objects COD, N and P in proportion to the existing tank volumes for COD elimination and nitrification (50.1%), denitrification (44.5%) and biological P elimination (5.4%), where the aerobic tank volume was allocated to the cost object COD, the anoxic tank volume to cost object N and the volume of the bio-P tank to cost object P. Normally one would carry out a reassessment for pure carbon elimination and nitrification/denitrification to determine the tank volumes attributable to COD elimination and the parameter N, which would result in much higher proportionate costs being assigned to cost object N. However, as the main focus of the present study was on

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Table 22.8. Breakdown of imputed costs by relevant cost centres

Cost centre	*€/a*	*Machinery*	*Biology*	*Sludge*	*Miscellaneous*
Mechanical pre-treatment	620,131	620,131			
Activated sludge plant	1,329,766		1,329,766		
Sludge treatment	1,961,521			1,961,521	
Miscellaneous	2,481,687				2,481,687
Sum imputed costs	6,393,104	620,131	1,329,766	1,961,521	2,481,687
Invest distribution key (%)	100	9.7	20.8	30.7	38.8

the additional treatment costs incurred with existing plants and equipment, the cost distribution described above was employed.

The imputed costs for the entire sludge treatment were allocated proportionately to the cost objects COD and P in accordance with the calculated sludge volume. To this end, the expected calculation quantities of surplus sludge and precipitation sludge were determined in accordance with Eq. 22.1 and Eq. 22.2 and the costs allocated according to their proportion in percent – 83.7% to COD and 16.3% to P. As the surplus sludge quantity from the growth of nitrificants is negligible, no sludge treatment costs were assigned to the cost object N; the imputed costs given in Table 22.8 are allocated to the individual cost objects as set out below (Table 22.9).

Allocation of Running Costs. Analogous to the allocation of the imputed costs, the individual items of the running costs account must be allocated to the corresponding sections of the plant, then broken down further and allocated to the various cost objects. The breakdown of running costs and their allocation to the respective costs centres is shown in Table 22.10.

Table 22.9. Allocation of the imputed costs to the relevant cost objects

		Cost object			
Cost centre	*€/a*	*Q*	*COD*	*N*	*P*
Mechanical pre-treatment	620,131	620,131	–	–	–
Activated sludge plant	1,329,766	–	666,857	591,363	71,546
Sludge treatment	1,961,521	–	1,641,793	–	319,728
Miscellaneous	2,481,687	2,481,687	–	–	–
Sum imputed costs	6,393,104	3,101,818	2,308,649	591,363	391,274
Proportion (%)	100	48,5	36,1	9,3	6,1

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Table 22.10. Allocation of running costs to the relevant cost centres

		Cost centre			
Running costs	*€/a*	*Machinery*	*Biology*	*Sludge*	*Miscellaneous*
1. Personnel	1,600,000	384,000	320,000	368,000	528,000
2. Administration	50,000	4,850	10,400	15,341	19,409
3. Structural maintenance	240,000	23,280	49,920	73,636	93,164
4. Maintenance equipment	34,000	3,298	7,072	10,432	13,198
5. Sludge disposal	1,200,000			1,200,000	
6. Consumables	950,000	35,150	387,600	527,250	
7. Energy	800,000	130,400	533,600	85,600	50,400
8. Sewage tax	190,000	190,000			
9. Miscellaneous	2,701,696	262,065	561,953	828,929	1,048,749
Sum running costs	7,765,696	1,033,043	1,870,545	3,109,189	1,752,920
Proportion (%)	100	13.3	24.1	40.0	22.6

The following methods were applied for the breakdown of running costs:

- In accordance with Günthert und Reicherter (2001), personnel costs were allocated as follows: 24% to "Machinery," 20% to "Biology," 23% to "Sludge" and 33% to "Miscellaneous."
- The items listed under 2, 3, 4 and 9 were allocated in accordance with the distribution key for investment-dependent costs from Table 22.8.
- All costs for sludge disposal were allocated in full to the cost centre "Sludge."
- Based on Beier (2003), consumables were allocated as follows: 4.5% to "Machinery," 41.5% to "Biology" and 50.5% to "Sludge."
- In accordance with Müller et al. (1999), energy costs were allocated as follows: 16.3% to "Machinery," 66.7% to "Biology," 10.7% to "Sludge" and 6.3% to "Miscellaneous."
- Sewage tax, as is customary and on condition that the discharge requirements are met, is assigned completely to the water volume and therefore allocated to "Machinery." In the event of limit values changing or being exceeded, however, a cost object-specific allocation would be more appropriate.

A breakdown of the individual running cost items from Table 22.10 and an allocation to the relevant respective cost objects is shown in Table 22.11. The following methods were applied:

- The sum of the costs for "Machinery" and "Miscellaneous" is allocated to the cost object Q.

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Table 22.11. Allocation of running costs to the relevant cost objects

		Cost object			
Running costs	*€/a*	*Q*	*COD*	*N*	*P*
1. Personnel	1,600,000	912,000	468,491	142,308	77,201
2. Administration	50,000	24,259	18,056	4,625	3,060
3. Structural maintenance	240,000	116,444	86,668	22,200	14,689
4. Maintenance equipment	34,000	16,496	12,278	3,145	2,081
5. Sludge disposal	1,200,000		1,004,400		195,600
6. Consumables	950,000	35,150	635,684	172,371	106,796
7. Energy	800,000	180,800	321,371	283,875	13,953
8. Sewage tax	190,000	190,000			
9. Miscellaneous	2,701,696	1,310,814	975,624	249,907	165,350
Sum running costs	7,765,696	2,785,963	3,522,572	878,431	578,730
Proportion [%]	100	35.9	45.4	11.3	7.4

- The costs for “Biology” and “Sludge” from Items 1, 2, 3, 4, 5, 6, 8 and 9 in Table 22.10 were assigned to the cost objects COD, N and P in analogy to the proportional allocation in Table 22.9 according to reactor volume and/or sludge quantity.
- Allocation of the energy costs for “Biology” was undertaken according to the calculated proportional oxygen consumption for COD degradation, nitrification and denitrification obtained by a re-dimensioning of the case study. 53.2% of the total oxygen consumption for nitrification was allocated to cost object N, and 46.8% of the oxygen consumption for COD removal, taking the oxygen gain from denitrification into account, to cost object COD.

Total Costs. If the imputed costs assigned to the individual cost objects (Table 22.9) and the running costs (Table 22.11) are added together, the resulting sum reveals the following cost object-specific total annual costs for the WWTP (Table 22.12).

Close consideration of the proportional costs assigned to the respective cost objects seems to lead to the putative conclusion that the costs allocated to the cost objects N and P are relatively low in comparison to the costs assigned to water quantity and COD elimination. As explained earlier, this circumstance is partly a result of the relatively high proportion of costs that can not be clearly assigned to a particular cost centre or cost object, and are therefore largely absorbed in the total costs. However, the resulting distribution of costs shown here is a significantly better reflection of the cost reduction that could be achieved by partial stream separation in currently existing plants than higher proportional weightings, as it has a much greater correlation with the actual costs of running and maintaining WWTPs.

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Table 22.12. Total annual costs for individual cost objects

		Cost object			
	€/a	*Q*	*COD*	*N*	*P*
Imputed costs	6,393,104	3,101,818	2,308,649	591,363	391,274
Running costs	7,765,696	2,785,963	3,522,572	878,431	578,730
Sum annual costs WWTP	14,158,800	5,887,781	5,831,222	1,469,794	970,004
Proportion [%]	100	41.6	41.2	10.4	6.9

22.5.4 Determination of Pollution Dependent Treatment Costs

Now a dynamic calculation of heavy pollution surcharges as applied here, based on ATV (1990), is presented. This dynamic calculation approach takes into account not only the proportional, pollution-dependent costs allocated to the respective cost objects (wastewater parameters), but also the concentrations of the parameters concerned present in the heavy polluter's wastewater, the mean concentration in household wastewater and a determined threshold value above which the heavy pollution surcharges is due. While ATV (1990) still contains some threshold concentrations that are higher by a factor of three than the mean concentrations of the relevant substances in household wastewater, since then the majority of the currently valid statutes of wastewater charges - if they actually include heavy pollution charges at all – have arrived at threshold concentrations that are either equal to, or only 20-30% higher than, the mean concentration values.

If the proportion of costs for the individual parameters (x) relative to the total costs of the WWTP is known, the following formula can be used to determine the pollution-dependent cost factor (f).

$$f = \frac{\text{costs WWTP}}{\text{total costs}} \cdot \frac{x}{100} \qquad \text{(Eq. 22.3)}$$

In accordance with Table 22.12 and the total costs shown in Section 22.5.3, the following pollution-dependent cost factors for the wastewater parameters COD, N and P are obtained (Table 22.13).

When the factor f, the mean annual concentration of the relevant parameter in the municipal wastewater of the location concerned and its concentration in the heavy polluter's wastewater are known, and the official threshold value stated in the wastewater statutes is taken into account, the surcharge rate (z) may be calculated as follows, in accordance with ATV (1990).

$$z_C = \frac{c_{hp} - c_k}{c_{av}} \cdot f \qquad \text{(Eq. 22.4)}$$

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Table 22.13. Cost factors for an individual allocation of pollution-relevant costs to the cost objects

Cost object	*x, proportional costs of WWTP (%)*	*f*
COD	41.2%	0.222
N	10.4%	0.056
P	6.9%	0.037

where c_{hp} = concentration of the parameter in highly polluted wastewater (mg/l); c_k = threshold value of the parameter for charging a heavy pollution charge (mg/l); c_{av} = average concentration of the parameter in municipal wastewater (mg/l); and f = pollution dependent portion of costs for the parameter.

In the present case study, the relevant threshold concentrations for a heavy pollution surcharge were assumed respectively at 20% above the mean concentrations of the relevant parameters in household wastewater. Following the same principle (Eq. 22.4), a factor z is calculated for each of the cost objects COD, N and P and used as the surcharge rate for the parameter in question (z_{COD}, z_N, z_P). The increased pollution charge (CH) is calculated using the regular wastewater charge (ch) and the respective surcharge rates z according to Eq. 22.5.

$$CH = ch + (ch \cdot z_{COD}) + (ch \cdot z_N) + (ch \cdot z_P) \tag{22.5}$$

In order to adapt heavy pollution surcharges if and when boundary conditions change, it is necessary to re-determine the following input parameters. The factors used for calculation must then be adapted accordingly, with the adaptation frequency in practice normally being determined by the required effort (recalculation, amendment of statutes etc.) on the one hand, and the anticipated benefits (e.g. potential number of customers liable to pay heavy pollution charges) on the other.

- Wastewater charge.
- Average annual concentration in wastewater of heavy polluter.
- Average annual concentration in household wastewater.
- Threshold concentration for levying of a heavy pollution surcharge (must be adapted to changed boundary conditions if necessary).
- Adaptation of allocation of annual costs.

22.5.5 Treatment Costs and Resource Economic Value of Partial Streams

Whereas Section 22.3 dealt with the relevant partial streams with regard to their respective concentrations and loads of relevant resources, this section is concerned with determining the parameter-specific costs of conventional wastewater

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Table 22.14. Resource potential and treatment costs of individual partial wastewater streams for 350,000 inhabitants

	Parameter	*Municipal wastewater*	*Yellow water*	*Brown water*	*Grey water*
Resource potential	N (€/m^3)	0.03	3.78	0.19	0.00
	P (€/m^3)	0.01	0.42	0.15	0.00
	K (€/m^3)	0.01	0.74	0.07	0.00
	COD (€/m^3)	0.05	0.84	1.43	0.02
Σ Resource potential (€/m^3)		0.10	5.78	1.84	0.02
Costs for wastewater treatment	N (€/m^3)	/	7.21	0.29	/
	P (€/m^3)	/	2.75	0.93	/
	COD (€/m^3)	/	3.68	6.51	/
General costs (€/m^3)		1.15	1.15	1.15	0.90
Σ Treatment costs (€/m^3)		1.15	14.79	8.88	0.90
Wastewater quantity (m^3/a)		22,776,000	175.000	400,750	22,200,250
Σ Treatment costs (€/a)		26,192,400	2,588,250	3,558,660	20,045,490

treatment and comparing them with partial stream- and parameter-specific economic resource potential. This allows the identification of principal cost drivers on a partial stream and parameter level on the one hand, and the determination of particularly valuable partial streams from a resource economic viewpoint on the other.

The respective loads and concentrations of the relevant partial streams as shown in Table 22.2 to Table 22.5 were used to determine the specific treatment costs and then converted to parameter-specific treatment costs (cf. Table 22.14) in accordance with the procedure described in Section 22.5.4, and the proportional costs set out in Table 22.13. The stated treatment costs include the annual costs for both the WWTP and the wastewater collection network.

The economic resource potential for organic substances in wastewater is founded on the premise of anaerobic treatment to produce biogas that is then used to generate electricity, and is based on calculations in accordance with the key figures given in Table 22.1. The respective resource equivalents for the plant nutrients nitrogen, phosphorus and potassium were determined on the basis of prices for commercially available complementary fertilizers (see Table 22.7).

Yellow water is predominant both for its resource potential in municipal wastewater and its attendant specific treatment costs (€/m^3). Although the volume flow accounts for only 0.77% of total wastewater, its treatment generates proportional costs of 9.9% in relation to the total costs of WWTP and sewer network. Yellow water treatment costs only attain a level of 18.3% proportional costs in relation to the total costs of the WWTP. Consequently, the partial stream yellow water, which is the real cost driver among the partial streams under

Table 22.15. Relevant cost centres within a municipal materials-flow management

Cost centre	*Stakeholder*	*Economic potential*
1. Wastewater treatment	Operating company; end user in households	Reduction of investment and operating costs
2. Resources in the partial streams	End user in households Recycling company	Commercialisation of resources
3. Drinking water	End user in households	Drinking water saving

consideration, is the preferential candidate from a resource economic point of view for partial stream separation and subsequent recycling. Interestingly enough, nitrogen – at least seen from a contemporary market economy angle – offers the largest economic resource potential, although phosphorus is undoubtedly the most important as far as resource conservation is concerned.

The total annual costs for treatment of the partial stream brown water are even higher than those for yellow water. With a proportional brown water volume stream of 1.8%, proportional total costs of 13.9% (in relation to costs for WWTP and sewer network) or 25.1% (WWTP costs only) must be considered. As one might expect, the predominant parameter for both the economic resource potential and the treatment costs of brown water is COD, as a result of its high load of organic substances.

Assuming that the complete separation of yellow water and brown water results in the cost reduction described in Table 22.15 (in accordance with the stated treatment costs for the partial streams yellow water and brown water), with the remaining total wastewater volume also being treated, the calculated treatment effort for grey water with existing WWTPs would be reduced from 1.15 €/m^3 to 0.90 €/m^3. Even assuming a continued use of existing WWTPs, the reduction of pollutant loads would provide economically exploitable leeway for the successive implementation of partial stream separation concepts. This is a decisive state of affairs inasmuch as it is almost impossible, both commercially and technically, to implement the complete replacement of existing systems in one go. This will force social and economic decision-makers to look for long-term opportunities to gradually supplement, and ultimately replace, existing disposal networks with new processing and recycling systems.

22.6 BALANCE SHEET CLASSIFICATION AND REDISTRIBUTION OF COST CENTRES

The chosen balance sheet classification and the distribution of costs centres will determine whether or not a stream separating concept with subsequent recycling will lead to an economic incentive for the stakeholders. In principle, the balance sheet classification should comprise – besides wastewater treatment – the

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Table 22.16. Exemplary wastewater treatment charge calculation for a household of four

1. Drinking water supply: 126 l/*PE* · d · 4 pers. · 365 d = 184 m^3/a · 1.60 €/m^3	294.00 €
2. Wastewater treatment charge: 184 m^3/a · 1.15 €/m^3	+211.60 €
3. Resources in urine: 4 pers · 0.5 m^3/a · 5.78 €/m^3	−11.56 €
4. Resource bonus for urine: 2 m^3 · 14.79 €/m^3	−29.58 €
5. Drinking water saving: 4 pers. · 2 l/flush · 5 flush/d · 365 d = 14.6 m^3/a · 1.60 €/m^3	−23.36 €
Total	441.11 €/a

components drinking water supply and recycling of resources instead of disposal. It is only with this permutation that benefits from theoretically existing synergies can be used. The following relevant cost centres can be identified within the scope of a materials-flow management in the sector of municipal wastewater treatment.

Within the chosen balance sheet classification, all costs centres and stakeholders have to be connected with each other. Considering the existing classification, the collectivity of end users does not benefit from water saving technologies, and neither do the consumers who use ecological sanitation techniques with subsequent recycling benefit from the reduced wastewater treatment costs to which they have contributed. In order to create a concrete incentive for the stakeholders, the system of municipal wastewater charging would have to be modified in such a way that a "resource bonus," so to speak, for separated and subsequently recycled partial streams is deducted from the general wastewater treatment charges. This "resource bonus," which has to be allocated to the general wastewater treatment charges, could be a promising control instrument for the enhanced implementation of stream separating concepts. The following exemplary calculation can be made for a household of four (Table 22.16) for separate urine collection and subsequent recycling.

In contrast to the conventional system, where the total costs for drinking water supply and wastewater treatment would amount to 505.60 €/a, the alternative scenario with urine separation and the allocation of a resource bonus would lead to a calculative annual saving of 16.13 € per person. Calculated for 350,000 inhabitants, the overall economic potential would theoretically amount to 5.6 million €/a.

Of course it cannot be expected that this newly introduced approach will bring about the *ad hoc* replacement of the existing systems for wastewater drainage and treatment. However, the approach identifies an economic potential for successively introducing sustainable concepts in spite of the long-term character of existing end-of-pipe systems. Especially locations where new sanitary and wastewater treatment facilities are realised, or where stream separating solutions with subsequent disposal of the resources already exist, are suitable for this purpose.

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22.7 CONCLUSION

Beside its many achievements, conventional modern wastewater treatment represents an elimination of essential and partly non-renewable resources under resource economic aspects. One main criterion of the existing systems is that particularly partial streams containing high concentrations of utilisable resources are diluted to such an extent that a recovery of the resources is economically no longer reasonable. Ecological sanitation concepts which include subsequent recycling may therefore outclass conventional systems. Especially the long term character of the existing systems with high investment costs and long depreciation periods makes their ad hoc replacement almost impossible.

The presented new approach to evaluation of the economic potential of resources contained in the different partial wastewater streams, in connection with the identification of the specific costs for conventional wastewater treatment of these streams, indicates an economic margin which can be used for a successive introduction of stream separating concepts with subsequent recycling. Urine source separation and recycling takes first priority within this approach due to its high resource potential, the large effort required for its treatment in conventional WWTPs and the comparatively low quantity of this partial stream. Although phosphorus has a major relevance under the aspect of resource protection, nitrogen represents the highest economic resource potential under current market economy conditions.

To enhance the usability of the economic potential that already exists, it will be a fundamental task to modify and extend the actual systems of wastewater charging in such a way that a pollution-dependent charge is introduced and a refund in form of a resource bonus is made possible. This will create an economic incentive for individual stakeholders to step up the realisation of stream separating systems in combination with re-use of the resources.

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CHAPTER 23

Wastewater: A Potential Resource of Energy

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23.1 INTRODUCTION

Inescapable growth in the global population is expected to exceed 9 billion by 2050. The world energy consumption rate is projected to double from 13.5 TW in 2001 to 27 TW by the year 2050 and to triple to 43 TW by 2100 (Lewis and Nocera 2006). This in turn brings about instability in the fossil fuel market and creates more greenhouse gas (GHG) emissions, which will ultimately change the global climate. Therefore, awareness of such deteriorating conditions of the world climate has driven scientists and technologists to consider different environmentally-friendly energy sources. One of the alternative sources of energy is nuclear fission. However, this alone cannot be a practical energy source, as it also depends on perishable source uranium which would be depleted within a few decades. Moreover, handling of radioactive material may also cause environmental damage (Lewis and Nocera 2006). In many countries, nuclear energy is not acceptable due to its destructive nature. The solar energy is another attractive renewable and widely available energy source, but real world application needs highly developed technologies. The other options for alternative energy are wind energy and bioenergy. Wind energy can be generated using turbines against the wind, but this energy entirely depends on the climate and also causes huge noise, which makes the place unsuitable for human inhabitance.

Recently, scientists are more interested in a source of energy, which is sustainable, renewable, economically viable and environmentally safe. In the last few decades, a major research emphasis has been directed towards the search for

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sustainable and economical sources of bioenergy, as is evident from the large rise in number of research publications from all over the world. This led to the utilization of various biomass feedstocks, from food crops, edible/non-edible oil seeds, algae to agricultural, domestic and industrial wastes and wastewaters. Among these sources of bioenergy, the energy recovery from wastewater in parallel with wastewater treatment has been proved to be the more energy-efficient process.

As a result of growing population, rapid urbanization and technology development, securing the water resource is becoming more and more challenging. The growing demand for large amounts of water in various sectors such as agricultural, industrial and domestic has put significant pressure on water resources. This may result in scarcity of water, even in areas that are traditionally rich in water. This enormous pressure on available water resources has put the sustainability of current living standards of the world at risk. Under such circumstances, awareness of all potential sources and their proper utilization are necessary. Wastewater both from domestic origins and industry are ubiquitous and a rich source of energy, nutrients and water. Therefore, several processes have been investigated for simultaneous wastewater treatment with a net energy recovery.

Anaerobic treatment is able to convert organics present in wastewater into biogas, which is a potentially renewable source of energy. The anaerobic conversion of sewage sludge to biogas is a complex process involving four phases of biochemical reactions catalyzed by anaerobic or facultative bacteria and archaea. These phases are hydrolysis, acidogenesis, acetogenesis, and methanogenesis (Tezel et al. 2011). Recently, microbial fuel cells (MFCs) and algae cultivations are also investigated for potential treatment and energy recovery from wastewater. The energy recovery from the wastewater treatment needs to be enough to overcome all energy dissipation in the total treatment process including water supply, distribution, collection, and treatment.

In this chapter, the energy production potential of different wastewater sources and various treatment processes are discussed, with an aim of establishing sustainable energy management systems.

23.2 ENERGY PRODUCTION POTENTIAL OF DIFFERENT WASTEWATERS

A major part of directly and commonly exploited energy source in wastewater is the organic fraction represented as chemical oxygen demand (COD), which indicates the amount of oxygen (O_2) required to oxidize the organic material to carbon dioxide (CO_2) and water (H_2O). Table 23.1 shows the typical COD values and methane yields from different wastewater sources. In general, each person produces wastes of about 40–80 g-BOD_5 every day, equating to around 60–120 g-COD/d (Kiely 1997). Considering the fact that 14.7 kJ energy is

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Table 23.1. Energy potential of different wastewaters

Type of wastewater	*COD concentration (mg/L)*	*TSS (mg/L)*	*VSS (mg/L)*	*Biogas production potential* $(LCH_4/g - COD_{removed})$	*Methane content (%)*
Brewery wastewater[a]	208.3	750	—	0.35	—
Brewery wastewater mixed with brewery yeast[b]	2739 ± 640	1740 ± 0.26	—	0.33	77.8
Slaughterhouse wastewater[c]	1100–7250	300–2300	—	0.28–0.34	—
Spoiled milk[d]	203,020 ± 60,250	1730 ± 340	1830 ± 255	0.315	69.18–60.6
Swine wastewater[e]	6978–11500	1221–2658	1264–2546	0.30–0.45 g CH_4–COD/g-VSS·d	74.7–78.4%
Municipal wastewater[f]	154	42	37	1.108 mol-CH_4/m^3 influent	54%
seafoodwastewater[g]	4000	—	—	500 mL-CH_4/g-$COD_{removed}$	—
Distillery wastewater[h]	150000	26000	—	270 mL H_2/g-MLVSS·d	34.7%
Landfill leachate[i]	2800–5000 mg dm^{-3}	—	—	0.45 dm^3-biogas/g $COD_{removed}$·d	—

Major references: [a]Alvarado-Lassman et al. (2008); [b]Zupancic et al. (2012); [c]Manjunath et al. (2000); [d]Sivakumar et al. (2012); [e]Masse and Masse (2001); [f]Yoo et al. (2012); [g]Kaosol and Sohgrathok (2012); [h]Searmsirimongkol et al. (2011); and [i]Bohdziewicz et al. (2008)

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produced per g-COD (Shizas and Bagley 2004), the total energy value of wastes produced by 6.8 billion people in the world would be 2.2–4.4 × 10^{18} J/yr. This energy is equivalent to the energy produced by burning 52–104 million tonnes of oil in a modern power station, or 12–24,000 of the world largest wind turbines working continuously year round (Heidrich et al. 2011). This estimation does not even include all the energy contained in agricultural and industrial wastewater.

Based on the theoretical calculations (1.47×10^7 J energy production per kg COD oxidized to CO_2 and H_2O), the energy density of wastewater is 0.74×10^7 J/m^3 (Owen 1982; Logan 2008) at an average COD of 0.5 kg/m^3. Heidrich et al. (2011) directly applied experimental methods to determine the internal chemical energy of wastewater which estimated to be 1.68×10^7 J/m^3 for combination of domestic and industrial wastewater, and 0.76×10^7 J/m^3 for pure domestic wastewater (Heidrich et al. 2011).

Therefore, a fair estimation of the theoretical energy density of wastewater is in the order of 10^7 J/m^3, which is 5 times as much as the energy consumed to treat the wastewater. The energy value of different wastewaters ranged from 17.7 kJ/g-COD to 28.7 kJ/g-COD (Heidrich et al. 2011). It has been shown that a methanogenic process could in some cases be endothermic, the combustion energy of the methane product being higher than that of the starting substrate. This is the case with the conversion of one mole of acetate (13.6 kJ/g-COD) to one mole of methane (13.9 kJ/g-COD). In this scenario, energy appears to have been created (McCarty et al. 2011). It is actually the Gibbs free energy (the amount of energy that can be extracted from a process occurring at constant pressure) which should be examined for this and other reactions as this parameter informs us of the amount of energy available to organisms for the generation of biomass and an energy-rich product. Methane thus produced from anaerobic treatment results only from the biodegradable fraction.

The problem arises when the influent COD concentration is very low. The Monod or Michealis-Menten kinetic model suggests that bacterial growth and the product formation are limited by the substrate concentration, leading to the substrate utilization approaching zero at the threshold substrate concentration (S_{crit}). The substrate concentration at which biological equilibrium is achieved (organisms growth and decay just balanced), is the minimum substrate concentration (S_{min}) for growth. This S_{min} can be correlated with the Gibbs free energy available for growth equilibrium (ΔG_E). McCarty and Bae (2011), in their study showed that the microorganisms involved in anaerobic reactions could survive at very low substrate concentration and worked syntrophically at close to thermodynamic equilibrium to capture and share the small quantities of energy available.

The refractory fraction of wastewater can be converted to energy through thermal, chemical, or electrical processes. In other ways, several pretreatment methods can be adapted to increase biodegradability and CH_4 production, but energy cost for this may offset the gains (McCarty et al. 2011). Thermal processes such as incineration have a potential to extract energy from both the biodegradable and refractory fractions of the sludge. However, unless water content can be reduced below ~30%, more energy is required for incineration than is produced

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through combustion (WEF-ASCE 1992). Thus, thermal processes are generally not a sustainable energy-generating process. In the case of MFCs, the measured voltage is directly related to Gibbs free energy. Importantly, it is the free energy of the organics that determines the maximum electricity yield. Apparently, not all the energy available in wastewater can be extracted in a useful form as no process is 100% efficient.

The importance of knowing the potential energy available lies in the choice of treatment methods so that most of the energy can be recovered. Some wastes which may be high in energy value, such as halogenated wastes, may be unsuitable or unattractive to some treatment methods. Although, these halogenated compounds are energy rich per gram of COD, but due to lack of hydrogen, this actually makes them unattractive for energy extraction in the form of methane or hydrogen. However, it may be possible to recover this energy using other treatment methods, which may be able to capture electrons directly. In this case, MFC technology could theoretically capture more of the energy available in complex or halogenated compounds than methanogenic treatment (McCarty et al. 2011).

23.3 SUSTAINABLE ENERGY MANAGEMENT SYSTEMS FOR WASTEWATER TREATMENT

The steadily increasing demand of water and energy brings out the concept of sustainable energy management systems for wastewater treatment. This in turn can solve the two major problems of society: first, water and second, energy. There are several systems for energy recovery with simultaneous treatment of wastewater. Some of them are discussed below.

23.3.1 Anaerobic Treatment

Anaerobic treatment is a combination of several degradation pathways of organic compounds through various organic intermediates into methane and CO_2 by a consortium of bacteria and archaea. The methane produced in an anaerobic treatment can be converted to electric energy through methane-driven engines. However, the low specific growth rate of methanogenic microorganisms causes instability of anaerobic treatment. The stability and performance of anaerobic reactors can be improved by complete retention of microbial consortium in the reactor. This can be achieved by using dense bacterial granules as in UASB reactors, microbial biofilm attached to inert carriers as in packed-bed reactors, fluidized bed reactors, and membrane reactors. The carrier medium in the packed-bed or fluidized bed reactor and the granular sludge in the UASB reactor allow rapid biofilm development by providing larger surface area thereby, preventing bacterial washout and improved methanogenesis. Few of these extensively studied reactors are discussed below. The following sections describe some of these reactors widely used for treating wastewaters.

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23.3.1.1 Anaerobic Sequencing Batch Reactor (ASBR)

Anaerobic sequencing batch reactors (ASBRs) containing granular biomass have been extensively studied for wastewater treatment. Better solids retention with efficient operating control and absence of primary or secondary settling make ASBR more acceptable than continuous processes (Rodrigues et al. 2003a). The ASBR involves a four-step repetitive cycle consisting of feeding, reaction, settling, and decanting phases (Figure 23.1a). As the performance of ASBR depends on internal solids separation, the reactor geometry, specifically the height to diameter ratio (H/D) (Sung and Dague 1995) is an important control parameter. Different reactor shapes or geometry impose distinct selective pressure on the microbial components of the biomass (Sarti et al. 2007a). Another important parameter affecting the process performance in ASBR is mixing, which can improve the mass transfer by providing efficient contact between the substrate and granulated biomass. The most economically sustainable way of mixing is by biogas recirculation that produces during the anaerobic treatment. However, for the treatment of low-strength wastewater such as domestic sewage, the biogas production is insufficient to provide suitable mixing. As a result, liquor recirculation or mechanical mixing should be implemented.

ASBRs with different H/D and mixing procedure (mechanical/effluent recirculation) have been successfully employed for treating domestic sewage from the University of Sao Paulo (Sao Carlos City, Brazil). The ASBR equipped with mechanical mixer showed better performance with 60% of COD and 80% of TSS removal than other ASBRs (mixed by liquor recirculation) with COD and TSS removal of 40% and 60%, respectively (Sarti et al. 2007a). ASBRs also provide high treatment efficiencies for dairy effluents. In a laboratory-scale study, the ASBR system treating synthetic wastewater containing non-fat dry milk was reported to provide soluble COD and BOD_5 removal of 62 and 75%, respectively, at an HRT of 6 h, at 5°C. In a temperature range between 5 and 20°C, and at an HRT range between 24 and 6 h, soluble organic removal rates ranged between 62–90% for COD, and 75–90% for BOD_5. In another pilot scale study, an average COD removal efficiency of 92.8% with 0.3117 m^3-biogas/kg-$COD_{removed}$ was observed by Sivakumar et al. (2012). A stable and efficient removal of organic matter at influent concentrations from 500 to 4000 mg-COD/L, corresponding to organic loads of 0.6–4.8 mg-COD/L·d was achieved in a mechanically stirred lab-scale ASBR. It was observed that a higher organic load causes decreased methane production due to increased accumulation of volatile acids. The authors suggested a reduction in the applied organic load (by reducing the feed, diluting the influent or gradual feeding of the reactor, i.e. fed-batch operation) or an increase of the cycle time might help to minimize volatile acids accumulation (Mockaitis et al. 2006).

An anaerobic sequencing batch biofilm reactor (ASBBR) containing immobilized biomass on inert support (polyurethane foam cubes) applied for the treatment of domestic sewage, was able to achieve COD removal efficiency of 66% (Sarti et al. 2007b). An ASBBR operated under fed-batch mode showed poor

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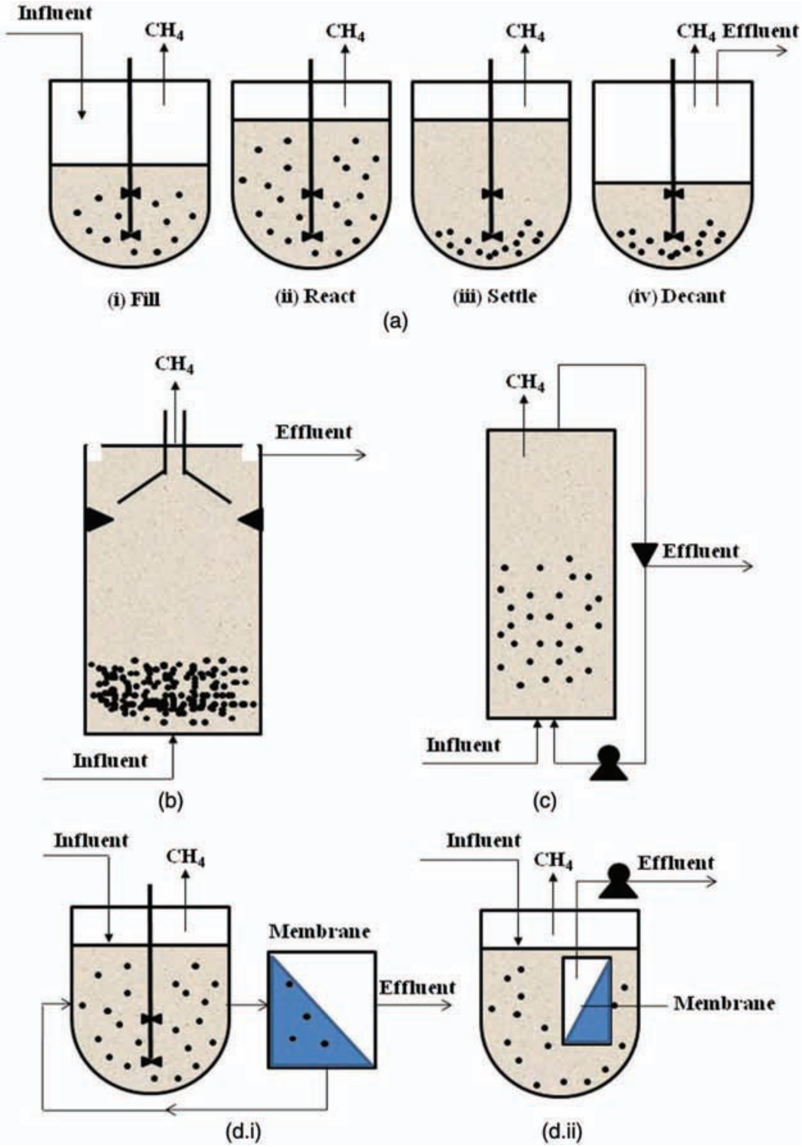

Figure 23.1. Schematic diagrams of main anaerobic reactor systems used in wastewater treatment: (a) ASBR, (b) UASB, (c) AFBR, (d.i) Sidestream AMBR, and (d.ii) Immersed AMBR

performance and instability when feeding time was more than 30 min. This may be due to the formation of considerable amounts of extracellular polymers, which hindered substrate-biomass mass transfer (Ratusznei et al. 2003). The influence of the size of carrier materials on ASBBR performance was also tested.

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A mechanically stirred 4.5-L ASBBR with biomass immobilized on cubical polyurethane foam matrices (0.5, 1.0, 2.0 and 3.0 cm sides) was employed for treating synthetic wastewater with 1000 mg/L of COD containing 50% suspended solids. The results showed maximum k_{1SS}^{app} (first order kinetic constant for suspended solid removal) was achieved for suspended COD at the particle size of 1 cm. However filtered COD displayed a maximum k_{1F}^{app} (first order kinetic constant for filtered solid removal) for the particle size of 2 cm (Pinho et al. 2005). The influence of different carbon sources and the carbon/nitrogen ratio (C/N) on the production and main composition of insoluble extracellular polymers (EPS) was studied in ASBBR with immobilized biomass in polyurethane foam. The authors observed that the yield of EPS was 23.6 mg/g-C, 13.3 mg/g-C, 9.0 mg/g-C and 1.4 mg/g-C when the reactor was fed with glucose, soybean oil, fat acids, and meat extract, respectively. The yield of EPS decreased from 23.6 to 2.6 mg/g-C as the C/N ratio was decreased from 13.6 to 3.4 g-C/gN, using glucose as carbon source (Miqueleto et al. 2010).

The EPS secreted by microorganisms helps in surface adhesion, aggregation of bacterial cells in flocs and biofilm, stabilization of the biofilm structure, formation of a protective barrier that provides resistance to biocides or other harmful effects, retention of water, sorption of exogenous organic compounds for the accumulation of nutrients from the environment, and accumulation of enzymes, such as those involved in the digestion of exogenous macromolecules, for nutrient acquisition. A recent theory is that EPS allows microorganisms to live continuously at high-cell densities in stable mixed microbial populations. In other words, the EPS matrix is a medium allowing cooperation and communication between cells in microbial aggregates (Miqueleto et al. 2010; Laspidou and Rittmann 2002).

Two integrated anaerobic/aerobic fixed-bed sequencing batch biofilm reactors (FB-SBBR) with volcanic pumice stones and a type of plastic media made of polyethylene applied for decolorization and biodegradation of azo dye Acid Red 18 (AR18). FB-SBBR with plastic media made of polyethylene showed better performance in terms of COD removal and dye degradation than the FB-SBBR with volcanic pumic stones (Koupaie et al. 2013). An ASBR operated at 6 h HRT with a filling cycle ranging from 60–320 min, showed stable performance with the average nonfiltered and filtered substrate removal efficiency of 78 and 84%, respectively, for all operating conditions (Rodrigues et al. 2003b). A high-rate ASBR was fed with swine waste containing 1.6 mg/L of tylosin A. The results showed the introduction of tylosin A in ASBR did not affect the COD removal or methane production. However, a substantial increase in MLS_B (macrolide antimicrobial tylosin) resistant biomass in ASBR was observed during initial stages of the operating period (Angenent et al. 2008). ASBR has also been successfully applied for hydrogen production from alcohol distillery wastewater containing high potassium and sulfate. The ASBR could achieve a maximum hydrogen yield of 172 mL-H_2/g-$COD_{removed}$ and a specific hydrogen production rate of 270 mL-H_2/g-MLVSS·d (or 3310 mL-H_2/L·d) with a COD loading rate of 60 kg/m^3·d and an HRT of 16 h without formation of methane gas. The higher

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organic loadings eventually decreased the hydrogen production due to potassium and sulfate toxicity (Searmsirimongkol et al. 2011).

Overall, it can be concluded that H/D of the reactor, mixing type, nature and size of carrier and reactor operation strategy affect the wastewater treatment performance, and therefore, directly influence the biogas production in ASBR.

23.3.1.2 Upflow Anaerobic Sludge Blanket (UASB)

UASB was first developed by Lettinga et al. (1979). The basic configuration of UASB is shown in Figure 23.1b. It has wide applications for treatment of both industrial and municipal wastewater. About 80% of total anaerobic systems in the world are based on UASB. The main component of UASB is anaerobic sludge granules which provide support to the microbes. The performance of UASB is improved on "maturing" with the formation of granules mainly consisted of acetate utilizing methanogens, especially *Methanothrix* and *Methanosarcina* (Rittmann and McCary 2001). The formation of granules is a critical factor for a successful operation of the UASB reactor. The granules not only support the active biofilms but also provide the buoyancy and the settleability necessary to enable very vigorous granule-liquid contact in the reactor. Granule formation in the reactor depends on several parameters such as type of wastewater, characteristics of seed sludge and cell surface, temperature, pH and organic loading rates (OLR) (Bhunia and Ghangrekar 2008) and favored by the combination of high liquid upflow velocity and short HRT (Alphenaar et al. 1993). Under the above favorable condition, the granulation is regulated by inoculum concentration and mixing in the sludge bed. To define favorable mixing conditions in the sludge bed of the UASB reactor and correlate biogas-induced mixing with percentage granulation, a dimensionless granulation index (GI) has been developed by Bhunia and Ghangrekar (2008). The GI helps in validation and verification of granule percentage prediction in UASB.

Several reports suggest that some divalent metal ions, such as Ca^{2+} and Fe^{2+}, enhance the granulation either by activating some enzymes in microbial cells for proper metabolism and cell aggregation (Mahoney et al. 1987; Kosaric and Blaszczyk 1990; Grotenhuis et al. 1991; Schmidt and Ahring 1993) or neutralizing negative charges on bacterial surfaces, serving as cationic bridges between bacteria (Liu et al. 2002; Chong et al. 2012). Yu et al. (2001) showed that introduction of Ca^{2+} at concentrations from 150 to 300 mg/L enhanced the biomass accumulation and granulation process. Massive granule formation was observed by Sponza (2001) within 1.5 months of start-up and fully grew in 7 months when the UASB reactor fed with wastewater containing tetrachloroethylene (TCE). The optimum concentration of iron (Fe^{2+}) at 300 and 450 mg/L accelerates the granulation process but higher Fe^{2+} concentrations in the feed (more than 450 mg/L) deteriorates the bacterial specific activity (Yu et al. 2000) due to excessive deposition of minerals on the granules. Fast start-up and granulation in UASB reactors can also be achieved by addition of some natural polymers, such as water extract of the Moringa Oleifera seeds (WEMOS) (Kalogo et al. 2001), Chitosan (Tiwari et al. 2004, 2005), Reetha extract (Tiwari et al. 2004, 2005) and powdered

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bamboo-charcoal (Cao et al. 2010); as well as commercial and synthetic polymers, such as the commercial cationic polymer "AA 180H" (Show et al. 2004; Wang et al. 2004) and organic-inorganic hybrid polymers (Jeong et al. 2005; Chong et al. 2012). USAB with imminodiacetic acid (IDA) polyacrylamide cryogel carriers was found to be more efficient for the treatment of seaweed leachate containing a high concentration of heavy metals (Nkemka and Murto 2010).

UASB reactors are reported to treat high-strength industrial wastewaters containing readily hydrolysable substrates (e.g., sugar industry wastes, distillery wastes, and brewery wastes) more successfully than complex substrates (e.g., phenols, effluents from food and milk processing plants, gelatin manufacturing plants, and slaughterhouse wastewaters) (Abbasi and Abbasi 2012). It is also much more challenging for low-strength wastewater treatment. The main challenges for treatment of sewage and other low-strength wastewaters in UASB are long start-up time, poor gas production, susceptibility to shock loading, and granule erosion (Abbasi and Abbasi 2012).

Several studies have showed that removal efficiencies of 40–60% for BOD and 50–70% for COD could be obtained for sewage treatment in UASB at 12–18°C and HRT of 7–12 h (Seghezzo et al. 1998). Nkemka and Murto (2013) studied the methane production from the mixture of wheat straw and seaweed hydrolysate co-digestion in the UASB reactor. The results suggest that the methane production rate increased from 0.82 to 1.47 $m^3/m^3 \cdot d$ when the OLR increased from 3.6 to 6.6 $kg\text{-}COD/m^3 \cdot d$, though the methane yield remained the same (0.22 $m^3/kg\text{-}COD_{removed}$). Pariwara et al. (2006) carried out a comparative study of potato waste leachate treatment in an anaerobic packed bed reactor (APBR) and a USAB. They observed the methane yield up to 0.23 $L\text{-}CH_4/g\text{-}COD_{removed}$ (at OLR 6.1 g-COD/L·d) and 0.16 $L\text{-}CH_4/g\text{-}COD_{removed}$ (at 4.7 g-COD/L·d) for treating potato waste leachate in the USAB and APBR, respectively. Improved anaerobic degradation with higher methanization efficiency could be obtained with the strategic intermittent operation of USAB. About 25% more methane conversion could be achieved with the intermittent USAB operation than continuous operation (Nadais et al. 2011). Also, there is a marked difference between the microbial consortium in the USAB reactor operated continuously or intermittently. Archaea organisms are abundant in the USAB reactor when operated intermittently.

Several full-scale UASB reactors have also been successfully used for treatments of different kinds of wastewater. The application of pilot and full-scale UASB reactors (Rao and Bapat 2006) for treating pre-hydrolysate liquor (PHL) emanating from a rayon grade pulp mill were able to achieve COD and BOD removals of 70–75% and 85–90%, respectively with a methane yield of 0.31–0.33 $m^3/kg\text{-}COD_{removed}$ at an OLR of 10 $kg\text{-}COD/m^3 \cdot d$. Likewise, two distinct full-scale UASB reactors were capable of treating alcohol distillery wastewaters with COD removal efficiencies of 90% and 60–80% at OLRs of 6–11 $kg\text{-}COD/m^3 \cdot d$ and 2.5–8.5 $kg\text{-}COD/m^3 \cdot d$, respectively with a same methanogenic activity of 350 and 376 $mL\text{-}CH_4/g\text{-}VSS \cdot d$ (Akarsubasi et al. 2006). A full-scale UASB reactor was applied for treating pharmaceutical

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wastewater containing 6-aminopenicillanic acid (6-APA) and amoxicillin with high COD concentrations with removal efficiencies of 26.3%, 21.6% and 52.2%, respectively (Chen et al. 2011).

The reactor performance could be further enhanced with a modified reactor design. Sometimes, two-stage treatment of wastewater containing large particulate organics is more advantageous, where the first reactor essentially hydrolyzes most suspended solids, and an enriched soluble organic matter containing effluent is fed to the second UASB/EGSB reactor (Seghezzo et al. 1998). Several kinds of reactors such as SBR, downflow-hanging sponge (DHS), activated sludge (AS), trickling filter (TF), stabilizing pond, rotating biological contractor (RBC), constructed wetland (CW) coupled with UASB have been studied for the post treatment of sewage sludge (Chong et al. 2012). The use of anaerobic filter after UASB enhances COD and TSS removal up to 86% and 85%, respectively. A two-step UASB system, in which one served as a hydrolytic unit and the other as a methanogenic unit, would provide better performance than a UASB reactor alone in a lower temperature range of 17–21 °C with overall HRTs of 9.3 to 17.3 h (Alvarez et al. 2008).

23.3.1.3 Anaerobic Fluidized Bed Reactor (AFBR)

The different anaerobic configurations are capable of treating different types of wastewater. The AFBR has been proved to be feasible for the treatment of low-strength wastewater like sewage. Several characteristics make AFBR very suitable for the treatment of domestic sewage (Diez et al. 1999). The process is able to maintain an enormous population of active microorganisms, which efficiently overcome the limits of low organic concentrations and low temperatures. The organic SS are entrapped in the fluidized bed forming granular pellets by fluid motion and/or tumbling action of the media (Figure 23.1c). The SS remain in the reactor until they are hydrolyzed. Turbulence around the particles increases substrate transfer by minimizing the clogging and mixing problems. Energy consumption is low since the pressure loss in the bed is minimal (Sanz and Fdz-Polanco 1989).

Though AFBR is the most suitable for treatment of sewage, it has also been employed for treating several types of wastewater like high-strength industrial wastewater, pink water (generated during handling and demilitarization of conventional explosives) (Davel 2002; Maloney et al. 2002; Atikovic et al. 2008), textile wastewater (Sen and Demirer 2003; Haroun and Idris 2009), pharmaceutical wastewater (Saravanane et al. 2001), brewery wastewater, palm oil mill effluent (Borja and Banks 1995). Sanz and Fdz-Polanco (1989) studied the sewage treatment in UASB and AFBR separately. The authors concluded that AFBR was very suitable for the treatment of low-strength domestic sewage (tCOD = 150–600 mg/L) in the temperature range of 15–25°C. COD and BOD_5 removals of 75 and 80%, respectively was achieved at an HRT of 2.7 h and the OLR of 2.5–3.5 g-COD/L·d with effluent COD and BOD_5 concentrations of 110 mg/L and 55 mg/L, respectively.

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The AFBR has an exceptional capacity for removing TSS, and it could achieve effluent TSS values lower than 20 mg/L (90% TSS removal). The fluctuations in OLR have a slight effect on the effluent quality of AFBR. Moreover, the start-up of AFBR after long non-operating periods (4 months) is reported to be shorter and with fewer problems. The AFBR behaves more stable in non-steady state conditions like start-up or fluctuations in OLR than the UASB. This stability in AFBR is pertained by a recycle line, which prevents the microorganisms from extreme changes. The methanogenic reaction utilizing acetate was observed to follow zero-order kinetics in an influent COD range of 1430–5340 mg/L, independently of the bed expansion (11–37%). The zero-order kinetic constant, K_0 was between 1180–1380 mg-COD/L·h on the fixed bed volume basis, and the maximum specific substrate utilization rate, k was between 145–198 mg-COD/g-VS·h (Diez et al. 1999). In another study, two anaerobic pretreatment technologies, AFBR and UASB, demonstrated that both have similar performance with regard to COD removal, SS removal and gas generation (Motta et al. 2008). In AFBR, 0.16 kg-SS/m^3·d were consumed, and 0.17 kg-SS/m^3·d accumulated in the bed and eventually would need to be removed at a solid loading of 1.02 kg-SS/m^3·d. Whereas, when the solids load of 1.15 kg-TSS/m^3·d applied to the UASB, 0.38 kg/m^3·d were consumed, and 0.054 kg/m^3·d accumulated in the unit (Motta et al. 2008). An AFBR with GAC achieved an overall COD removal efficiency of 97.2% to treat a synthetic high strength industrial wastewater containing acetate, phenol and 2-CP (2-chloro-phenol) (Suidan et al. 1996). The average removal efficiencies of acetate, phenol, and 2-CP were found to be 99.3%, 99.9%, and 99.2%, respectively with about 90% conversion of COD to CH_4.

Another GAC containing AFBR could achieve 99.9% removal efficiency of pentachlorophenol (PCP) at a loading rate of 4 g/kg-GAC·d and influent PCP concentrations as high as 1333 mg/L. Though complete mineralization of PCP to CO_2 and CH_4 was not observed, PCP was stoichiometrically converted into equal-molar concentrations of 3-CP and 4-CP after exhaustion of the GAC adsorptive capacity (Suidan et al. 1996). Xing et al. (2010) attempted to enhance the performance of GAC-containing AFBR for treatment of primary treated sewage effluent (PTSE) with or without refractory organic pollutants (ROPs) by addition of a new starch-based flocculant (NSBF) with a natural starch-based cationic flocculants. Their results indicated that the addition of NSBF in AFBR attained improved organic (9–10%) and nutrient removal (10–20%), higher biomass growth (3.0 g-biomass/L-GAC) and net bed expansion (18 cm). A double critical flux (from 15 L/m^3·h to 30 L/m^3·h) could be achieved when the system used as pretreatment for the microfiltration system. The GAC containing AFBR has also been used to investigate the removals of COD, BOD, and color of textile wastewater. This GAC-AFBR was fed continuously with or without supplemented with glucose at HRTs ranged from 4 to 2 h. The results showed that the anaerobic treatment of the textile wastewater is favorable with the addition of an external carbon source (600 mg/L glucose with the influent COD concentration of 2200 mg/L). The COD, BOD, and color removals achieved in this GAC-AFBR were around 98%, 95%, and 65%, respectively (Haroun and Idris 2009).

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Shin et al. (2012) reported that a high quality effluent could be achieved with acetate and propionate concentrations near or below their detection limits of 0.4 mg-COD/L with influent COD of 200 mg/L, 17 min HRT, and the OLR at 17 kg-COD/m^3·d, or with influent COD values ranging from 45 to 2010 mg-COD/L and OLRs of 4.2–4.5 kg-COD/m^3·d for treatment of dilute wastewater in the GAC-AFBR system. In another study, Shin et al. (2011) concluded that a high influent DO concentration with a DO/COD ratio of 0.12 has adverse impacts on organic removal efficiency, methane production, and effluent SS concentration in the GAC-AFBR system treating low strength wastewater. Even though initially organic removal appeared satisfactory at the higher DO/COD ratio at an HRT of 0.30 h, but soon a rapid growth of oxygen-consuming zoogloeal-like organisms resulted in a high effluent SS concentrations in the system. The AFBR with pumice stone as support material have also been employed for treating cotton textile wastewater with or without supplemented with synthetic municipal wastewater and glucose. The corresponding maximum COD, BOD_5 and color removals were found to be around 82%, 94% and 59%, respectively, at an HRT of 24 h and the OLR of 3 kg-COD/m^3·d (Sen and Demirer 2003).

The AFBR with natural zeolite could achieve COD removal up to 90% at OLRs of up to 20 g-COD/L·d. The methane yield coefficient was 0.29 L-CH_4/g-COD at STP and was virtually independent of the OLR applied. Scanning electronic microscopy (SEM) image of biomass attached zeolite showed that it possesses excellent physical characteristics as a support medium in AFBRs (Fernández et al. 2007). A fluorescence in situ hybridization (FISH) analysis showed that *Methanosaeta* and *Methanosarcinaceae* were the predominant anaerobic microorganisms that colonized the zeolite, with a reduced number of sulfate-reducing bacteria irrespective of the particle size (Fernández et al. 2007). This could further help in improving the biogas yield. Zeolite containing AFBR was also employed to treat the high-strength distillery wastewater at different OLRs, fluidization level (FL) and particle diameter (Dp) of the natural zeolite. The OLR and FL were shown to have only a slight influence on COD removal, whereas they had a stronger influence on the methane production rate. It was also observed that both COD removal and methane production increased linearly with the OLR, independently of the Dp used (Fernández et al. 2008; Montalvo et al. 2012). The use of the zeolite-AFBR for treatment of landfill leachate could achieve COD removals of up to 90% at OLRs as high as 18 g-COD/L·d after 80 days of operation (Turan et al. 2005). A good biogas production yield of 0.53 L-biogas/g-$COD_{removed}$ with a methane content of 75% was obtained. The attached biomass concentration increased along the column height from bottom to top, and its mean value was found to be 6065 mg/L after 100 days of operation (Montalvo et al. 2012).

A laboratory-scale AFBR containing activated carbon particles was evaluated for treating the cephalexin containing pharmaceutical factory effluent with bioaugmentation, which could be used to promote biological treatment to applications where conventional operation might be difficult or unfavorable. The effluent, with COD of 12,000–15,000 mg/L, was diluted and studied in single and multiple inoculation experiments with HRTs of 3–12 h. Continuous COD removal efficiency attained a maximum value of 88.5% using bioaugmentation through the periodic addition of acclimated cells every 2 days with 30–73.2 g of cells from an off-line enricher-reactor (Saravanane et al. 2001).

The operation of an AFBR using biolite as substratum and fed with acetic acid as the sole carbon source showed several important parameters such as fluidization percentages, formation of denser biofilm zone at the bottom of the reactor, particle size and density, and composition of wastewater, which may affect the performance of the reactor and methane yield (Hidalgo and Garcia-Encina 2002). For example, the denser biofilm zone at the bottom of the reactor caused substrate diffusion problems hence lowered the methanogenic activity in this zone than upper levels, thereby reducing the overall biogas production.

In addition to the general wastewater treatment, AFBRs have also been used for treating munitions specific waste. Davel (2002) evaluated the treatment of TNT (trinitrotoluene), RDX (royal demolition explosive, or hexahydro-1,3,5-trinitro-1,3,5-triazine), and HMX (high melting explosive, or octahydro-1,3,5,7-tetranitro-1,3,5,7- tetrazocine) using AFBRs and found almost complete transformation of the compounds. Others have shown similar results using dinitrotoluene (Cheng et al. 1996). Atikovic et al. (2008) showed that AFBRs could effectively remove RDX and perchlorate both separately and in combination. A study was also performed for treatment of pink water containing TNT. In that study, Maloney et al. (2002) found that the AFBRs were effective in removing TNT and RDX, despite widely varying concentration loads (Platten III et al. 2010).

23.3.1.4 Anaerobic Membrane Bioreactor (AMBR)

The granule- and biofilm-based technologies are the well-developed traditional way for biomass retention to enable the operation of bioreactors at high biomass concentrations and high OLR (Skouteris et al. 2012). However, under certain specific conditions, such as high salinities or thermophilic temperatures, biofilm and granule formations may not be as effective as under normal condition. Anaerobic membrane bioreactors (AMBRs) can be used to achieve the required sludge retention in non-conventional conditions. The basic configuration of AMBR is shown in Figure 23.1d. The operation of AMBRs at longer SRTs significantly improves the anaerobic treatment with retention of all microorganisms (Skouteris et al. 2012). The higher methane content has been observed in AMBRs, in comparison with other conventional anaerobic treatment processes, due to the fact that shorter HRTs can be achieved by applying membranes for sludge separation. The major problem related to anaerobic treatment is the slow-growth rate (doubling time from 12 h to 1 week) of microorganisms involved in the process (Zayen et al. 2010). AMBRs are able to solve this problem with complete retention of the microorganisms within the reactors.

Skouteris et al. (2012) reported that since 2006, there have been only few scientific studies that dealt with pilot-scale AMBRs (Saddoud et al. 2006; Wong et al. 2009), while most of the studies are limited to the laboratory-scale only.

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AMBRs have been employed to treat a wide variety of wastewaters. Most of the studies have been carried out with synthetic or real municipal wastewaters (Skouteris et al. 2012) and raw domestic wastewaters (Baek and Pagilla 2006; Saddoud et al. 2006; Kocadagistan and Topcu 2007). AMBRs have also been used to treat white waters from pulp and paper mills (Gao et al. 2010; Lin et al. 2011) and petrochemical effluents (Van Zyl et al. 2008). Depending on the source of wastewater, COD concentrations in the influent usually vary from very low values (162 mg/L) to very high values (10,000 mg/L) such as for kraft evaporator condensate (Lin et al. 2009) or even as high as 18,000 mg/L, for high-strength petrochemical effluent (Van Zyl et al. 2008). The removal efficiencies of AMBRs have varied from 76% (Saddoud et al. 2006) to 99% (Huang et al. 2008; Lin et al. 2009) with biogas conversion up to 98% (Van Zyl et al. 2008).

AMBRs are capable of producing biogas of excellent fuel quality, with a composition of 80–90% methane (Hu and Stuckey 2006; Liao et al. 2006; Xie et al. 2010) in particular cases, which can then be burnt to produce electric power and sometimes able to cover all of the energy demand required for membrane filtration and provide net energy for the wastewater treatment plant (Van Zyl et al. 2008). However, biogas with 70% methane content has also been reported in the literature (Skouteris et al. 2012). Van Zyl et al. (2008) reported energy recovery of 2.02 kWh/kg-$\text{COD}_{\text{removed}}$, which is 7 times higher than the amount of electricity required for the reactor operation for treating synthetic wastewater. Martinez-Sosa et al. (2012) studied the application of anaerobic submerged membrane bioreactor (ASMBR) on low-strength wastewater treatment under psychrophilic condition (20°C). The authors observed COD removal efficiencies of up to 94% with a methane yield of 0.29 L-CH_4/g-$\text{COD}_{\text{removed}}$, which is 85% of the maximal theoretical value at 20°C (0.34 L-CH_4/g-$\text{COD}_{\text{removed}}$). A similar COD removal efficiency with a higher methane yield could be achieved in a similar ASMBR operated at 35°C (Martinez-Sosa et al. 2011). A lower methane yield than the theoretical value indicates that the organic compounds were not completely degraded but physically retained by the membrane in the reactor (Martinez-Sosa et al. 2012).

An AMBR treating the landfill leachate could attained the highest COD removal efficiency of 90% with a biogas yield of 0.45 dm^3/g-$\text{COD}_{\text{removed}}$·d at an HRT of 2 days and an OLR of 2.5 kg-COD/m^3·d (Bohdziewicz et al. 2008). A cross-flow membrane bioreactor could achieve methane yields in the range of 0.17–0.30, 0.20–0.34, and 0.12–32 L/g-COD_{fed} at STP from the treatment of artificial wastewater, sauerkraut brine, and animal slaughterhouse wastewater, respectively (Fuchs et al. 2003). Methane yields up to 0.30 m^3-CH_4/kg-$\text{COD}_{\text{removed}}$ at STP could be achieved by an AMBR treating wastewater containing Mecoprop up to 200 mg/L (Yuzir et al. 2013). This difference in methane composition is due to the characteristics of the organic compounds present in wastewater to be treated (Chernicharo et al. 2007). For example, organic wastes rich in carbohydrates, such as bio-waste and corn silage, has improved the biogas production and the proportion of methane (Skouteris et al. 2012). In addition, the overall composition of the biogas varies according to the conditions

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prevailed in the AMBR (Skouteris et al. 2012). The methane recovery efficiency of an ASMBR treating urban sulfate-rich wastewater was mainly affected by the influent wastewater COD/S–SO_4 ratio. In the absence of sulphate, the recovery efficiency of methane from synthetic wastewater could reach up to 83% and 77% at 33°C and 20°C, respectively. While, the methane recovery efficiency was 57.4% and 53.6% at 33°C and 20°C for real wastewater (Giménez et al. 2012).

The membrane fouling is the major drawback of all MBRs, and appeared to be more intense in AMBRs than in aerobic ones (Spagni et al. 2010). This limits full-scale applications of AMBR as it hinders the continuous and reliable operation of the systems. Potential foulants in AMBRs are inorganic precipitates, or biological–organic material like SMP (soluble microbial protein), EPS (mainly bound protein-based EPS), biopolymer clusters (BPC) and microbial cells (Lin et al. 2009, 2011; Skouteris et al. 2012). The main components of the organic matter in the membrane foulants were identified by Fourier transform infrared spectroscopy (FT-IR) as proteins, polysaccharides and humic acids (Gao et al. 2010). Membrane fouling can be either internal, due to membrane pore clogging/blocking, or external, due to cake formation. Protein-like substances and soluble microbial by-product-like materials were observed as main foulants in both external and internal foulants of an ASMBR treating supermarket wastewater. Gel filtration chromatography analysis demonstrated that the external foulants had much broader distributions of molecular weight (MW) than the membrane effluent, while the internal foulants were mainly comprised of low MW molecules. The different distributions of MW between the external and internal foulants indicated the formation of them at two distinct stages (Zhu et al. 2011). Two important operational parameters for AMBR that affect membrane fouling and impact reactor performance are HRT and SRT. For low-strength wastewater, a low HRT is desirable to reduce AMBR size and the overall footprint of the operation. While, a high SRT may be required to achieve the necessary treatment performance under the constraints of discharge limits, especially at lower temperatures (O'Flaherty et al. 2006). However, increasing the SRT with a constant HRT increases the suspended biomass concentration, leading to a decreased permeate flux (Liao et al. 2006; Huang et al. 2011; Smith et al. 2012). Thus, a considerably high SRT may lead to irreversible membrane fouling such as internal pore blocking (Huang et al. 2008).

Different measures can be applied to mitigate membrane fouling. A short-term operation of the AMBR as a conventional anaerobic reactor during the start-up process to waste some of the fine particles of the feed can be an effective strategy to reduce membrane fouling (Liao et al. 2010). Cross-flow operation of AMBRs is also able to reduce particle deposition on the membranes but still have some limitations with respect to cost and performance of the reactor (Skouteris et al. 2012). Ultrasonic irradiation had also been used effectively to control membrane fouling in several studies. However, this method is not economical as longer ultrasound irradiation times or higher amounts of ultrasound energy required for removing membrane fouling (Skouteris et al. 2012). Another way of in situ membrane cleaning is sparging with biogas that are produced during the

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reactor operation. However, membrane scouring with gas may not be very efficient at high membrane flux. Addition of activated carbon such PAC and GAC helps to minimize the membrane fouling and maintain a lower trans-membrane pressure even at higher membrane permeate fluxes (Hu and Stuckey 2006). PAC seems to have a better performance than GAC as PAC leads to greater absorbance of low and high MW biodegradable matter and fine colloidal particles on the carbon surface (Skouteris et al. 2012).

AMBR has also been coupled with other reactors to produce high-quality effluent with a lesser degree of membrane fouling problem. Periodic 6-min backwashing (twice a day) and intermittent membrane effluent were adopted to reduce membrane fouling, and maintain the permeate flux as high and constant as possible in a EGSB reactor coupled with membrane filtration unit for treating domestic wastewater (Chu et al. 2005). It was observed by the authors that EPS has a higher tendency of depositing on membrane surface than granules of EGSB. An AMBR at membrane flux of 6–11 LMH equipped with scouring effect of the fluidized GAC particles (AFMBR) coupled with AFBR for treating domestic wastewater could be operated for 192 days without membrane fouling (Yoo et al. 2012). AMBRs coupled with other reactors have also achieved improved COD removal efficiencies and biogas yields. For example, an integrated system composed of an AFBR for the acidogenesis step followed by the AMBR for the methanogenesis step was successfully able to overcome the problem of drastic decrease in COD removal and biogas conversion efficiencies of only AMBR while treating the slaughterhouse wastewater at a high OLR (16.32 kg-tCOD/m^3·d) (Saddoud and Sayadi 2007). An integrated UASB-MBR system for treatment of berberine antibiotic wastewater could achieve overall removals of 99.0% and 98.0% of berberine and COD, respectively (Qiu et al. 2013).

The energy production from anaerobic treatment is through methane production. Therefore, the conversion of methane to electrical energy always incurs some energy loss. This loss of energy can be omitted by direct conversion of organics to electricity like in MFCs.

23.3.2 Microbial Fuel Cell (MFC)

MFCs are new types of bioreactors for the production of electrochemical energy using exoelectrogenic biofilms (Oh et al. 2010). The typical MFCs consist of two chambers: an anaerobic anode chamber and an aerobic cathode chamber separated by an ion conducting membrane. Anaerobic respiring bacteria on the anode oxidise organic matter (substrates) and produce electrons and protons. The bacteria transfer electrons to the anode which passes through an external circuit producing current. Protons migrate through the solution across the membrane to the cathode, where they combine with oxygen and electrons to form water (Figure 23.2). This basic design of MFC has been modified further for the ease and better performance of reactor like one-chambered air cathode (Cusick et al. 2010; Cheng et al. 2006; Cheng and Logan 2007), up-flow mode MFC (Jang et al. 2004; Moon et al. 2004; Tartakovsky and Guiot 2006), stacked MFC (Aelterman et al. 2006).

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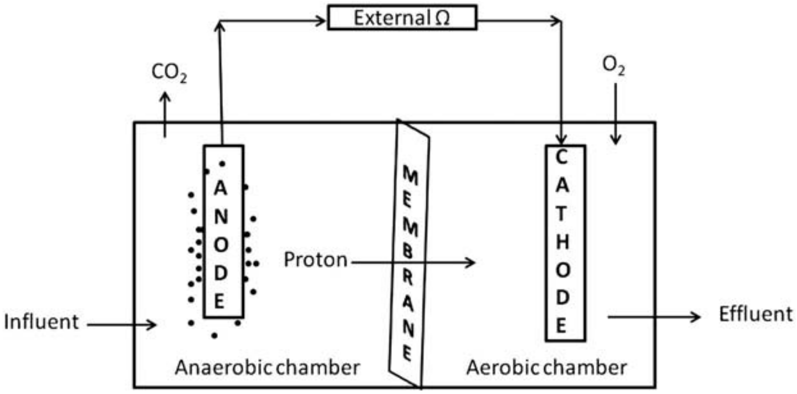

Figure 23.2. Schematic diagram of the microbial fuel cell system

The earliest MFC concept as demonstrated by Potter in 1910 (Ieropoulos 2005) is that the electrical energy can be produced from living cultures of *Escherichia coli* and *Saccharomyces* by using platinum electrodes (Potter 1912). This did not generate much interest until 1980s when it was discovered that current density and the power output could be greatly enhanced by the addition of electron mediators (Du et al. 2007). Recently, MFCs have been gaining increasing attention as devices are able to produce electric power while simultaneously treating industrial, agricultural or municipal wastewater (Rozendal et al. 2008). Compared to other treatment technologies, MFCs have the advantage of being able to achieve the theoretical value of energy efficiencies. The underlining rationale is that fuel cells do not use heat as an intermediate form of energy for electricity production (Virdis et al. 2011).

The MFCs started to be considered a useful method for treating wastewater since early 1991 (Habermann and Pommer 1991). The amount of power generated by MFCs in the wastewater treatment process is always higher than any conventional treatment process. A hybrid incorporating both electrophiles and anodophiles are especially suitable for wastewater treatment as more organics can be biodegraded by a variety of microorganisms. MFCs using certain microbes have a unique ability to remove sulfides without compromising the electricity generation whereas in anaerobic treatment sulfate removal obtained at the cost of less methane (energy) production (Rabaey et al. 2006). MFCs can enhance the growth of bioelectrochemically active microbes during wastewater treatment; thus they have good operational stabilities. Continuous flow and single-compartment MFCs and membrane-less MFCs are favored for wastewater treatment as these are easy to scale-up (Jang et al. 2004; Moon et al. 2005; He et al. 2005). Sanitary wastes, food processing wastewater, swine wastewater and corn stover are all excellent biomass sources for MFCs as they are rich in organic matter (Suzuki et al. 1978; Liu et al. 2004; Min et al. 2005; Oh and Logan 2005; Zuo et al. 2006; Oh et al. 2010). The performances of different types of MFCs treating various wastewaters are shown in Table 23.2.

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Table 23.2. Applications of MFC technology to treat different wastewater streams

Type of MFC	*Type of wastewater*	*Inf COD (mg/L)*	*Maximum Voltage (mV)*	*Maximum Power density*	*current density (mA/m^2)*	*CE (%)*	*COD removal (%)*	*References*
Single chambered	Winery	—	441 ± 17	31.7 Wh/m^3	—	18	65 ± 7	Cusick et al. (2010)
Single chambered	Domestic	—	381 ± 10	22.5 Wh/m^3	—	18	83 ± 10	Cusick et al. (2010)
Single chamber air-cathode	Domestic	—	—	115 W/m^3	—	60	—	Cheng and Logan (2007)
Dual chambered	Chemical wastewater	—	271.5 and 304	—	747.96 and 862.85	—	62.9 and 35.4	Mohan et al. (2008)
single- and dual chambered air cathode	Swine wastewater	tCOD: 494–4470sCOD: 359–2840	—	261 mW/m^2	—	—	tCOD 85, sCOD: 91	Min et al. (2005)
Two-chambered	Domestic wastewater	—	70	40 mW/m^2	—	80	—	Kim et al. (2005)
Single-chamber	Domestic wastewater	180–570	261	300 mW/m^2	—	—	—	Liu et al. (2011)
two- and one-chambered	Cereal wastewater	595 mg COD/L		371 mW/m^2			95	Oh and Logan (2005)
Single chambered	Synthetic domestic wastewater	420	478 V	155.6 mW/m^2	325.51		66.67	Mohan et al. (2009)

(Continued)

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Table 23.2. Applications of MFC technology to treat different wastewater streams (Continued)

Type of MFC	*Type of wastewater*	*Inf COD (mg/L)*	*Maximum Voltage (mV)*	*Maximum Power density*	*current density* (mA/m^2)	*CE (%)*	*COD removal (%)*	*References*
dual-chamber	Mustard tuber wastewater	550–2968	570	246 mW/m^2		67.7	85	Guo et al. (2013)
Plug-flow single chamber	Domestic wastewater		70.6	281.74 mW/m^2		3.04	70	Karra et al. (2013)
Complete mixing single chamber	Domestic wastewater		50.4	239.56 mW/m^2		1.70	81	Karra et al. (2013)
Osmotic MFC	Domestic wastewater	154		4.5 W/m^3	37 A/m^3	83.8	82.9	Ge et al. (2013)
Dual chamber-earthen pot	Rice mill wastewater	1100–2250	304	48.64 mW/m^2 (2310.4 mW/m^3)		18.6	96.5	Behera et al. (2010)
Proton exchange membrane MFC	Rice mill wastewater	1100–2250	172	15.57 mW/m^2, (528.3 mW/m^3)		8.5	92.6	Behera et al. (2010)
Dual Chamber	cyanide laden Cassava mill wastewater	16000		(1771 mW/m^2), (18.2 W/m^3)		20	88	Kaewkannetra et al. (2011)
single-chamber air–cathode 2010	Domestic wastewater	450–470		422 mW/m^2 (12.8 W/m^3)		1.7	25.8	Ahn and Logan (2010)
Membrane less-MFC	artificial wastewater		~480	1.3 mW/m^2	6–9		90	Jang et al. (2004)

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two-compartment continuous flow MFC	Synthetic wastewater	936	340–350	22 mW/m^2	68.2			Tartakovsky and Guiot (2006)
Submerged MFC	Synthetic/ domestic wastewater	100	418–695	191–754 mW/m^2		5–21	80–95.7	Yu et al. (2012)
Column type MFC	Landfill leachate	555		0.62 mW/m^2, (600 mW/m^3)			5	Yu et al. (2012)

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MFC has been successfully used for bioelectricity generation from brewery wastewater treatment with a COD removal efficiency of 40–43% at an HRT of 2.13 h. The maximum coulombic efficiency (CE) of 19.75% was documented at the external resistance of 20 Ω. The model established based on polarization curve for the MFC showed that the most important factors, which influenced the performance of the MFC, were reaction kinetics and mass transport loss. Increasing reactant concentrations and reaction temperature, employing more effective and cheaper electrode catalysts and rough electrodes, and improving the flow structure are several methods for decreasing mass transport losses (Wen et al. 2009). A COD removal of 83% was achieved for the treatment of winery and domestic wastewater by MFCs with energy recovery of 1.22 ± 0.006 kWh/kg-COD (Cusick et al. 2010). The maximum voltages of 271.5 mV (5.43 mA) and 304 mV (6.08 mA) (measured at 50 Ω external resistors at stable operating conditions) with COD removal efficiencies of 35.4% and 62.9% were achieved at OLRs of 1.165 kg-COD/m^3·d and 1.404 kg-COD/m^3·d, respectively in a dual chambered MFC treating chemical wastewater.

Single-chamber air-cathode MFCs have been employed for treating domestic wastewater. The highest power density of 422 mW/m^2 (12.8 W/m^3) and COD of 25.8% were achieved under continuous flow and mesophilic conditions at an OLR of 54 g-COD/L·d. Energy recovery was found to depend significantly on the operational conditions (flow mode, temperature, OLR, and HRT) as well as the reactor architecture (Ahn and Logan 2010). A submerged type MFC system consisted of six readily exchangeable air-cathode MFCs, operated under continuous mode, was fed with synthetic domestic wastewater (COD 100 mg/L) at OLRs of 0.20–0.40 kg/m^3·d. The maximum power densities from 191 to 754 mW/m^2 and COD removal efficiencies of 66–80% could be achieved by the system (Yu et al. 2012).

An air-cathode MFC with membrane electrode assembly was employed for treating starch processing wastewater containing 4852 mg/L of COD operated over four batch cycles (a total period of 140 d). The maximum voltage output and power density of 490.8 mV and 239.4 mW/m^2 (a current density of 893.3 mA/m^2) were approached in the third cycle, which also had the minimum internal resistance of about 120 Ω and maximum CE of 8.0%. The removal efficiencies of COD and NH_4^+-N increased as a function of time, and the maximum amounted to 98.0% and 90.6%, respectively (Lu et al. 2009).

A two-chambered MFC using anaerobic sewage sludge with a porous carbon paper anode electrode was able to generate 8 mW/m^2 of power within 50 h with a CE of 40%. When an iron oxide-coated electrode was used, the power and the CE improved to 30 mW/m^2 and 80%, respectively. While a methanogen inhibitor (2-bromoethanesulfonate) increased the CE to 70%. The maximum power was increased to 40 mW/m^2 by applying biofilm scraped from the anode of a working MFC to a new anode electrode (Kim et al. 2005).

A single-chambered air cathode MFC treating animal wastewater produced the maximum power density of 261 mW/m^2 (200 Ω resistor), which was 79%

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higher than that previously obtained with the same system using domestic wastewater (146 ± 8 mW/m^2) (Min et al. 2005). Power generation as a function of substrate concentration was modeled according to saturation kinetics, which provided the maximum power density of 225 mW/m^2 (fixed 1000 Ω resistor) and half-saturation concentration of 1512 mg/L (tCOD). Further, pretreatment of wastewater such as dilution (1:10), sonication and autoclaving generated 16% more power (Min et al. 2005).

Mustard tuber wastewater (MTWW) was utilized as fuel in the typical dual-chamber microbial MFCs to recover bio-energy and to obtain effluent treatment simultaneously. The whole experiment was divided into four phases characterized by increasing contents of primary clarifier effluent (PCE). Results showed that MFC generated a maximum power density of 246 mW/m^2 and the most appropriate fuel in terms of power recovery and the internal resistance and CE were 121 Ω and 67.7 ± 1%, respectively when fed with 550 mg/L COD. The maximum 85% COD removal could be achieved with much lower the power retrieve efficiency when fed with 1561 mg/L COD concentration as influent (Guo et al. 2013).

Karra et al. (2013) compared the two flow patterns i.e. plug flow (PF) and complete mixing (CM) of MFCs with multiple anodes-cathodes in continuous flow mode for wastewater treatment and power generation. The PF-MFC had higher power generation and CE whereas the CM-MFCs had higher COD removal than PF-MFCs. Behera et al. (2010) compared the performance of a proton exchange membrane (PEM) MFC for rice mill wastewater treatment with that of an earthen pot MFC. The maximum COD removal efficiencies of 96.5% and 92.6% were obtained in earthen pot MFC and PEM-MFC, respectively. The lignin removals were 84% and 79%, and the phenol removals were 81% and 77%, for earthen pot MFC and PEM-MFC, respectively. Maximum sustainable volumetric powers of 2.3 W/m^3 and 0.53 W/m^3, with 100 Ω external resistances, were obtained in earthen pot MFC and PEM-MFC, respectively. More effective treatment of rice mill wastewater and higher energy recovery was demonstrated by earthen pot MFC as compared to MFC incorporated with PEM.

In order to achieve both wastewater treatment and bioenergy production, biological hydrogen and electricity production using MFCs were successfully linked together. Hydrogen was generated from the bacterial fermentation of sugar in the food processing wastewater. Hydrogen yields were in between 0.61 and 0.79 mol/mol for the cereal wastewater. The maximum power density of 81 ± 7 mW/m^2 (normalized to the anode surface area) with a 95% COD removal was achieved when the two-chambered MFC and the cereal wastewater (diluted 10 × 595 mg-COD/L) treatment was linked together. Coupling of a one-chambered MFC and the biohydrogen reactor effluent could produce the maximum power of 371 ± 10 mW/m^2 (Oh and Logan 2005).

These studies demonstrate that different types of wastewaters can be used for power generation in MFCs while at the same time achieving wastewater treatment.

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23.3.3 Simultaneous Algal Biomass Production and Wastewater Treatment

Although, anaerobic treatment and MFC can effectively remove COD and BOD from wastewater, these methods are inadequate at removing nutrients (Tchobanoglous et al. 2003; Dahiya et al. 2012). In order to attain the effluent quality thresholds for discharge into surface waters, the treated wastewater effluent coming out of a biodigester needs to undergo further treatment, for which aerobic processes are normally employed. Algae are known to utilize many components found in these effluents, including nitrogen, phosphorus, potassium, heavy metals, and other organic compounds (Oswald 1990; Wilkie and Mulbry 2002; Kebede-Westhead et al. 2003; Pizarro et al. 2006; Mulbry et al. 2008).

Cyanobacteria and *Chlorophyceae* can grow with up to 18% dissolved CO_2 in the cultivation medium. *Cyanobacteria* can also be grown in organic substances, such as sugars, fatty acids, and amino acids. Nitrogen can be utilized as NO_3, NO_2 or NH_4 and also as N_2. Some *Cyanobacteria*, such as *Oscilatoria*, *Anabaena* and *Spirulina*, are diazotrophic, which means that they are capable of utilizing elemental nitrogen as their sole nitrogen source by the reduction of N_2 to NH_4. Apart from carbon, nitrogen and phosphorous, microalgae can also utilize sulphur, calcium, magnesium, potassium, molybdenum, iron, nickel, copper, zinc, cobalt, boron, manganese and chloride as macro or micro nutrients (Markou and Georgakakis 2011).

Algae have also been widely researched and employed successfully to treat a variety of commercial and industrial wastewater streams. Dosnon-Olette et al. (2010) used immobilized cultures of *Scenedesmus obliquus* and *Scenedesmus quadricauda* to phytoremediate the agricultural fungicides dimethomorph and pyrimethanil and the herbicide isoproturon. Many metals can be bioremediated and biosorbed from wastes using algae such as *Chlorella sp*. and *Scenedesmus sp*. (Markou and Georgakakis 2011). *Chlamydomonas reinhardtii* was grown in synthetic and influent, effluent and centrate from a wastewater treatment plant in flask and biocoil. About 83.0% of the N and 14.45% of the P were removed from the centrate wastewater with an initial concentration of 120 mg/L-P, 128.6 mg/L-TKN and 67 mg/L-NH_3 (Kong et al. 2010).

Currently, algae have also received an enormous amount of attention as an alternative biofuel feedstock due to their high photosynthetic and growth rate than any of terrestrial plants. Algae may contain up to 70% of lipid on a dry weight basis. Integrated systems for algae feedstock production with wastewater treatment hold high potential for cutting costs and generating new revenue and products for farmers (Dahiya et al. 2012). Algae harvested in wastewater can also be used for the production of high-energy fuels and compounds such as acetone, butanol, and ethanol (ABE) (Ellis et al. 2012). Several algae species such as *Botryococcus braunni*, *Chaetocero scalcitrans*, several *Chlorella sp*., *Isochrysis galbana*, *Nanochloropsis*, *Schizochytrium limacinum*, *Scenedesmus sp*. have been studied as a potential source of biofuel (Chisti 2007; Rodolfi et al. 2008; Singh and Gu 2010).

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Table 23.3 shows the treatment of different wastewaters by cultivating different oleaginous algae with their potential lipid productivity. Sturm and Lamer (2011) suggested that biofuel production is energetically favorable for open pond reactors utilizing wastewater as a nutrient source, even without an energy credit for nutrient removal. The energy content of algal biomass was also considered as an alternate to lipid extraction and biodiesel production. Direct combustion of algal biomass may be a more viable energy source than biofuel production, especially when the lipid content of dry biomass (10% in this field experiment) is lower than the high values reported in lab-scale reactors (50–60%) (Sturm and Lamer 2011). Wang and Lan (2011) observed that *N. oleoabundans* was a promising candidate for integrated microalgal biofuel production and wastewater treatment. *N. oleoabundans* is able to deplete N and P completely from secondary municipal wastewaters while achieving high biomass productivity of 233.3 mg-DCW/L·d (Wang and Lan 2011).

Mixed cultures of algae employed for pulp and paper industry could achieve removal up to 58% for COD, 84% for color and 80% for absorbable organic xenobiotics (AOX). No remarkable differences were observed in COD and color removal when light intensity and wastewater strength were changed, while AOX removals were strongly affected. In the presence of organic carbon in the medium, algae exhibit mixotrophic growth and mainly green algae, diatoms and flagellates can survive and grow in the pulping effluents. In the case of higher initial COD, diatoms grow more; however, under higher light intensity, green algae are more dominant than diatoms (Tarlan et al. 2002). Mahapatra et al. (2013) demonstrated *Euglena sp.* as a suitable source of lipids for potential use as biofuel and sustainable wastewater treatment. *Euglena sp*. grown in municipal wastewater could achieve 98% removal of NH_4-N, 93% of total nitrogen, 85% of orthophosphate, 66% of total phosphate and 92% total organic carbon with a mean specific growth rate of 0.28/d, biomass productivity 132 mg/L·d and maximum lipid content of 24.6% (w/w).

An attempt to grow *Chlorella pyrenoidosa* in dairy wastewater at different stages (influent and effluent) and different dilution (25–100%) showed that nitrate removal was better in the influent whereas nitrite removal was better in the effluent. The maximum growth rate of *C. pyrenoidosa* could be observed in 75% of dairy wastewater. A better biomass yield of Chlorella was achieved in the influent (fresh weight 18.8 g/L) than that in the effluent (14.1 g/L) with a higher biodiesel production potential (Kothari et al. 2012).

A 6-day batch cultivation of *Auxenochlorella protothecoides* UMN280 in concentrated municipal wastewater showed that the maximal removal efficiencies for total nitrogen, total phosphorus, COD and TOC were over 59%, 81%, 88% and 96%, respectively, with a high growth rate (0.490/d), high biomass productivity (269 mg/L·d) and high lipid productivity (78 mg/L·d). Further fatty acid methyl ester (FAME) analysis showed that the microalgal lipids were mainly composed of C16/C18 fatty acids, which are suitable for high-quality biodiesel production.

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Table 23.3. Treatment of different wastewaters by cultivating different oleaginous algae with their potential lipid productivity

Type of wastewater	*Algae sp*	*Inf. COD (mg/L)*	*Inf. N (mgN/L)*	*Inf. P (mgP/L)*	*COD removal (%)*	*N removal (%)*	*P removal (%)*	*Biomass productivity (g/L·d)*	*Max. Biomass conc. (g/L)*	*Lipid productivity*
Artificial wastewater[a]	*Neochloris oleoabundans*	—	218	47	—	100	100	0.233	2.91	—
Municipal wastewater[b]	*Chlamydomonas reinhardtii*		64–128	6.9–120	—	83	15.4	2	2	0.505 g/L·d
Municipal wastewater[c]	*Euglena sp.*	600	32	18	—	93	66	1.2	—	24.6%, 16.15 mg/L·d
Dairy wastewater[d]	*Chlorella pyrenoidosa*		60–82	80–85	—	—	—	—	18.8	3.5 mg/L·d
Concentrated municipal wastewater[e]	*Auxenochlorella protothecoides* UMN280	2344	134	211	88	59	81	0.269–51	—	78 mg/L·d
Pretreated piggery wastewater[f]	*Botryococcus braunii* UTEX 572	284	836	40	—	43	—	—	0.0085	0.045–0.053 g hydrocarbon/ L·d, 0.95 g–hydrocarbon/L
Centrate from activated sludge process[g]	*Chlorella kessleri*	—	—	—	89	83	92	—	2.1	24%
	Chlorella protothecoides	—	—	—	87	86	82	—	1.31	25%

Note: Inf. = Influent; Max. = Maximum; Conc. = Concentration

Major references: [a]Wang and Lan (2011); [b]Kong et al. (2010); [c]Mahapatra et al. (2013); [d]Kothari et al. (2012); [e]Zhou et al. (2012a); [f]An et al. (2003); [g]Li et al. (2011)

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The system could be scaled up from 100 mL flasks to 25 L BIOCOIL reactors, and semi-continuously operated at an HRT of 3 d with a net biomass productivity of 1.51 g/L·d of dried algae (Zhou et al. 2012a). In another study, *Botrytiscoccus braunii* cultivated in pretreated piggery wastewater could achieve dry cell weight of 8.5 mg/L and hydrocarbon level of 0.95 g/L with a nitrate removal rate of 620 mg-N/L (An et al. 2003). A sequential two-stage mixo-photoautotrophic culture strategy developed for simultaneous biofuel and animal feed production from swine wastewater treatment using two newly isolated microalgal strains UMN 271 and UMN 231. The maximal biomass concentration and lipid content reached 2.03 g/L and 23.0%, and 0.83 g/L and 19.0% for UMN 271 and UMN 231, respectively. The maximal nutrient removals for total phosphorus and ammonia after second-stage cultivation were 100 and 89.46%, respectively (Zhou et al. 2012b). *C. zofingiensis* cultivated in tubular bubble column photobioreactor for 10 days treating piggery wastewater could achieve COD, TN and TP removals ranging from 65.81% to 79.84%, from 68.96% to 82.70% and from 85% to 100%, respectively (Zhu et al. 2013). The highest biomass, lipid and biodiesel productivities of 296.16 mg/L·d, 110.56 mg/L·d and 30.14 mg/L·d, respectively were obtained at the influent COD concentration of 1900 mg/L (Zhu et al. 2013). Woertz et al. (2009) reported 2.8 g/m^2·d of lipid productivity from an algal polyculture (*Scenedesmus* > *Micractinium* > *Chlorella* > *Actinastrum*) treating dairy wastewater and lipid productivities of 9.7 mg/L·d (air-sparged) to 24 mg/L·d (CO_2-sparged) treating municipal wastewater (predominately genera *Chlorella*, *Micractinium*, and *Actinastrum*).

23.4 ENVIRONMENTAL IMPACT

Appropriate wastewater treatment strategy reduced GHG emissions and considered as a global warming mitigation factor. Full wastewater treatment with biomass sequestration and biogas energy recovery can be a net carbon sequestration process. The emission of methane in the environment should be avoided since the global warming potential (GWP) of methane is 23 times the GWP of CO_2, and therefore methane leakages can impose a negative carbon footprint of the process (Martinez-Sosa et al. 2012). Methane recovery should also include the dissolved methane in the liquid phase. Up to 95% of dissolved methane recovery had already been achieved by using a down-flow hanging sponge reactor operated at 20°C (Hatamoto et al. 2010). The selective membranes have been used to improve the dissolved methane recovery. In a study, up to 97% dissolved methane recovery was achieved using the hollow fiber degassing membrane at 25°C (Martinez-Sosa et al. 2012).

De Meester et al. (2012) compared the reference electricity production from the grid with electricity production from anaerobic digestion of domestic waste and energy crops. A saving of over 90% resources was achieved for biobased

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electricity compared to conventional electricity, except for the fossil fuel use in domestic organic waste digestion. The life cycle assessment (LCA) showed that, the latter was mainly caused by the transport distances necessary for a selective municipal organic waste collection. However, a positive balance was still achieved with a consumption of 0.59 MJ fossil energy/MJ electricity. Furthermore, waste collection is a service to society, which is indispensable and independent of the final fate of waste (De Meester et al. 2012). Unlike other sources of bioenergy, usage of organic waste as a feedstock does not have direct land necessity, and the digestion of this biomass source can thus be seen as a valorization pathway with an overall positive energy balance.

A maximum amount of energy contained in the form of biogas should thus be used as the waste heat would detract from the efforts to obtain the biomass resources. This is logical from a thermodynamic point of view but causes difficulties in reality, since both the agricultural and organic waste digesters are mainly located in rural and non-industrial areas. Nevertheless, solutions should be sought for this problem, where heat demanding processes can be executed in the proximity of digesters (e.g. drying steps, domestic and rural heating such as greenhouses, stables). An alternative is a transportation of the heat or the biogas itself. An upgrade to biomethane, for example, is stated to have a positive environmental effect when being burned in a small-scale combined heat and power generation plant (CHP) unit (Pöschl et al. 2012), whereas the biomethane could be transported in the currently available gas supply. Ozone depletion and photochemical oxidant formation are mainly caused by transport, which results in the highest impact for the organic waste digestion due to a transport intensive waste collection step (Bacenetti et al. 2013). In a proposed LCA model of ethanol conversion from municipal solid waste, Kalogo et al. (2007) showed its better performance in terms of net energy and GHG savings compared to corn ethanol or cellulosic biomass-ethanol.

Although MFC technology has the advantage of direct electricity production from wastewater treatment, a recent study (Foley et al. 2010) concluded that it does not provide a significant environmental benefit relative to the anaerobic treatment processes. The adverse environmental impacts associated with anaerobic treatment or MFC are mainly due to electricity consumption in the various process units and transportation/disposal of biosolids. In the case of anaerobic treatment, these negative impacts can be balanced by benefits that can be achieved by the displacement of fossil-based natural gas, with the produced biogas. On the other hand, the positive environmental impacts in MFC arise solely from the displacement of grid electricity. However, the main demerits lie in the construction of MFC, which requires emissions-intensive materials such as stainless steel, membrane materials, carbon fibers, polyvinyl chloride. In future, appropriate materials selection and development may make MFC environmentally competitive relative to the existing anaerobic treatment technology (Foley et al. 2010).

In the case of algal biofuels, further reduction in GHG can be obtained as CO_2 produced in the fermentation process can be recycled as a carbon source for algae

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cultivation (Singh and Gu 2010). The recycling of nutrients by converting the sewage to algal biomass and then to biofuel is a significant environmental benefit to the system. This would also help in mitigating GHGs through assimilation of carbon (as algae are photosynthetic organisms). Algae-based pond systems deployed in the rapidly growing cities would aid in the sustainable management of wastewater through low-cost treatment with the prospects of biofuel in addressing the regional energy demand (Mahapatra et al. 2013). The problem with wastewater treatment ponds is that they are limited in providing carbon for algal growth. The heterotrophic oxidation of organic material by bacteria is one way that CO_2 is made available to algae (Oswald et al. 1953). Collet et al. (2011) studied the life-cycle of biogas production from the algae *Chlorella vulgaris*. They emphasized that high productivity of algae enabled by recycling CO_2 from flue gas and the algae also had the capacity to carry out anaerobic digestion directly, to produce methane and recycle nutrients (N, P and K). Their results suggested that the production of methane from algae can directly correlate and mitigate the electric consumption, and further improvements could be realized by decreasing the mixing costs and circulation between different production steps, or by improving the efficiency of the anaerobic process under controlled conditions (Collet et al. 2011).

CO_2 addition can also impact biomass and lipid productions. Gouveia et al. (2009) showed a slight increase in lipid contents when CO_2 was added to the algae culture media. The addition of CO_2 has been shown to increase algae biomass (Benemann 2003; Woertz et al. 2009; Craggs et al. 2012). High-rate algae ponds fed with clarified domestic wastewater and CO_2-rich flue gas are expected to remove nutrients to concentrations similar to those achieved in mechanical treatment technologies, such as activated sludge; however, the energy intensity of wastewater treatment with CO_2-supplemented high-rate ponds (HRPs) would be less than that of mechanical treatments (Craggs et al. 2012). This approach would require robust oleaginous strains capable of tolerating high CO_2 concentrations. Some studies have shown that *Cyanidium caldarium*, *Scenedesmus* sp., *Chlorella* sp. and *Eudorina* spp can tolerate CO_2 concentrations of 100%, 80%, 40% and 20%, respectively (Seckbach et al., 1971; Hanagata et al., 1992; Dahiya 2012). Many studies have used either wastewater or CO_2 from the respective point sources as nutrient streams for growing algae biomass. Very few studies have actually taken the advantage of both combined CO_2 and wastewater from point sources for algae production. For instance, Yun et al. (1997) cultured *C. vulgaris* in steel manufacturing wastewater effluent under high concentrations of 15% (v/v) CO_2 supply captured from a power plant and removed 0.92 $g/m^3 \cdot h$ ammonia and 26 $g/m^3 \cdot h$ CO_2. One of the possible reasons behind the lack of combining CO_2 and wastewater supplies from point sources in culturing algae is the distance between the locations of respective point sources may not be close enough; as such, if an algae production facility is utilizing CO_2/flue gas from a point source, hauling wastewater from a distant location would increase the costs of biomass production. This area of research needs special attention.

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23.5 SUMMARY

The outlook of waste management is going to change in the future since waste will no longer considered as an inconvenient burden to dispose of but as a source of alternative energy. Wastewater represents a valuable source of nutrients (primarily nitrogen and phosphorus), energy (organic matter), and water itself. In the future, we will no longer refer to wastewater treatment plants but rather to bioenergy recovery plants or biorefineries. The treatment stages of wastewater will depend on the final usage of the water. The treatment plant may be the combination of more than one technology including anaerobic treatment for the production of biogas, MFCs for bio-electricity and algae cultivation for biofuel. Methane can be directly and effectively used as a replacement of natural gas. Among the aforementioned technologies, anaerobic treatment is the only renewable energy technology, which is fully mature, completely scalable, and generates an energy product that can be stored as produced. In particular, this technology is applicable in all sectors like domestic, industrial and agricultural whenever and wherever there is a need for wastewater treatment and energy. A large part of organics are being emanated as methane, which is currently lost with a consequent GHG impact contributing to global warming. It is very likely that other technologies such as MFC and algae biofuel, once standardized, would also be implemented at a large scale as a partner to anaerobic digestion.

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CHAPTER 24

Fermentative Biohydrogen Production from Wastewaters: An Exploration for Sustainable Green Energy

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24.1 INTRODUCTION

In this 21st century, sustainable development is the main factor governing the economic growth of a country. A rapid transition from the fossil-fuel driven energy sector to new, sustainable, energy systems is one of the key challenges faced by mankind in this century (Mullai et al. 2013a). Reducing energy demand by improving energy efficiency, heightening environmental stewardship and development of alternative energy sources, must be merged to defuse the crisis of fossil fuel depletion threatening both climate change and environmental pollution (Hallenbeck 2005; Hallenbeck et al. 2012; Mullai et al. 2013b). A systematic planning of research and development activity is required for all renewable energy-based research in order to transfer comprehensively the acquired lab-based knowledge to industry-scale production. The acclivitous demand for sustainable alternate energy sources and the changing global policies have facilitated basic and applied research in biohydrogen production. Biohydrogen, a fuel generated through microbial metabolism will pave the way for a prognosticating avenue for the large-scale sustainable generation of hydrogen to fuel the rising world demand. Accordingly, biohydrogen is considered as the key solution to meet the persisting global energy crisis and is presently being considered as a versatile fuel for many future applications (Kothari et al. 2012; Mullai et al. 2013a).

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Recently, several approaches for biohydrogen production had been experimented and reported in the literature. Biohydrogen can be made from water, either directly or indirectly, using solar driven photosynthesis (bio-photolysis) and through anaerobic fermentative processes using hybrid biotechnologies. Among these processes, fermentative hydrogen production is a promising technology. In this chapter, the microbiology, different biochemical pathways involved, the critical process parameters dictating the performance of batch and continuous bioprocesses, and modeling of biohydrogen production are discussed in detail.

24.2 MICROBIOLOGY AND BIOCHEMISTRY OF HYDROGEN PRODUCTION

The microbial degradation of organic material under anaerobic environment is accomplished in the absence of free oxygen using sulfate, nitrate or carbon dioxide as electron acceptors (Gray 2004). This anaerobic decomposition ultimately results in the production of a biogas consisting of methane, carbon dioxide, hydrogen, nitrogen, and hydrogen sulphide. The overall chemical reaction (Eq. 24.1) is often simplified and expressed as follows:

$$\text{Organic matter} \rightarrow CH_4 + CO_2 + H_2 + N_2 + H_2S \qquad \text{(Eq. 24.1)}$$

The anaerobic degradation of organic material is chemically a very complicated process involving hundreds of possible intermediate compounds and reactions, each independently catalyzed by specific enzymes or catalysts (Mullai 2002; Mullai et al. 2011).

24.2.1 Microbiology of Hydrogen Production

There are four major sub-processes that regulate the anaerobic conversion of complex organic substrates to elemental hydrogen (H_2), *viz.*, disintegration, hydrolysis, acidogenesis and acetogenesis, respectively. Each sub-process is mediated by one or more specific microbial groups.

24.2.1.1 Disintegration and Hydrolysis

By disintegration and hydrolysis processes, the breakdown of large, complex and insoluble organics into simple substances is achieved. Disintegration of composite particulate material into smaller carbohydrate, protein and lipid fractions is catalyzed by extracellular enzymes like cellulase, amylase, protease, and lipase. Hydrolysis is accompanied by the release of energy. In this process, organic waste is converted into a soluble form, but often not stabilized (Parkin and Owen 1986; Batstone et al. 2002).

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24.2.1.2 Acidogenesis

The acidogenesis process is a complex process involving acid forming fermentation, hydrogen production, and an acetogenic step. Sugars, long chain fatty acids and amino acids from hydrolysis act as substrates, and acidogens or acid formers produce organic acids (acetic, propionic, butyric, and others), alcohols, hydrogen, and carbon dioxide. The end-product of this process varies with the types of bacteria as well as with the environmental conditions (Mosey 1983). Bacteria responsible for acid production include facultative anaerobic bacteria, strict anaerobic bacteria, or both (*e.g.*, *Bacteroides, Bifidobacterium, Clostridium, Lactobacillus,* and *Streptococcus*). Organisms that produce fermentation products, such as propionate, butyrate, lactate and ethanol, generally exhibit obligate proton-reducing metabolism, *i.e.*, they produce hydrogen as a fermentation product.

The accumulation of lactate, ethanol, propionate, butyrate and higher volatile fatty acids is responsible for the bacteria to increase hydrogen concentration in the medium (Schink 1997). Acidogenesis can occur without an additional electron donor or acceptor (Gujer and Zehnder 1983). Eqs. 24.2 and 24.3 show the production of acetic and butyric acid from glucose by acidogenesis with H^+ ions acting as an electron acceptor. Theoretically, a maximum of 4 moles of hydrogen is obtained from acetic acid and 2 moles of hydrogen from butyric acid. The production of volatile fatty acid (VFA) and the lack of H_2 scavengers are responsible for the accumulation of dissolved H_2 in the system. Besides, as shown in the literature, microorganisms are able to play an active role in controlling the redox potential (Mosey 1983).

$$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 4H_2 + 2CO_2 \qquad \text{(Eq. 24.2)}$$

$$C_6H_{12}O_6 \rightarrow CH_3CH_2CH_2COOH + 2H_2 + 2CO_2 \qquad \text{(Eq. 24.3)}$$

Acidogenesis of amino acids usually occurs *via* Stickland oxidation where different amino acids are fermented pair-wise, with one amino acid in a pair acting as an electron donor, while the other acts as an electron acceptor (Gottschalk 1986). There is typically a 10% shortfall of electron acceptor and therefore ~10% of amino acid acidogenesis occurs by uncoupled oxidation with H^+ ions or CO_2 acting as an electron acceptor (Nagase and Matsuo 1982). Thus, the products of amino acid digestion will be VFA, CO_2, NH_3, H_2 and reduced sulphur, respectively, depending on which of the 20 amino acids have been degraded (Batstone et al. 2002).

24.2.1.3 Acetogenesis

In the acetogenic process, acetogens will degrade organic acids such as propionic, butyric and valeric acids from the acidogenesis step into acetate and hydrogen, respectively. Acetogenic microorganisms can also tolerate a wide range of environmental conditions (Novaes 1986; Parkin and Owen 1986). However, in most of the cases, each group of acetogens can ferment only one type of VFA. This

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is often considered as a separate step to acidogenesis since no large pH effect is associated with the conversion of higher acids to acetic acid, and there is no internal electron acceptor (Batstone et al. 2002). Eq. 24.4 shows the acetogenesis of butyric acid using H^+ ions as an electron acceptor to produce acetic acid and H_2.

$$CH_3CH_2CH_2COOH + 2H_2O \rightarrow 2CH_3COOH + 2H_2 \qquad \text{(Eq. 24.4)}$$

24.2.2 Biochemistry of Hydrogen Production

Pyruvate plays an important role in the fermentation pathway leading to hydrogen from the glycolytic breakdown of carbohydrate rich materials (Hallenbeck 2005). Based on the metabolic types, the process is mediated by two different enzymes namely pyruvate:formate lyase in enteric type mixed acid fermentation and pyruvate:ferredoxin oxidoreductase in clostridial type fermentation. Though their metabolic types are different, the acetyl-CoA produced could be converted to acetate with adenosine triphosphate (ATP) synthesis from acetyl phosphatase intermediate. Strict anaerobes like *Clostridial* species convert pyruvate to acetyl-CoA and CO_2 by the reduction of ferredoxin. The reduced ferredoxin transfers electron to a Fe-Fe hydrogenase in order to produce hydrogen (2 mol H_2/mol glucose). Some microorganisms contain Hnd hydrogenase in addition to heteromeric Fe-Fe hydrogenase that can couple directly with NAD(P)(H), since they contain sub-unit homologues of some complex I proteins (Hashesh et al. 2011).

Since two moles of nicotinamide adenine dinucleotide (NADH) are produced during the glycolysis of glucose, up to a maximum of two additional molecules of hydrogen could be generated by this pathway. Hence, these organisms are capable of producing 4 mol H_2/mol glucose consumed theoretically (Hawkes et al. 2007). Usually many organisms contain genes encoding both pyruvate: formate lyase and pyruvate:ferredoxin oxidoreductase. Pyruvate:formate lyase plays a major role in the fermentation step, while the pyruvate:ferredoxin oxidoreductase acts in the latter pathways. Interestingly, in some cases, these genes play an entirely different role that is not related to hydrogen production. It is, therefore, impossible to predict the fermentation pathways of a particular microorganism from its complement encoding genes. Anew, it appears that hydrogen production depends not only on the active hydrogen producers, but also on the co-metabolism of the whole microbial community involved.

24.2.2.1 Enzymology

Molecular hydrogen is produced by hydrogenases (EC 1.12.99.6, EC 1.12.7.2), which catalyzes the reduction of protons; thereby releasing the reducing equivalents that are formed during the anaerobic degradation of organic substrates. Hydrogenases can also perform the reverse reaction (Eq. 24.5), which allows microorganisms to use H_2 as a source of reductant (Vazquez and Varaldo 2009).

$$H_2 \leftrightarrow 2H^+ + 2e^- \qquad \text{(Eq. 24.5)}$$

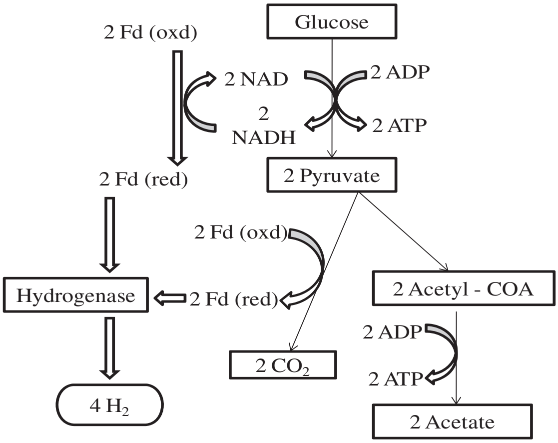

Figure 24.1. Clostridial *type hydrogen fermentation*
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Two main types of hydrogenases can be distinguished based on their metal content, *viz.*, the Fe-only hydrogenases and the [Ni-Fe] hydrogenases (Hallenbeck 2009; Hallenbeck et al. 2012). Fe-only hydrogenases seem to be restricted to strictly anaerobes, whereas the [Ni-Fe] hydrogenases are found wide-spread in anaerobes, facultative anaerobes, and aerobes, respectively. Both types of hydrogenase play a crucial role in the fermentative production of H_2 which is discussed in this section (Figure 24.1).

The two main oxidation steps during anaerobic sugar degradation (either EM- or PP-pathway) are the conversion of glyceraldehyde-3-P to 3-P-glycerate and the conversion of pyruvate to acetyl-CoA, respectively. Recycling of the reduced carriers occurs by different enzymatic steps. Generally, the reduced ferredoxin is used for proton reduction. Hydrogen formation from NADH requires an NADH-dependent hydrogenase. Alternatively, NADH may transfer its electrons first to ferredoxin by an NADH:ferredoxin reductase, and the reduced ferredoxin is subsequently used for proton reduction. Hydrogen can also be produced in (facultative) anaerobes without ferredoxin or separate hydrogenases. For instance, the facultative anaerobic *Enterobacteria* differ in their hydrogen enzymology by the sequential use of a pyruvate formate lyase and a formate hydrogen lyase.

24.3 FACTORS INFLUENCING BIOHYDROGEN PRODUCTION

24.3.1 Substrate

The sustainability of biohydrogen production mainly depends on the type of substrate used, and it has been shown that the physicochemical properties of the

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substrate strongly determine the overall efficiency of the process. For sustainable biohydrogen production, the feedstock has to meet the following criteria:

- Rich in carbohydrates;
- Require less pre-treatment;
- Sustainable sources;
- Low cost; and
- Energy recovery should be actively favourable.

The substrates commonly exploited and commercially used for biohydrogen production can be divided into four main groups, namely, pure substrates (*e.g.*, glucose, cellulose, starch), energy crops (*e.g.*, *Miscanthus*, amaranth, grass, sugar beet), solid waste (*e.g.*, food waste, organic fraction of municipal solid waste), and wastewaters.

24.3.1.1 Pure Substrates

Carbohydrates are the main source of hydrogen. Pure monosaccharides like glucose (Mullai et al. 2013a, b), fructose (Lin et al. 2012a), disaccharides like sucrose, maltose, lactose (Chen and Lin 2003; Zhang et al. 2005; Mu et al. 2006a), and polysaccharides like starch, cellulose, hemicelluloses (Lin et al. 2008; Ren et al. 2009a) have been used. Similarly, monomeric carbohydrates like xylose, cellobiose (Adav et al. 2009; Ngo et al. 2012) have also been used. It appears to be quite obvious that hydrogen conversion capability from different substrates is related to the microbial species and their metabolic profiles as the hydrogen yields from the same cultures obtained under the similar operating conditions are rather inconsistent. On the contrary, it takes a relatively longer fermentation time to degrade starch and cellulose, since they have to be hydrolyzed into mono-saccharides before being used for hydrogen production. Nevertheless, pure carbohydrate sources are expensive raw materials for full-scale hydrogen production, which can only be viable when they based on renewable and low-cost sources.

24.3.1.2 Energy Crops

Energy crops usually comprise of green wastes. Based on their elemental composition, energy crops can be divided into sugar-based crops (*e.g.* sweet sorghum, sugar cane and sugar beet), starch-based crops (*e.g.* corn and wheat), lignocellulose-based crops (*e.g.* switch grass and fodder grass) and wood-based (*e.g.* *Miscanthus* and poplar). Several energy crops that have been used in different studies include lignocellulosic materials (Kumar and Das 2001; Ren et al. 2009b), sweet potato starch residues (Yokoi et al. 2001), *Miscanthus* (Vrije et al. 2002), wheat straw (Fan et al. 2006), grass silage (Pakarinen et al. 2008), sweet sorghum (Antonopoulou et al. 2010), poplar leaves (Cui et al. 2010), agricultural wastes (Guo et al. 2010), corn wastes (Wang et al. 2010), and beet sugar (Zhu et al. 2013). Green wastes are complex polymers consisting of lignin, cellulose and hemicellulose. Cellulose and hemicellulose are readily converted to biohydrogen whereas lignin is not.

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Delignification is the critical step in biohydrogen production. Several factors have shown to limit the use of green wastes: process viability, economics, continuously rising food prices, suspecting real sustainability, optimizing sugar recovery during pretreatment, process costs, and environmental impacts.

24.3.1.3 Solid Wastes

The use of solid wastes for biohydrogen production could be considered as a feasible option from an environmental and economic viewpoint. Complex solid wastes include wastes from kitchens, food processing, mixed wastes, and municipal wastes, amongst others (Ntaikou et al. 2010). Several studies have been performed to investigate the feasibility of hydrogen recovery from the processing byproducts, including bean curd and noodle manufacturing wastes (Mizuno et al. 2000), rice and wheat bran (Noike and Mizuno 2000), municipal wastes (Okamoto et al. 2000), starch manufacturing wastes (Yokoi et al. 2002), sewage sludge's (Cai et al. 2004), sugar beet (Hussy et al. 2005), rice slurry (Fang et al. 2006), and market wastes (Jaitalee et al. 2010). Though these wastes are rich in carbohydrates, they have enormously high contents of proteins and fats. This leads to lower hydrogen yield since they are heterogeneous in nature.

24.3.1.4 Wastewaters

Among all the above-mentioned substrates, wastewater as a potential substrate has been tested in bioreactors, both under batch (Table 24.1) and continuous (Table 24.2) operations. Batch studies have dealt with biohydrogen production from various types of industrial wastewaters: condensed molasses wastewater (Wu and Lin 2004), confectionery and potato processing wastewater (Van Ginkel et al. 2005), cattle wastewater (Tang et al. 2008), palm oil effluent (Chong et al. 2009), probiotic wastewater (Sivaramakrishna et al. 2009), vinasse wastewater (Fernandes et al. 2010), brewery wastewater (Shi et al. 2010a), sulfate and ferrous-rich wastewater (Hwang et al. 2011), cassava wastewater (Leano and Babel 2012), and distillery wastewater (Wicher et al. 2013). It was reported in these studies that higher substrate concentrations could increase biohydrogen production efficiency, but at higher concentrations, substrate or product inhibitions would occur. In addition, there is no optimal substrate concentration for the fermentation of various substrates to produce biohydrogen (Lin et al. 2012b). In some studies, higher hydrogen production rates were obtained at lower substrate concentrations.

Continuous hydrogen production is usually envisaged as organic loading rate (OLR) dependent which could be controlled either by increasing the substrate concentration or reducing the hydraulic retention time (HRT) (Table 24.2).

For biohydrogen production, different wastewater streams have been tested in the literature: rice winery wastewater (Yu et al. 2002), sugar industry wastewater (Hussy et al. 2005), olive pulp wastewater (Koutrouli et al. 2006), citric acid wastewater (Yang et al. 2006), chemical wastewater (Venkatamohan et al. 2007), dairy wastewater (Venkatamohan et al. 2008a), distillery wastewater

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Table 24.1. Comparison of biohydrogen production from batch reactors using wastewater as the substrate

Wastewaters	*Seed sludge*	*Substrate conc. (g COD/L)*	*pH*	*Temp. (°C)*	*Hydrogen yield (mol H_2/mol hexose)*
Condensed molasses wastewater[a]	Anaerobic sewage sludge	10–160	4.0–8.0	35	1.5
Confectionery processing wastewater[b]	Soil	6.5	6.1	23	6.94 mmol/g COD
Potato processing wastewater[b]	Soil	20	6.1	23	5.71 mmol/g COD
Cattle wastewater[c]	Sewage sludge	1.324	4.5–7.5	30–55	12.41 mmol/g COD
Distillery effluent wastewater[d]	*C. freundii* 01, *E. aerogens* and *R. palustric* P2	10	5.2–7.0	26–39	2.76
Palm oil effluent wastewater[e]	*C. butyricum*	100	5.0-8.5	3.–55	1.30 mmol/g COD
Condensed molasses wastewater[f]	*C. sporosphaeroides* F 52 and *C. pasterinum* F40	10–160	7.0	35	1.78
Probiotic wastewater[g]	Anaerobic digested sludge	2–8	45–7.0	37	1.8
Vinasse wastewater[h]	Anaerobic digested sludge	0.25	5.5	25	24.97
Brewery wastewater[i]	Anaerobic sewage sludge	2–12	4–8	25–45	6.11 mmol/g COD
Sulfate and ferrous wastewater[j]	Anaerobic digested sludge	15	5.5–6.2	35	1.9
Cassava wastewater[k]	Anaerobic sludge	50 mL	—	37	5.02 mol H_2/g COD
Distillery wastewater[l]	Anaerobic digested sludge	40% *v*/*v*	5.5	35	—

Note: Conc. = Concentration; Temp. = Temperature

Major references: [a]Wu and Lin (2004), [b]Van Ginkel et al. (2005), [c]Tang et al. (2008), [d]Vatsala et al. (2008), [e]Chong et al. (2009), [f]Hsiao et al. (2009), [g]Sivaramakrishna et al. (2009), [h]Fernandes et al. (2010), [i]Shi et al. (2010a), [j]Hwang et al. (2011), [k]Leano and Babel (2012), and [l]Wicher et al. (2013)

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Table 24.2. Comparison of biohydrogen production from continuous reactors using wastewater as the substrate

Wastewaters	*Reactor*	*Substrate Conc. (g COD/L)*	*pH/Temp (°C)*	*HRT (d)*	*HPR (L/L/d)*
Sugar wastewater[a]	CSTR	31.85	6.8/60	0.5–7	4.85
Rice winery wastewater[b]	Upflow reactor	14–36	5.5/55	2–24	3.81
Sugar wastewater[c]	CSTR	10	5.2/32	14.2	—
Olive pulp wastewater[d]	CSTR	17.8–19.6	4.9/35	7.5–30	0.48
Citric acid wastewater[e]	UASB	5.0–19.2	7/35–38	8–48	0.72
Chemical wastewater[f]	Biofilm configured reactor	9.84	6.0/28 ± 2	10	6.076 mmol H_2/m^3 min
Cheese whey wastewater[g]	CSTR	5.0–7.0	4.79/35–38	12–24	1
Synthetic wastewater[h]	FBR	10–30	4.0/37	1–4	2.36 L/Lh
Dairy wastewater[i]	ASBR	2.4–4.7	4.56–6.28/28	24	0.03
Distillery wastewater[j]	ASBR	9.6	5.2–7.0/28	24	5.15
Cheese whey wastewater[k]	CSTR	21–47	5.5/55	24–84	1.5
Cheese whey wastewater[l]	CSTR	—	5.2/35	—	2.9 ± 0.2 L/L reactor/d
Coffee processing wastewater[m]	UASB	20	5.5/35	4–8	4.64
Soluble condensed molasses wastewater[n]	CSTR	40–320	5.5/35	3–24 h	390 mmol H_2/L d
Organic wastewater[o]	AFBR	10 g glucose	5.5/35	2–0.25	6.8
Soft drink wastewater[p]	Upflow PBR	1.94	6.4/25 ± 1	0.5	0.4
Tapioca wastewater[q]	ABR	15.92–16.88	9/32.3 ± 1.5	3–24	883.19 mL H_2/L · d
Soy bean protein processing wastewater[r]	ABR	5	7/35 ± 1	16	165 L H_2/kg VSS · d
Beet sugar factory wastewater[s]	CSTR	12–18	4.1–4.5/35	6–10	0.1 L/gVSS · d

Note: Conc.-Concentration; Temp.-Temperature; HRT-hydraulic retention time; HPR-hydrogen production rate; COD-chemical oxygen demand; CSTR-continuous stirred tank reactor; UASB-upflow anaerobic sludge blanket; ASBR-anaerobic sequencing batch reactor; AFBR-anaerobic fluidized bed reactor; FBR-fluidized bed reactor; PBR-packed bed reactor; ABR-anaerobic baffled reactor

Major references: [a]Ueno et al. (1996), [b]Yu et al. (2002), [c]Hussy et al. (2005), [d]Koutrouli et al. (2006), [e]Yang et al. (2006), [f]Venkatamohan et al. (2007), [g]Yang et al. (2007), [h]Zhang et al. (2007), [i]Venkatamohan et al. (2008a), [j]Venkatamohan et al. (2008b), [k]Azbar et al. (2009), [l]Venetsaneas et al. (2009), [m]Jung et al. (2010), [n]Lay et al. (2010), [o]Show et al. (2010), [p]Peixoto et al. (2011), [q]Thanwised et al. (2012), [r]Zhu et al. (2012), and [s]Zhu et al. (2013)

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(Venkatamohan et al. 2008b), cheese whey wastewater (Azbar et al. 2009), coffee drink manufacturing wastewater (Jung et al. 2010), organic wastewater (Show et al. 2010), soft drink wastewater (Peixoto et al. 2011), tapioca wastewater (Thanwised et al. 2012), and soy bean protein processing wastewater (Zhu et al. 2012).

24.3.2 Inoculum

24.3.2.1 Pure Cultures

Clostridium genus is a gram-positive bacterium, fast growing and capable of forming spores and easy to handle in industrial application. *Clostridium* species are typically acid and hydrogen producers which ferment carbohydrate to acetate, butyrate, hydrogen, carbon dioxide and organic solvent. *Clostridium* species, between a pH range of 5.0 and 6.5, produce hydrogen gas during the exponential growth phase and after reaching stationary phase, their metabolism shifts from hydrogen/acid production to solvent production. *Clostridium thermocellum* is a thermophilic anaerobic bacterium that has the capability of producing hydrogen from lactose with acetate, ethanol and lactate in the liquid-phase. Facultative anaerobes produce ATP by aerobic respiration if oxygen is present and are capable of switching to anaerobic fermentation. *Enterobacter* species is the most common gram-negative and facultative anaerobe with the ability to produce hydrogen. Enteric bacteria such as *Escherichia coli* and *Enterobacter aerogenes* are also interesting test species for biohydrogen fermentation. Among the reported *Enterobacter cloacae* IIT-BT 08, *Citrobacter freundii* IIT-BT L139 and *Bacillus coagulans* IIT-BT, as stand-alone microorganisms, *Enterobacter cloacae* gave maximum biohydrogen yield (276 mL H_2/g COD reduced) than *Citrobacter freundii* IIT-BT L139 and *Bacillus coagulans* IIT-BT. Pure cultures such as *Citrobacter intermedius*, *Caldicellulosiruptor* species, *Clostridium saccharoperbutylacetonicum* N1-4(ATCC13564), *Clostridium acetobutylicum*, *Clostridium butyricum* CGS2, *Clostridium beijerinckii*, *Clostridium pasteurianum*, *Clostridium thermocellum*, *Clostridium fruendii*, *Clostridium sporoshaeroides*, *Clostridium acetobutyricum JM, Enterobacter aerogenes, Escherichia coli, and Bacillus coagulans* are some representative examples of spore forming hydrogen producers (Vatsala et al. 2008; Chong et al. 2009; Hsiao et al. 2009).

24.3.2.2 Mixed Cultures

Mixed cultures are obtained from natural sources, and they are able to operate in non-sterile feedstocks. Mixed microbial cultures are often considered to be more cost-effective and promising to achieve large-scale biohydrogen installations. Applying the concept of mixed cultures is one of the techniques for improving hydrogen production because complex microbial communities are likely to contain the required hydrolytic activities and are potentially more robust to changes in operational conditions. Enriched mixed cultures predominantly include *Clostridia* species. Heat-treated sludge is also commonly used as it avoids the presence of organisms utilizing hydrogen, in specific methanogens. Microflora

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from various sources has been used as inoculums for hydrogen production. However, the selection of microflora might be difficult due to the co-existence of hydrogen consuming bacteria. Removal of hydrogen consuming bacteria can be achieved by heat treatment or acid treatment method as most of the hydrogen producing bacteria have the tendency to produce spores under harsh operating conditions. Anaerobic granular sludge can also be used for hydrogen production processes. Various mixed cultures used in biohydrogen production for both batch and continuous processes are mixed anaerobic cultures (Wang and Wan 2008a; Prakasham et al. 2009), anaerobic sludge (Hao et al. 2006), soil (Niessen et al. 2006), and mangrove sediments (Mullai et al. 2013c).

24.3.3 Nutrients

Biohydrogen production requires some of the basic, yet essential nutrients for bacterial metabolism during fermentation. These include the common elements of carbon, nitrogen, phosphorus, potassium, sodium, calcium and magnesium, plus over a dozen of trace elements such as iron, sulfur, chlorine, manganese, zinc, nickel, molybdenum, copper, iodine, selenium and cobalt, among others. Carbon is the main constituent of cellular material, and there are different carbon sources: carbohydrates such as hexoses, pentoses and organic-rich wastewater (Mullai et al. 2013c). Nitrogen is essential for protein synthesis and primarily required in the mineral medium. C/N ratio plays a crucial role in biohydrogen production. Some optimal C/N ratio are 50 (Tao et al. 2007), 22–25 (Bouallagui et al. 2009). Iron is considered as an important element to form hydrogenase or other enzymes required for biohydrogen production (Wang and Wan 2008a). As reported in the literature, the optimum concentration of Fe^{2+} for maximum biohydrogen yield were 4000 mg $FeCl_2$/L (Lee et al. 2001), 1600 mg $FeSO_4$/L (Zhang et al. 2005), 150 mg/L $FeSO_4$ (Yang and Shen 2006), 25 mg/L $FeSO_4 \cdot 7H_2O$ (Alshiyab et al. 2008), 350 mg/L (Wang and Wan 2008a), and 100 mg/L $FeSO_4 \cdot 7H_2O$ (Mullai et al. 2013c). Nickel is another trace metal which is also important, equivalent to iron (Fe), as these two metals combine together to form the hydrogenase enzyme complex. [Ni-Fe] hydrogenase complex exists in hydrogen producing bacteria, where as Ni^{2+} affects the activity of hydrogenases and thus an appropriate concentration of Ni^{2+} should be maintained during the process (Wang and Wan 2008b). Wang and Wan (2008b) have reported a maximum biohydrogen production of 288.6 mL/L at Ni^{2+} concentration of 100 mg/L. Optimum concentration of other nutrients like sodium of 1000 to 2000 mg/L (Xialong et al. 2006), and magnesium of 177.3 mg/L has also been reported (Guo et al. 2009).

24.3.4 Hydrogen Ion Concentration (pH)

Hydrogen ion concentration (pH) is one of the important parameter that has significant effect on hydrogen production. The medium pH influences the hydrogen production rate, hydrogen yield, and types of organic acid produced, due to its effect on the hydrogenase activity and on the metabolic pathways. It has

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been confirmed that, within an appropriate range, increasing pH could increase the yield of hydrogen production, but pH at much higher levels could also decrease hydrogen yields. Many studies have reported that pH in the range of 5.5–6.0 as the best operational pH for biohydrogen production (Yasin et al. 2011; Infantes et al. 2012). At pH 5.5, however, a maximum hydrogen yield of 2.1 ± 0.1 mol H_2/mol glucose using mixed culture was observed by Fang and Liu (2002), while the hydrogen yield reported by Nicolau et al. (2008) was 0.37 mol H_2/mol carbohydrate. Using *Clostridium butyricum* CWBI1009, the maximum hydrogen yield of 1.7 mol H_2/mol glucose, at pH 5.0, from glucose and 2.0 mol H_2/mol hexose from starch, at pH 5.6, was reported by Lee et al. (2008). Antonopoulou et al. (2010) obtained a maximum hydrogen yield of 0.93 mol H_2/mol glucose at pH 5.3 using sweet sorghum as the substrate. Under thermophilic conditions (55 °C), Yasin et al. (2011) observed a maximum hydrogen yield of 79 m mol H_2/L media/d at pH 5.5 using food waste, whereas it was 0.57 m mol H_2/g COD at pH 7.0 using kitchen waste as the substrate (Lee et al. 2008). At mesophilic temperatures and at pH 6.5, Ferchichi et al. (2005) and Tang et al. (2008) observed 28.3 mL H_2/h using cheese whey as the substrate, and 368 mL H_2/h using cattle waste as the substrate, respectively. The difference in the hydrogen production and yields in these studies might be due to the difference in inoculum, substrate and pH range. However, briefly stating, hydrogen production was not reported in the pH range of 4.0–5.0, because when the pH of the fermentation medium was too low, either metabolic activity of the hydrogen producing bacterial population would be inhibited or there would be a switch in the metabolic pathway resulting in the termination of biohydrogen generation.

24.3.5 Volatile Fatty Acids

Anaerobic fermentation involves the acidogenesis phase, during which various end-products such as volatile fatty acids (VFAs) and hydrogen would be produced depending on the microbial strain used and the environmental conditions (Vazquez et al. 2008; Gadhamshetty et al. 2009). Hydrogen and VFA can be produced at high rates during the exponential growth phase and decrease during the stationary phase due to alcohol production. Accumulation of VFA could cause hydrogen producing bacteria to switch over to solvent production and cell death, resulting in decreased hydrogen production (Hawkes et al. 2007). All VFAs are first degraded to HAc (acetate) and their conversion rates also vary according to the order: HEt (ethanol) > HBu (butyric acid) > HPr (propionic acid). Such hydrogen associated VFA production has been reported in several biohydrogen fermentation studies (Belokopytov et al. 2009; Cubillos et al. 2010). On the other hand, increase in substrate concentration could also lead to increase in the VFA production rates, which in turn has shown to decrease hydrogen production (Prakasham et al. 2009; Cubillos et al. 2010). The increase of VFA concentration indicates that the process is overloaded. Nevertheless, above the optimum level, the reduction of hydrogen and VFA production could be attributed to either the formation of a catabolic byproduct of the substrate used or to intracellular VFA accumulation that inhibits the hydrogenase enzyme (Lin and Lay 2004). VFA

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production and their concentrations can be significantly affected due to an increase in the surface area of the sludge and decrease in biomass concentration in the reactor (Halalsheh et al. 2011). Anew, it has been reported that, acidic pH (pH 5.0 and 4.5) does not necessarily always favor the production of VFA or other soluble metabolites.

24.3.6 Surfactants

Recent studies aimed at improving biohydrogen production have shown that reverse micelle (surfactant and organic solvents) could be employed. Reverse micelles are thermodynamically stable and micro-meter in size, wherein, amphibhilic surfactants are used to entrap a hydrophilic biological catalyst, and each micelle acts as a micro-reactor for the microorganisms. Entrapment of microorganisms within the micelle protects them from denaturing. Within the reverse micelle, the stability and kinetics of the enzyme increases. Until now, only a few researchers have focused on enhancing hydrogen production using reverse or micro micelles (Zhi et al. 2008, 2010). The studies revealed that hydrogen production depend upon the water content and the pH of reverse micelles. Pandey and Pandey (2008) studied the efficiency of hydrogen production by heterotrophic bacteria (*Citrobacter* Y-19) and photosynthetic bacteria (*Rhodobacter sphaeroides* 2.4.1) together with AOT iso-octane reverse micelle and a specific rate of hydrogen production of 69 mmol H_2/mg protein h was achieved. Zhi et al. (2008) obtained 3.51 mol H_2/mol glucose, at pH 7.5, using AOT isooctane reverse micelles.

24.3.7 Temperature

Temperature is an important environmental parameter affecting biohydrogen production in terms of substrate degradation rate, and hydrogen producing bacterial counts (Wang and Wan 2009a). Mesophilic temperatures (30–40°C) are ideal and stable for the effective functioning of the hydrogen production process (Wang and Wan 2009a). According to Khalid et al. (2011), lower temperatures decreases microbial growth, substrate utilization rates and hydrogen production, leading to the exhaustion of cell energy, leakage of intracellular substances, and in some cases complete cell lysis. Thermophilic temperatures (45–65°C) lowers biogas yield due to the production of volatile gases like ammonium (Wang and Wan 2009a). Some advantages of thermophilic temperatures can be stated as follows: faster degradation of organic wastes, higher biomass growth and high gas production potential and less effluent viscosity (Khalid et al. 2011). Mu et al. (2006a) envisaged that, when the temperature increased from 33 to 40°C, the substrate degradation increased from 97.8 to 98.9% and biohydrogen production from 3200 to 4280 mL.

24.3.8 Nanoparticles

The use of nanomaterials is widespread as they have unique physical and chemical properties and have significant implications in the field of medical science, optics,

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magnetics, mechanics, catalysis and bioenergy production. Nanoparticles, especially in the range 1 to 10 nm, would display electronic structures, reflecting the electronic band structure of a nanoparticle. The application of gold nanoparticles (Zhang and Shen 2007), hematite iron nanoparticles (Zhao et al. 2011) and nickel nanoparticles (Mullai et al. 2013a) have shown to enhance biohydrogen yield. Higher concentrations of metal nanoparticles cause toxicity and produces reactive oxygen species which decrease the growth of microorganism (Buzea et al. 2007). Ferrous and nickel nanoparticles have also shown to affect the hydrogen production, mediated through hydrogenases enzymes, as these metals combine to form enzyme complexes (Kothari et al. 2012).

24.4 BIOREACTORS

Bioreactors such as anaerobic batch reactor (ABR), anaerobic continuous stirred tank reactor (CSTR), anaerobic fluidized bed reactor (AFBR), anaerobic packed bed reactor (APBR), upflow anaerobic sludge blanket (UASB) reactor, hybrid upflow anaerobic sludge blanket (HUASB) reactor have either been tested in the lab-scale or used at the industrial scale for the digestion of organic wastes for biohydrogen production (Show et al. 2008).

24.4.1 Anaerobic Batch Reactor

According to its operational characteristics, an ideal batch reactor holds the reactant mixture in a process vessel, maintains the mixture under ideal conditions for reaction to occur and selective permeation to take place, and after a desired amount of time, expels the desired byproducts. Different wastewaters studied in batch reactors for biohydrogen production are confectionery and potato processing wastewater (Van Ginkel et al. 2005), cattle wastewater (Tang et al. 2008), palm oil effluent (Chong et al. 2009), condensed molasses wastewater (Hsiao et al. 2009), probiotic wastewater (Sivaramakrishna et al. 2009), vinasse wastewater (Fernandes et al. 2010), brewery wastewater (Shi et al. 2010a), sulfate and ferrous wastewater (Hwang et al. 2011), cassava wastewater (Leano and Babel 2012), distillery wastewater (Wicher et al. 2013). The most commonly studied operating parameters in batch reactors are pH (Hwang et al. 2011), temperature (Mu et al. 2006a), addition of nanoparticles (Mullai et al. 2013a) and surfactants (Zhi et al. 2010).

24.4.2 Anaerobic Continuous Stirred Tank Reactor (Anaerobic CSTR)

Anaerobic CSTR is a typical representation of suspended cell system that provides excellent mass transfer among the different reactant species. It is widely applied in biohydrogen production because it offers the following advantages: complete mixing of biomass, easy process control and rapid start-up of the reactor. The hydraulic retention time (HRT) influences the

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performance of this reactor type. At shorter HRTs, wash out of microorganism takes place; eventually leading to reduced reactor performance and operational instability (Zhu et al. 2013).

24.4.3 Anaerobic Fluidized Bed Reactor (AFBR)

AFBR was initially developed in the 1970's (Jeris et al. 1974). In AFBR, the feed is passed upward through a continuously fluidized bed comprising spherical activated carbon, silicone-immobilized cell, expanded clay or celite that supports microbial growth. The purpose of using immobilization techniques such as cell entrapment and cell attachment in fluidized bed reactors is to improve the cell retention time (Zhang et al. 2007). However, during its operation, adequate care should be taken for reactors that are operated under turbulent flow conditions (Barros et al. 2010). AFBR offers the following advantages: high biomass concentrations, high organic loadings, high mass transfer characteristics, ability to handle shock loads due to continuous mixing and dilution with the recycle stream, and minimal space requirements.

24.4.4 Anaerobic Packed Bed Reactor (APBR)

APBR can be operated in upflow or down flow mode. Generally, the upflow reactors are called filters and the down flow reactors are called fixed film reactors. The packed bed, while retaining biological solids, also acts as a medium for separating the solids and gas produced during the digestion process. The major disadvantages of the APBR are the problems associated with flow distribution, heating, and plugging. The most commonly used packing materials are low-density polyethylene balls, ceramic rings, pumice stone and in some cases immobilized biomass. Lima and Zaiat (2012) reported a maximum hydrogen yield of 4.22 mol H_2/mol sucrose at 2h HRT; while, Peixoto et al. (2011) reported a maximum yield of 3.5 mol H_2/mol sucrose at 0.5 h HRT. In some APBRs, lower hydrogen production was attributed to the accumulation of hydrogen in the aqueous phase, leading to product inhibition (van Ginkel and Logan 2005). This problem could easily be overcome by maintaining optimal concentrations of organic matter in the influent and by adjusting the HRT. Concerning energy yields, APBRs have higher energy yield than fluidized bed reactor (Wu et al. 2007) and a six-fold better energy yield than a continuous stirred tank reactor operated in series (Keskin et al. 2011).

24.4.5 Upflow Anaerobic Sludge Blanket (UASB) Reactor

In UASB reactor, anaerobic bacteria form dense granules that settle and remain as a bed at the bottom of the reactor. When the wastewater flows upward through a blanket of biologically formed granules, they consume the waste and produce hydrogen and traces of carbon dioxide, and other trace gases. The advantages of UASB reactor can be summarized as follows: (i) production of valuable biogas which can be collected, upgraded and used commercially; (ii) less bio-solid generation; (iii) low energy requirements; (iv) requires the addition of only minimal (trace) nutrients; (v) UASBs can be shut down for extended periods

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without serious deterioration in reactor performance; and (vi) ability to withstand shock loads (Karim and Gupta 2006; Sabry 2008). Despite their overwhelming advantages, UASBs also pose some operational limitations, that includes: (i) inability to achieve surface water discharge quality limits without a post-treatment step; (ii) the formation of reduced sulphur compounds that can lead to corrosion, and odour related problems; (iii) long start-up periods (Escudie et al. 2011); and (iv) need for an adequate temperature control system in cold countries, in order to maintain the optimal mesophilic temperatures (20 to 35b°C) for microbial activity. In the UASB reactor, the maximum hydrogen production rate and hydrogen yield of 6.8 L H_2/L reactor/h at 0.25 h HRT with organic wastewater (Show et al. 2010) and 3.6 mol H_2/mol sucrose at 4 h HRT and 20 g COD/L with synthetic wastewater (Chang and Lin 2006), respectively, was reported. Anew, the hydrogen production rate increased with increase in the substrate concentration or loading, but decreased with increase in the HRT (Poontaweegeratigarn et al. 2012).

24.4.6 Hybrid Upflow Anaerobic Sludge Blanket (HUASB) Reactor

The HUASB reactor was aimed at improving the "gas-liquid-solid" separation within the reactor. In this hybrid reactor configuration, the upper 20–30% of the reactor is filled with either floating or stationary materials, such as polyurethane (PU) foam, polymer balls or random-packed plastic rings, to retain some of the escaping fine biomass. Thus, the HUASB reactor is actually a combination of UASB unit at the lower part and an anaerobic filter at the top portion. The top anaerobic filter section retains the suspended sludge within the reactor. Another advantage of this kind of design is its ability; even without granular sludge it has the ability to hold large amounts of biomass inside the reactor and the packed zone acts as a gas-liquid-solid separator. Although HUASB reactor design is expected to work efficiently without the granular sludge, it is desirable to cultivate the granular biomass. The HUASB reactor is also referred in the literature as sludge blanket filter (SBF), upflow blanket filter (UBF), anaerobic hybrid reactor (AHR), sludge blanket anaerobic filter (SBAF) or simply a hybrid reactor (Tilche and Vieira 1991). In terms of COD removal efficiencies, HUASB have shown to achieve 80-100% removal, and hydrogen production of 1.72–2.25 mol H_2/mol glucose has been reported for synthetic, and confectionery wastewaters (Sudha and Mullai 2010; Mullai et al. 2013b; Yogeswari et al. 2013; Yogeswari 2013).

24.5 KINETICS OF BIOHYDROGEN PRODUCTION

Kinetic models are used to describe the progress of a batch fermentative hydrogen production process to study the relationship among the substrate degradation rate, the hydrogen producing bacterial growth rate and the product formation rate. Cell growth kinetics in a batch system consists of following growth phases: (i) lag

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phase, (ii) logarithmic phase, (iii) stationary phase, and (iv) death phase. During the lag phase, no cell growth occurs and it is the phase wherein the cells adapt to new environment. The cell concentration (x) increases (proportional) with operational time (t) and is given Eq. 24.6.

$$\frac{dx}{dt} \alpha x$$

$$\frac{dx}{dt} = \mu x \tag{Eq. 24.6}$$

$$\mu = \frac{1}{x} \cdot \frac{dx}{dt} \tag{Eq. 24.7}$$

where, μ is the specific growth rate (1/h); x is the biomass concentration (g/L).

24.5.1 Monod Model

The Monod model is a simple and empirical model, which relates the effect of substrate concentration on specific growth rate. It can be emphasized that, the Monod model is applied when the substrate is present in limited amount. This condition is stated as "nutrient controlled growth". The effect of the limiting factor on specific growth rate is given by Monod equation.

$$\mu = \frac{\mu_{\max} S}{K_s + S} \tag{Eq. 24.8}$$

$$\frac{1}{x}\frac{dx}{dt} = \frac{\mu_{\max} S}{K_s + S}$$

$$\frac{dx}{dt} = \frac{\mu_{\max} S}{K_s + S} x \tag{Eq. 24.9}$$

where, S is the substrate concentration (g/L); μ_{max} is the maximum specific growth rate; K_s is saturation constant (g/L of substrate).

Linearizing Eq. 24.8;

$$\frac{1}{\mu} = \frac{K_S}{\mu_{\max}} \cdot \frac{1}{S} + \frac{1}{\mu_{\max}} \tag{Eq. 24.10}$$

The kinetic parameters $\mu_{\max}$ and K_s can be calculated using Eq. 24.10.

24.5.2 Logistic Model

The growth rate characteristics of stationary phase and exponential phase are described by the logistic curve. It relates the change of specific growth rate with

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respect to change in cell concentration (x). The yield of cell concentration depends on substrate utilization and is expressed as yield co-efficient ($Y_{x/S}$):

$$Y_{x/S} = -\frac{\Delta x}{\Delta S}$$

$$Y_{x/S} = -\frac{x - x_0}{S - S_0} \quad \text{(Eq. 24.11)}$$

where, x_o is the initial cell concentration (g/L), and S_o is initial substrate concentration (g/L).

Rearranging Eq. 24.11 gives:

$$S = \frac{x_0 + Y_{x/S}S_0 - x}{Y_{x/S}} \quad \text{(Eq. 24.12)}$$

The maximum cell concentration (x_{max}(g/L)) is equal to sum of the initial cell concentration and the coefficient yield multiplied by substrate concentration in the inoculum, assuming the conversion of substrate into biomass.

$$x_{\max} = x_0 + Y_{x/S}S_0$$

Substituting $x_0 = x_{\max} - Y_{x/S}S_O$ in Eq. 24.12, we get:

$$S = \frac{x_{\max}}{Y_{x/S}}\left(1 - \frac{x}{x_{\max}}\right) \quad \text{(Eq. 24.13)}$$

Assuming the change of substrate concentration with respect to time and applying chain rule principle on the right-hand side of the above rate equation gives:

$$\frac{dS}{dt} = \frac{dS}{dx} \cdot \frac{dx}{dt} \quad \text{(Eq. 24.14)}$$

$$\textit{Substituting}\ \frac{dx}{dt} = kY_{x/S}S \quad \textit{and} \quad S = \frac{x_{\max}}{Y_{x/S}}\left(1 - \frac{x}{x_{\max}}\right)$$

$$\frac{dS}{dt} = \frac{dS}{dx} \cdot k \cdot Y_{x/S}\frac{x_{\max}}{Y_{x/S}}\left(1 - \frac{x}{x_{\max}}\right)$$

$$\frac{dx}{dt} = kx_{\max}\left(1 - \frac{x}{x_{\max}}\right) \quad \text{(Eq. 24.15)}$$

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Assuming the inhibition is second order (x^2), at $t = 0$ and $x = x_0$, we get:

$$\frac{dx}{dt} = kx(1 - \beta x) \qquad \text{(Eq. 24.16)}$$

where k is the apparent specific growth rate (h^{-1}), and $\beta = \frac{1}{x_{\max}}$. Eq. 24.16 is called the Riccatti equation and on integration, a logistic curve is obtained. Integrating Eq. 26.16, we get:

$$\int_{x_0}^{x} \frac{dx}{x\,(1 - \beta x)} = k \int_{0}^{t} dt \qquad \text{(Eq. 24.17)}$$

Splitting the terms on the left-hand side using the partial fraction method, we get:

$$\frac{1}{x(1 - \beta x)} = \frac{A}{x} + \frac{B}{1 - \beta x}$$

$$A(1 - \beta x) + Bx = 1$$

$$\begin{gathered} If\ x = 0; \quad A = 1 \\ If\ x = 1/\beta; \quad B = \beta \end{gathered}$$

$$\frac{1}{x(1 - \beta x)} = \frac{1}{x} + \frac{\beta}{1 - \beta x}$$

On integrating and applying the limits, we get:

$$\int_{x_0}^{x} \frac{dx}{x(1 - \beta x)} = k \int_{0}^{t} dt \qquad \text{(Eq. 24.18)}$$

$$\int_{x_0}^{x} \frac{dx}{x} + \int_{x_0}^{x} \frac{dx}{1 - \beta x} = k \int_{0}^{t} dt$$

$$\ln \frac{x}{x_0} - \ln \frac{(1 - \beta x)}{(1 - \beta x_0)} = kt$$

$$\ln \frac{x(1 - \beta x_0)}{x_0(1 - \beta x)} = kt \qquad \text{(Eq. 24.19)}$$

$$e^{kt} = \frac{x(1-\beta x_0)}{x_0(1-\beta x)} \qquad \text{(Eq. 24.20)}$$

Rearranging the above equation, the cell concentration (x) is given by:

$$x = \frac{x_0 e^{kt}}{1-\beta x_0(1-e^{kt})} \qquad \text{(Eq. 24.21)}$$

The kinetic parameters x_{max} and k are calculated from the above equation, where k apparent specific growth. The logistic equation fails to predict the lag phase and the decay phase, while it explains cell growth rate when the population reaches its maximum under limited nutrient condition.

24.5.3 Luedeking-Piret Model

The Luedeking-Piret model is used to describe the relationship between hydrogen producing bacterial growth rate and product formation rate. Significant product formation is observed in late log phase. Luedeking-Piret model involves both growth-associated and non-growth associated terms.

$$r_{fp} = \alpha r_{fx} + \beta x$$

$$\frac{dP}{dt} = Y_{P/x}\frac{dx}{dt} + \beta x \qquad \text{(Eq. 24.22)}$$

$$Y_{P/x} = \frac{(Mass\ of\ products\ formed)(g\ products)}{(Mass\ of\ cells)(g\ dry\ weight\ biomass)}$$

$$\frac{dP}{dt} = \alpha\frac{dx}{dt} + \beta x \qquad \text{(Eq. 24.23)}$$

where, α is the yield co-efficient and is growth associated product; β is the non-growth associated product.

Several research works have reported biohydrogen production using kinetics models (Mu et al. 2006b; Wang and Wan 2009b). The kinetic constants obtained are used to find out the predicted data and can be useful as design parameters for various configurations of bioreactors producing biohydrogen. If the correlation coefficient R^2 between the experimental and predicted data is close to unity, it can be concluded that the kinetic models were able to describe the experimental data satisfactorily, except for deviations.

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24.6 ARTIFICIAL NEURAL NETWORK (ANN) MODELING OF BIOHYDROGEN PRODUCTION

The production of biohydrogen is usually a very complex process that is influenced to a large extent by the composition and activity of the prevailing microbial community. Anew, parameters such as inoculum size, substrate, reactor type, metal ion concentrations, temperature and pH will also affect the quantity of biohydrogen yielded through fermentative bioprocesses. Several lab- and pilot-scale studies have investigated the influence of these process parameters on both productivity (μmol H_2/mg protein h) and biohydrogen yield. One of the best strategies followed in most of these studies is to identify and delineate the effects of these parameter(s) and the interactions amongst different process parameters for a proper experimental design. Experimental design is a process by which certain selected factors are varied in a well-controlled manner, from low to high levels, to get the response of the bioprocess, which then is followed by analysis of the results (Sinha and Pandey 2011). Tools such as factorial design of experiments and response surface methodology (RSM) will be beneficial to understand and optimize the performance of the biohydrogen process; this methodology also helps the user to improve the performance of an already operating system and optimize its state variables in a statistically significant way (Chaganti et al. 2012; Mullai et al. 2013b).

Alternate modeling strategies followed to model and optimize the performance of batch and continuous biohydrogen processes use artificial neural networks (ANNs), which is a mathematical representation of the human brain. ANNs are universal approximates for Boolean and continuous functions and have the inherent capacity to learn 'by example', in which an actual measured set of input variables and the corresponding outputs are presented to determine the rules that govern the relationship between the variables. ANNs are able to depict the interactive effects among different process variables in complicated bioprocesses, and has been successfully applied in multivariate non-linear bioprocess as a useful tool for constructing the desired model (Wang and Wan 2009c). The impetus of employing ANNs to model dynamic biological systems is due to their advantages over other non-linear modeling paradigms (Rene et al. 2011a). As stated earlier, a typical fermentation biohydrogen process can have characteristics including non-linearity, which render conventional mathematical models difficult to predict the performance. Although several mathematical and empirical models have been proposed in the literature, some of them however fail to predict the data of other researchers as they were originally developed and validated with the experimental data from a particular biohydrogen process. Therefore, there exist good prospects to model a biohydrogen production process using ANNs, due to their process complexity, changing microbial characteristics, pH, concentrations, etc. among others. Neural networks are also superior and sometimes more accurate compared to statistical methods such as RSMs. Considering their use in environmental engineering and applied sciences, they have gained an increasing

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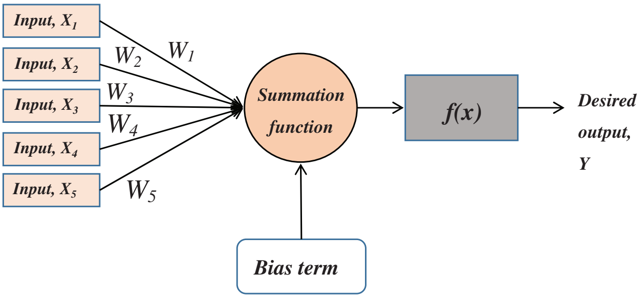

Figure 24.2. Structure of an artificial neuron. X_1 to X_5 correspond to the different inputs, while W_1 to W_5 are the connection weights; $f(x)$ is the activation function, and Y is the output from the neuron

consideration in wastewater treatment and biogas production and modeling (Boger 1992; Çinar et al. 2006; Rene et al. 2006; 2011b; Rene and Saidutta 2008).

24.6.1 Structure of a Typical Artificial Neuron

ANNs consist of densely interconnected processing units called the neurons that utilize parallel computation algorithms (Alalayah et al. 2014). The structure and functioning modes of an artificial neuron in a neural network are shown in Figure 24.2.

It consists of processing elements that receives numerous signals from other neurons through thousands of paths called dendrites. The input signals flow through a gain or weight called synaptic weight, whose function is analogous to that of the synaptic junction in a biological neuron. The connection weights can be positive or negative, corresponding to acceleration or inhibition of the flow of electrical signals in a biological cell. The summing node accumulates all the input weighted signals, adds a bias signal and then passes to the output through the activation function, which is usually non-linear in nature. Among the scientific community, ANNs are also known as connectionism, parallel distributed processing, neuron-computing, natural intelligent systems and machine learning algorithms (Boger 2007; Han et al. 2013).

24.6.2 Types of Neural Networks

The inter-connections between the biological neurons are not well understood, and thus, numerous neural network models have been developed over the past few years. These networks are generally classified as feed-forward and recurrent types. In the feed-forward type network, signals from one neuron to another flows only in the forward direction. The most common type of feed-forward type neural network is the multi-layer perceptron (MLP) that consists of an input layer, a hidden layer and the output layer. The main function of neurons in the hidden layer is to interact between the external input and network output in some useful manner, using a set of governing rules or algorithms in order to extract higher

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statistics. Recurrent type network can be defined as a feed-forward neural network having one or more hidden layers with at least one feedback loop. In general, feedback networks are considered to be powerful and can get extremely complicated depending on the computational task involved. Feedback networks are dynamic; their 'state' is changing continuously until they reach an equilibrium point. They remain at the equilibrium point until the input changes and a new equilibrium needs to be found. Other network models developed include the following: (i) radial basis function (RBF) network, (ii) Kohonen self-organizing network, (iii) learning vector quantization, (iv) fully recurrent network, (v) Hopfield network, (vi) Boltzmann machine, (vii) stochastic neural networks, (viii) modular neural networks, (ix) associative neural network (ASNN), (x) dynamic neural networks, (xi) cascading neural networks, and (xii) neuro-fuzzy networks (Bishop 1995; Haykin 2008).

24.6.3 Multilayer Perceptron

Multi-layer perceptrons (MLPs) belong to the class of supervised feed-forward network wherein the processing elements (PE) are arranged in a multi-layered structure. The structure of MLPs consists of an input layer, one or more hidden layers and an output layer (Figures 24.3 and 24.4). The input from each PE in the previous layer is multiplied by a connection weight (W_i). These connection weights are adjustable and may be linked to the coefficients in statistical models. At each PE, the weighted input signals are summed, and a bias value is added or subtracted. This combined input is then passed through a non-linear transfer

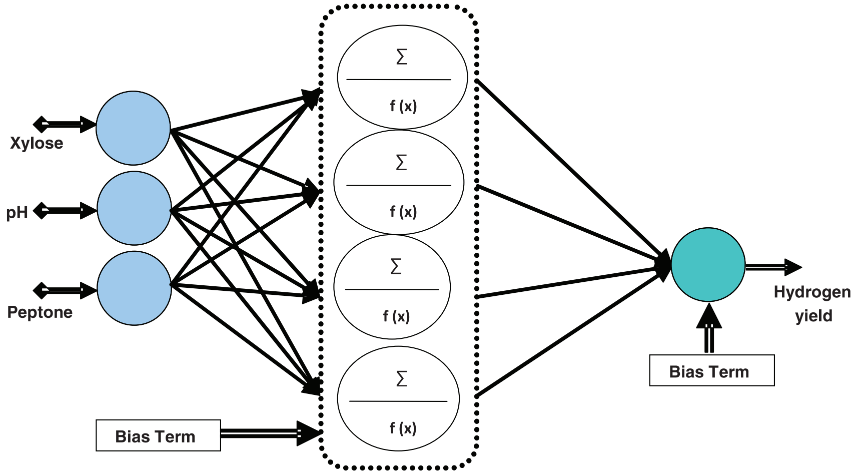

Figure 24.3. Schematic of ANN network architecture with one hidden layer. Xylose concentration, peptone concentration and pH are used as the inlet parameters for predicting biohydrogen yield

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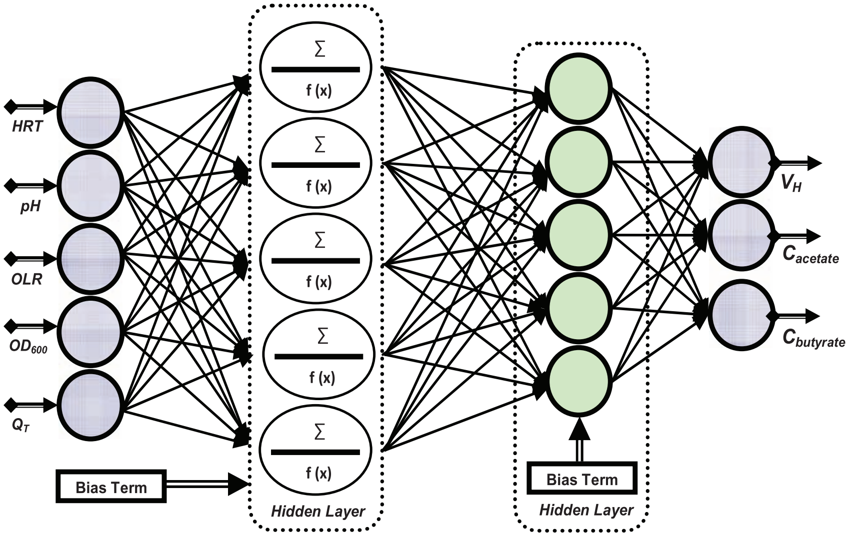

Figure 24.4. Schematic of ANN network architecture with two hidden layers. Hydraulic retention time (HRT), pH, organic loading rate (OLR), optical density (OD_{600}) and flow rate (Q_T) are used as the inlet parameters for predicting the hydrogen production rate (V_H), and acetate ($C_{acetate}$) and butyrate ($C_{butyrate}$) concentrations in the effluent of a packed-bed bioreactor

function to produce the output of the PE. The output of one PE provides the input to the PEs in the next layer.

24.6.4 Activation Function

The most commonly used activation functions are non-linear, continuously varying between two asymptotic values 0 and 1 or −1 and +1. Typical example of an activation function is the sigmoid function which can be defined by Eq. 24.24;

$$f(\mathrm{x}) = \frac{1}{1 + \mathrm{e}^{-\mathrm{x}}} \qquad \text{(Eq. 24.24)}$$

24.6.5 Selecting the Appropriate Network Topology

Figure 24.5 illustrates the step-wise procedure involved in the neural modeling process. The appropriate input and output parameters are first screened and selected. The number of nodes in the input layer is fixed by the number of model inputs, whereas the number of nodes in the output layer is decided by the number of model output parameters. The next task involves in suitable training the network, where the prime objective is to minimize the errors between the predicted and actual outputs. This minimization process can be achieved by the

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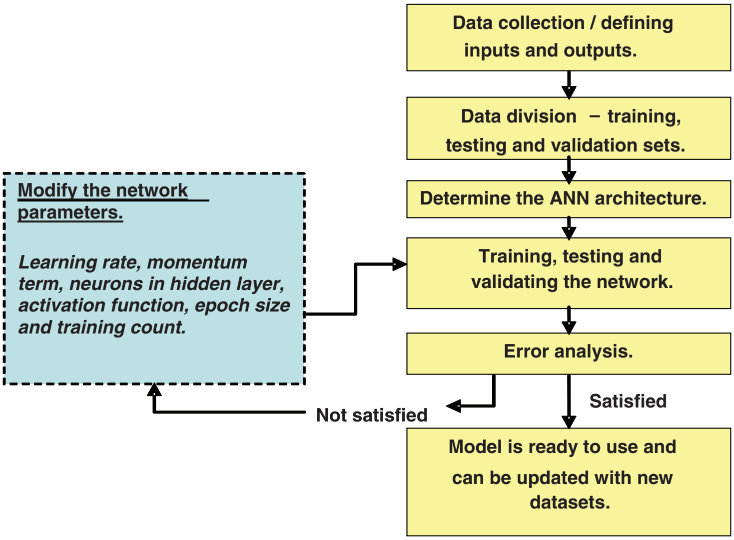

Figure 24.5. Flow chart showing the different steps involved in ANN modeling
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error function with respect to all variables in the neural network (e.g. connection weights, network architecture, learning rate and threshold).

Rumelhart et al. (1986) proposed the back error propagation (BEP) training algorithm in which the error function is minimized with respect to the connection weights only. The back-propagation algorithm uses the gradient descent technique to adjust the weights in which the global error function (E) is minimized by modifying the weights using the following equation:

$$\Delta W_{ji} = -\eta \frac{E}{\partial W_{ji}} \qquad \text{(Eq. 24.25)}$$

where, ΔW_{ji} = weight increment from node i to node j; and η = learning rate, by which the size of the step taken along the error surface is determined.

The weights are then updated by adding the delta weight, Δw_{ji}, to the corresponding previous weight as follows:

$$W_{ji}(\mathrm{n}+1) = W_{ji}(\mathrm{n}) + \Delta W_{ji}(\mathrm{n}+1) \qquad \text{(Eq. 24.26)}$$

where, $W_{ji}(n)$ = the value of a weight from node i to node j at step n (before adjustment); and $W_{ji}(n+1)$ = the value of the weight at step $(n+1)$ (after adjustment).

The weights between the hidden layer and the output layer are adjusted first, followed by the weights between the hidden layer and the input layer. The choice

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of the learning rate is usually determined by trial-and-error. If the learning rate is selected to be small, convergence will be achieved, however, it will be very slow and subject to the local minima in the error surface that is closest to the random starting position. On the other hand, if the learning rate is selected to be large, the weight changes will also be large, causing the error to go up rather than down and thus, convergence might never occur (Maier and Dandy 1998). However, greater learning rates might enable the model to jump out of the local minima. Rumelhart et al. (1986) described a process to solve the above problem without leading to any discrete oscillations during training. This process simply adds a momentum term (μ) to the weight adjustment that is proportional to the amount of the previous weight change. The momentum term may be considered to increase the effective step size in shallow regions of the error surface (Hassoun 1995) and can speed up the training process by several orders of magnitude (Masters 1993). It should be noted that the momentum term must be less than 1 for better convergence. Once an adjustment is carried out, it is saved and used to modify all subsequent weight adjustments. This means that the weight change of the current step should carry some momentum of the weight change from the previous step. The modified adjustment of the delta weight, Δw_{ji}, is as follows;

$$\Delta W_{ji} = -\eta \frac{\partial E}{\partial W_{ji}} + \mu \Delta \mathrm{W}_{\mathrm{ji}} \qquad \text{(Eq. 24.27)}$$

The above process is repeated, which propagates the error term needed for weight adjustment until the network can obtain a set of weights that result in the input/output mapping that has the minimum error. Once the desired learning is achieved, the weights are fixed and the neural network can be deployed and used in practice.

24.6.6 Error Estimation Indices

In order to estimate the predictive accuracy of the developed ANN model, the standard deviation (SD), error and average relative error (ARE) terms can be used. These can be defined using the following equations:

$$SD,\% = \left[\frac{\sum_{i=1}^{N} \frac{(Y_{meas} - Y_{model})}{Y_{meas}}}{N-1}\right]^{0.5} \times 100 \qquad \text{(Eq. 24.28)}$$

$$Error,\% = \frac{(Y_{meas} - Y_{model})}{Y_{meas}} \times 100 \qquad \text{(Eq. 24.29)}$$

$$ARE,\% = \frac{\sum_{i=1}^{N} Error}{N} \times 100 \qquad \text{(Eq. 24.30)}$$

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where, Y_{meas} is the experimental value; Y_{model} is the ANN model fitted value; and N is the sample size or number of data points used.

24.6.7 Types of Back Propagation Algorithms

Selection of the back propagation algorithm is an important component of the modeling task. Some commonly tested back propagation algorithms can be summarized as follows; resilient (R_{prop}), one step secant, Powell-Beale conjugate gradient, BFGS quasi-Newton, Fletcher-Powell conjugate gradient, gradient descent with momentum and adaptive learning rate, Levenberg-Marquardt, scaled conjugate gradient, Polak-Ribiere conjugate gradient, gradient descent with adaptive learning rate, gradient descent with momentum and batch training with weight and bias learning rules.

24.6.8 Examples of Modeling Biohydrogen Production Using Artificial Neural Networks

There are several recent studies that have reported the use of ANN models to predict the biohydrogen yield or the biohydrogen production rates (Table 24.3). The data points used for developing these models were obtained from a series of batch and continuous experiments; and in all instances, ANNs were reported to be very effective in capturing the non-linear relationships between multi-component variables (inputs and outputs) and showed high predictive potential. Studies by Wang and Wan (2009c) reported the ANN model developed using temperature, pH and glucose concentrations as the input parameters to predict the fermentative biohydrogen production by mixed consortium of microorganisms. In another study, Shi et al. (2010b) predicted the steady-state performance of bioreactors (integrated stirred tank reactor and an UASB reactor) for biohydrogen production using sugar refinery wastewater. OLR, HRT and influent bicarbonate alkalinity were used as the model inputs, while the hydrogen concentration, hydrogen production rate, hydrogen yield, effluent total organic carbon concentration, and several aqueous end-products (acetate, butyrate, etc.) were used as the model outputs. Mullai et al. (2013b) predicted the hydrogen production using anaerobic sludge blanket filter using glucose concentration, pH, acidity and biogas production rate as inputs and hydrogen production rate as output with two hidden layers. The main advantages of using ANNs to model bioprocesses, compared to other modeling techniques is the fact that ANNs does not require a prior specification of suitable fitting functions, and ANNs have universal approximation capability. Table 24.3 gives an overview of the recent literatures wherein ANNs were used to model fermentative biohydrogen process. From a practical application viewpoint, the concept of ANN modeling combined with real-time control strategy of biohydrogen production processes has significant implications. Programmable logic controllers (PLCs) and expert systems for process fault diagnosis can also be used to control processes and predict the real-time behavior of the system.

Table 24.3. Application of ANN to model fermentative biohydrogen production process

Input parameters	*Output parameter*	*Network architecture*	*Data points used*	*References*
HRT, substrate concentration, biomass concentration, organic acids, ORP, pH, recycle ratio, alkalinity	Hydrogen production rate	12-20-1	NA	Nikhil et al. (2008)
T, pH, glucose concentration	Hydrogen yield	3-4-1	15	Wang and Wan (2009c)
HRT, pH, OLR, OD_{600}, flow rate	Hydrogen production volume, acetate concentration, butyrate concentration	5-10-6-3	90	Jo et al. (2011)
T, pH, substrate concentration	Hydrogen yield	3-6-4-2-1	15	Alalayah et al. (2014)
Substrate concentration, biomass concentration, pH, temperature, time	Hydrogen profiles	5-6-4-1	313	Nasr et al. (2013)

Note: T-temperature; HRT-hydraulic retention time; ORP-oxygen and reduction potential; OLR-organic loading rate; OD-optical density; NA-Not available

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24.7 SUMMARY

Presently, hydrogen is produced from non-renewable energy sources which can lead to the depletion of fossil fuel-based sources in the near future. Based on the extensive literature review carried out in this chapter, it is articulated that the production of biohydrogen from green energy sources or waste matrices is crucial to meet the rising energy demands. The biohydrogen generation during anaerobic wastewater treatment involves hydrolysis, acidogenesis, acetogenesis, and solventogenesis, of which hydrolysis is often conceived as the rate limiting step. The kinetics describing biomass growth and hydrogen production provide valuable information for bioreactor design and scale-up.

Evaluating the performance and economics of continuous biohydrogen process (bioreactors) will provide useful information for future development of commercially viable bioprocesses for large-scale hydrogen production. Future research on biohydrogen research should focus on emerging fields/research directions such large-scale fermentative hydrogen production, the use of nanoparticles for enhancing hydrogen production and in developing artificial intelligence based control systems to monitor and supervise industrial bioprocesses.

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CHAPTER 25

Anaerobic Membrane Bioreactors for Future Green Bioprocesses

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25.1 INTRODUCTION

With ever-increasing consumption and pollution of our limited water resources, water scarcity has been brought rising levels of public concern on a global scale. However, this worsening situation could be alleviated through sustainable water reuse schemes, which include using suitable wastewater treatment technologies to treat and reclaim wastewater. Starting from the last century, anaerobic wastewater treatment technology has been recognized as a more promising alternative to conventional aerobic bioprocesses due to its prime advantages in pollution reduction, net energy production (methane generation) and sludge minimization. To date, anaerobic treatment processes have been successfully utilized for treating agricultural and industrial sewages, particularly in the mesophilic or thermophilic temperature conditions.

Nevertheless, the applicability of anaerobic bioprocesses has been proven to be limited with the major concern on poor biomass retention. In the conventional anaerobic digestion processes, the slow-growing nature of methanogenic microbes together with the poor settling properties of the biomass lead to a low yield of net biomass production and the loss of biomass to the effluent (Lin et al. 2013). As a

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result, anaerobic effluent can rarely meet the standards for water reuse and aerobic treatment or other processes are usually required as a post-treatment to further polish the effluent from anaerobic processes (Chan et al. 2009).

As advanced membrane-based separations are well suited for water recycling and reuse, membrane bioreactor (MBR) technology is now experiencing rapid growth in a wide variety of applications and has become one of the most promising technologies for the 21st century. Being an alternative to the conventional activated sludge (CAS)-membrane filtration process by combining both activated sludge process and membrane separation into one single unit, MBRs can provide superior performance such as high effluent quality, excellent microbial separation ability, absolute control of hydraulic retention time (HRT) and sludge retention time (SRT), high biomass content and less sludge bulking problem, relatively low-rate sludge production, small footprint and limited space requirement and possibilities for a flexible and phased extension of existing wastewater treatment plants (Ngo et al. 2012).

To solve the problems associated with poor retention of anaerobic microbes in conventional anaerobic treatment processes and high energy requirement in aerobic MBRs owing to aeration, anaerobic membrane bioreactor (AnMBR) technology has been considered as an attractive approach. The main advantages of AnMBR include higher biomass retention to attain a full growth of slow-growing methanogenic consortia and probability of bioenergy recovery, thereby improving treatment and energy efficiency. Moreover, compared with conventional anaerobic processes that require large capacity reactors to hold the slow-growing anaerobic microorganisms, AnMBR processes can operate with a significantly reduced reactor footprint to ensure efficient anaerobic biodegradation of nutrients, suspended solids, colloidal organics, bacteria, etc., as well as achieve sustainable biosolids management. However, membrane fouling of AnMBR remains as a main impediment to its worldwide application, and its economic consequences deserve serious consideration when applying AnMBR technology, in terms of plant maintenance/operation as well as membrane cleaning and replacement (Lew et al. 2009; Yoo et al. 2012; Lin et al. 2013).

As membrane fouling has been extensively reviewed by many researchers, this chapter mainly focuses on the comprehensive overview of the recent progress in AnMBR applications, including the fundamental aspects and development of AnMBR processes. As a future green bioprocess, biogas production and waste minimization, opportunities, future perspectives and research needs are also discussed.

25.2 FUNDAMENTALS OF ANMBR

25.2.1 Evolution of AnMBR Technology

The very first concept of AnMBR technology was proposed by Hans E. Grethlein in 1978 in Hanover, New Hampshire, USA, when a flat sheet ultrafiltration (UF) membrane module and a Helicore reverse osmosis (RO) unit were used to treat

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effluent from a septic tank. The flow was directed to one or two modules in parallel, and the concentrated solution was returned back to the septic tank (Grethlein 1978). Based on the patented Membrane Sewage Treatment System (MSTS), Dorr-Oliver Inc., USA has developed the first commercially-available AnMBR (the Membrane anaerobic Reactor System (MARS)) in 1984, which was composed of an activated sludge reactor followed by an UF step for solid-liquid separation under anaerobic operation (Li et al. 1985). In 1985, a 6-year R&D program was initiated in Japan in order to develop various pilot-scale AnMBR systems by utilizing different kinds of membranes and bioreactor configurations (suspended growth and attached growth) for industrial wastewater and sewage treatment (Kimura 1991). During 1987 and 1988, research on combining anaerobic digestion with locally manufactured UF membranes has been carried out in South Africa to treat wine distillery wastewater with high chemical oxygen demand (COD). After that, a number of pilot- and full-scale systems, known as Anaerobic Digestion Ultrafiltration (ADUF) systems, have been implemented successfully for treatment of organic industrial effluents (Ross et al. 1990).

Since then, research and investigations on AnMBRs have been focused on membrane materials, filtration performance, membrane fouling characterization and strategies for fouling control (Lin et al. 2013). In the last decade, Kubota submerged Anaerobic Membrane Biological Reactor (KSAMBR) has been proposed by Kubota Corporation, Japan, which has been successfully applied in 15 full-scale plants (Kanai et al. 2010). As reported by McMahon (2010), the largest AnMBR system in the world is the ADI-AnMBR developed by ADI Systems, Inc. in cooperation with Kubota. Table 25.1 lists the important milestones of AnMBR development and applications. At present, the focus of AnMBR research has been mainly on energy recovery, nutrient recovery, membrane fouling control and application implementation.

25.2.2 Membrane and Process Design

An AnMBR can be defined as a biological treatment process, which is operated without the presence of oxygen and using a membrane to achieve complete retention of microorganisms and solid-liquid separation. However, Liao et al. (2006) discussed in their critical review that this definition is too broad because there are a wide variety of alternatives existed for both the anaerobic process and the membrane process. The effectiveness of AnMBRs is usually dependent upon which alternatives are adopted in the process design. Therefore, it would be useful to overview the current available alternatives before looking into the process design of AnMBRs.

Available anaerobic reactors can be generally classified into two categories based on the criteria whether there is biomass retention. Continuous stirred tank reactor (CSTR) is a classic example of reactor designs that do not provide biomass retention. In this case, the HRT remains the same as the SRT in CSTR and hence suspended solids concentration of the effluent remains the same as the solids concentration in the bulk reaction zone. This type of reactor is mainly utilized in treating high solids wastes including sludge from municipal wastewater treatment systems and animal manures and food processing wastewater. On the other hand, the most commonly

Table 25.1. The milestones of AnMBRs' evolution

Year	*Highlights*	*Reference*
1978	• The first AnMBR application achieved the reduction of E. coli, turbidity, BOD, nitrate and orthophosphate by 100, 100, 85–95, 72–75 and 24–85, prospectively. • The anaerobic digestion rate of organic carbon in the septic tank was enhanced by 3–4 times due to the increased concentration of microorganisms and substrate caused by membrane. • The stability of pH was excellent even with intermittent loading and the sludge accumulation was less than that in the ordinary septic tank. • High practical flux (400 to 600 L/m^2·d with UF module for over 900 pump hours or 1500 hours of real time without frequent cleaning of the membrane.	Grethlein (1978)
1985	• The first commercially available AnMBR—pilot-scale MARS, was developed for treating dairy and wheat starch wastewater. The system was capable of removing 95.1 and 99.2% of COD at a volumetric loading of 14.6 and 8 kgCOD/m^3·d, respectively. • SS were well handled by this process and less than 10 mg/L effluent SS was obtained with influent SS up to 13,300 mg/L. • The average observed methane yield rate varied from 0.28 to 0.34 m^3 CH^4/kg COD removed.	Li et al. (1985)
1987	• Pilot-scale ADUF was completely enclosed non-odor process and has been applied for food-processing and beverage wastewater treatment. • For the digester, no strict SRT control and complete mixing were required. Sludge could be withdrawn from the digester and returned to the external UF unit at different levels. • It was also highlighted that ADUF was a high-rate process with high space load rates ($>$10 kgCOD/m^3·d), which led to reduced digester volume and capital cost.	Ross et al. (1990)
1999	• Based on ADUF process, pilot- and full-scale BIOREK® system has been developed by BIOSCAN Engineering A/S, Denmark to treat pig manure. The system comprised six unit operations (pre-separation, the ADUF process, ammonia stripping process, RO, gas purification and power generation).	Norddahl and Rohold (2000)

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Table 25-1. The milestones of AnMBRs' evolution (Continued)

Year	*Highlights*	*Reference*
	• More than 80% of water was recovered from the slurry and more than 90% COD was removed through the mesophilic anaerobic digestion reaction with a HRT of 6 days. • Results from full-scale plant showed that it was possible to produce energy from biogas recovery and fertilizer from potassium and phosphate recovery, as well as potable demineralized water.	
2009	• KSAMBR process has been successfully applied in a number of full-scale food and beverage industries, which consisted of a solubilization tank and a thermophilic or mesophilic digestion tank coupled with submerged membranes. • One of the main advantages of KSAMBR is that membranes retain the methanogenic bacteria while dissolved methane fermentation inhibitors (e.g. ammonia) are filtered out with the permeate. The digester volumes can be scaled down to 1/3 to 1/5 of the conventional digesters due to concentrated biomass. • COD removal efficiency was between 75 to 92% and the biogas (60% CH_4 and 40% CO_2 with a few minor components such as H_2S) generated could be utilized for water heating via boilers.	Kanai et al. (2010)
2010	• ADI-AnMBR has been applied in Ken's Foods of Marlborough, MA, USA for upgrading one of its three WWTPs in order to maximize biogas production and treat high-strength organic content wastewater, containing high levels of fat, oil and grease. • The ADI-AnMBR system can remove 99.4% COD and produce effluent free of SS, allowing 378 m^3/d treated water to be discharged into the municipal system. • As part of the system upgrade, the AnMBR has been operated together with previously installed low-rate anaerobic reactor (developed by ADI). The combined system produces approximately 5660–8500 m^2 biogas every day, which can not only satisfy 100% heating requirements of the WWTPs, but also provide more than 50% of power supply for the company's manufacturing facility.	McMahon (2010)

BOD: biological oxygen demand; COD: chemical oxygen demand; RO: reverse osmosis; SS: suspended solids; WWTP: wastewater treatment plant

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recognized reactors that offer biomass retention are upflow anaerobic sludge bed (UASB), anaerobic filter (AF), expanded granular sludge bed (EGSB), fluidized bed (FB), etc. In this case, the suspended solids concentration in the effluent is dramatically reduced as compared with that in the reactor ozone (Liao et al. 2006).

Membranes used in anaerobic treatment can be classified into metallic, polymeric and inorganic (ceramic) based on what material used to manufacture membrane. Ceramic membranes have been used most extensively in the early studies of AnMBRs due to less membrane fouling and their ability of being backwashed without affecting their longevity adversely. As for metallic membranes, they can demonstrate better fouling recovery, higher endurance to an impact force, and tolerance to high temperature and oxidation. Moreover, it has been observed that both metallic and ceramic membranes show their advantages in better hydraulic performance and easier fouling control over polymeric membranes. However, they cost much more compared to polymeric counterparts. Therefore, polymeric membranes have attracted more interests in both research and commercial development of AnMBR, especially when the economic concern becomes the major consideration for the commercialization of a system in the recent years. Regarding the membrane materials, the preferred ones are polyvinylidene fluoride (PVDF) and polyethersulfone (PES) which present a significant fraction of the total products on the market (75%) (Skouteris et al. 2012; Lin et al. 2013). Commonly, microfiltration (MF, 0.1–10 μm) and UF (0.01–0.1 μm) membranes are the most popular membranes used for AnMBRs with three common configurations, namely hollow fiber, flat sheet (plate or frame) and tubular. The key features of each type can be found in the book chapter of Guo and Ngo (2012).

The AnMBR configurations are generally divided into two major groups depending upon whether membrane operation is under vacuum or under pressure. For those requiring a pump to push anaerobic bioreactor effluent to the membrane unit and permeate through the membrane, they are normally called external crossflow AnMBR (Figure 25.1a), of which the membrane system is separated from anaerobic bioreactor. AnMBR can also be operated under a vacuum to draw effluent through membrane and this configuration is often named submerged AnMBR (SAnMBR). In this case, the membrane could be either directly placed in the anaerobic bioreactor (Figure 25.1b) or immersed in a separated bioreactor (Figure 25.1c).

Early studies of AnMBR have been focused on the external configuration exclusively. However, this configuration has its own inherent weaknesses. First of all, extensive energy consumption due to the high hydraulic shear force reduces the economic efficiency of AnMBR applications (Choo and Lee 1998; Stuckey 2012). The high shear force can also cause the disruption of anaerobic biosolids, leading to aggravated membrane fouling and harming the biological activities of anaerobic microbes. Compared to external configuration, submerged types can have substantial energy savings because no recirculation pump is required. Thus, SAnMBR has become a promising alternative due to its relatively lower energy consumption, fewer rigorous cleaning procedures, and milder operational conditions with lower tangential velocities (Brockmann and Seyfried 1996; Lin et al. 2013).

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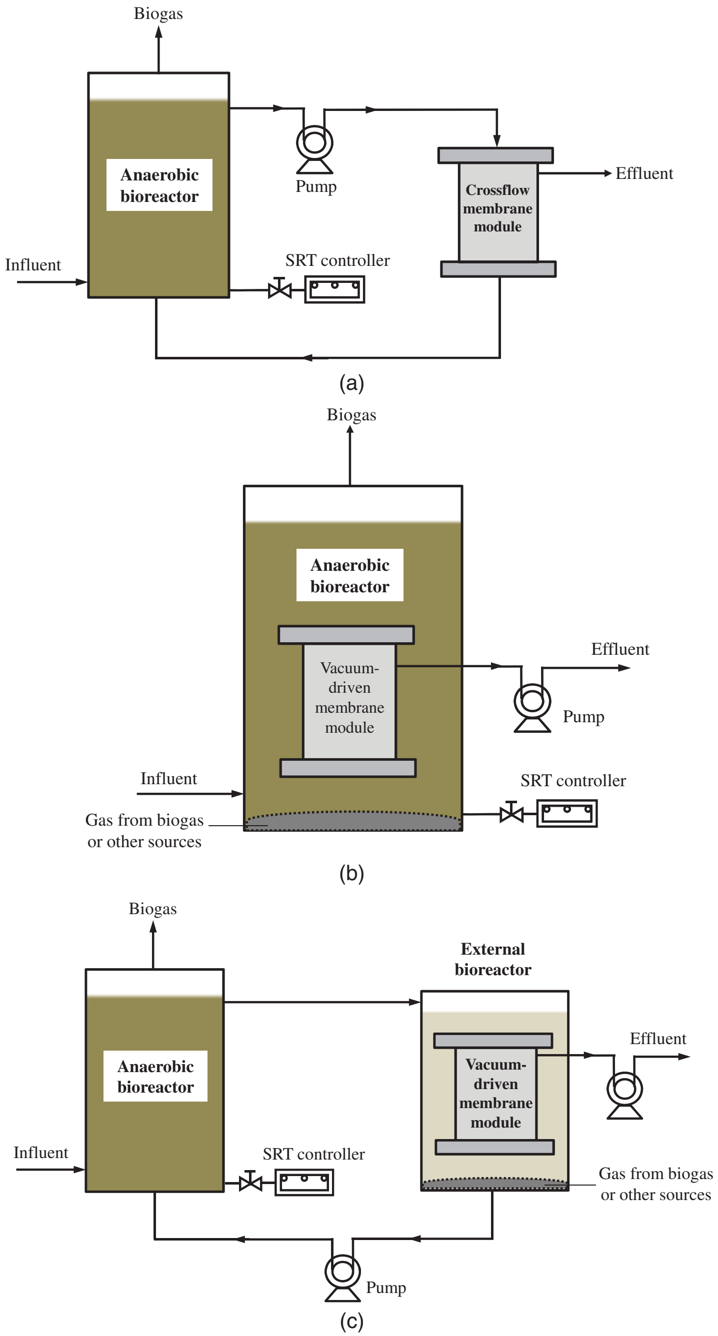

Figure 25.1. Schematic of AnMBR configurations: (a) external crossflow AnMBR; (b) SAnMBR with the membrane placed directly in the reactor; (C) SAnMBR with the membrane immersed in a separated bioreactor

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It is well known that hydrolysis, acidogenesis, acetogenesis and methanogenesis are the four fundamental steps of anaerobic digestion. However, as a result of the difference in the rate of acidogenesis and methanogenesis, acid inhibition usually occurs and acid inhibitors such as ammonia and volatile fatty acids (VFAs) generated during acidogenesis can limit the methane yield and destruct the process stability, thereby leading to the insufficient anaerobic digestion (Kanai et al. 2010). Moreover, all of the three principal anaerobic microbes, namely the hydrolyzing and fermenting microorganisms, the obligate hydrogen-producing acetogenic bacteria and the methanogenic archaea, have extremely sensitive pH ranges. For example, both acetogens and acidogens need the pH range from 5.5 to 7.2, while methanogens bacteria require strictly the optimal pH between 6.8 and 7.8 (Visvanathan and Abeynayaka 2012). Additionally, acidogenic organisms are found to grow much more rapidly compared to methanogenic bacteria. The production of acids during acidogenesis can reduce pH of the bioreactor, which can adversely affect methanogenic bacteria. Therefore, it would be better to separate acetogens/acidogens and methanogens into different reactors to offer desirable circumstances that allow each type of bacteria to perform at its optimal condition (Chen et al. 2008a; Zhao 2011).

Furthermore, although aerobic MBRs can produce high quality of treated effluent to meet controlled levels of organics and nutrients (nitrogen and phosphorus) and achieve almost complete nitrification, denitrification always requires the addition of an anoxic tank prior to the aeration tank with conventional recycle (Gander et al. 2000). Moreover, the concept of simultaneous nitrogen and phosphorus removal significantly depreciated the most favourable characteristics of long SRT control in aerobic MBR. Although various designs of treatment processes associated with aerobic MBR have been reported through applying various combinations of anaerobic, anoxic and aerobic or multiple compartments (e.g., anoxic/anaerobic/oxic/anoxic MBR or anoxic/aerobic MBR, sequencing anoxic/anaerobic MBR, alternating of anoxic and anaerobic MBR process, anaerobic/anoxic/oxic MBR, etc.), the additional pumping, pipeline and recirculation configurations of either mixed liquor or permeate lead to higher capex, operational costs and energy consumption (Guo et al. 2010). Table 25.2 summarizes the performance comparison of conventional aerobic treatment, anaerobic treatment, aerobic MBR and AnMBR, indicating that AnMBR possesses the advantages of both anaerobic treatment and MBR technology (Lin et al. 2013).

In order to provide sufficient treatment to meet stringent effluent requirements, as well as fulfill the complete decomposition of complex organic wastes into the end-products (e.g. methane, carbon dioxide, etc.), researchers have started investigating and developing the hybrid anaerobic systems with multistage treatment involving the AnMBR process. The purposes of using the hybrid AnMBR systems are to improve effluent quality, enhance the stability of the anaerobic process, reduce waste biosolids production, reduce high energy and operating expenditure due to membrane fouling problem and maximize methane production (Yushina and Hasegawa 1994; Trzcinski and Stuckey 2009; Kanai et al. 2010; Yoo et al. 2012). Tables 25.3 and 25.4 list a number of hybrid AnMBR systems that have been employed in treating various sources of wastewater.

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Table 25.2. Comparison of the performance of conventional aerobic treatment, anaerobic treatment, aerobic MBR and AnMBR

Indicator	*Conventional Aerobic Treatment*	*Conventional Anaerobic Treatment*	*Aerobic MBR*	*AnMBR*
Organic removal efficiency	High	High	High	High
Effluent quality	High	Moderate to poor	Excellent	High
Organic loading rate	Moderate	High	High to moderate	High
sludge production	High	Low	High to moderate	Low
Footprint	High	High to moderate	Low	Low
Biomass retention	Low to moderate	Low	Total	Total
Nutrient requirement	High	Low	High	Low
Alkalinity requirement	Low	High for certain industrial stream	Low	High to moderate
Energy requirement	High	Low	High	Low
Temperature sensitivity	Low	Low to moderate	Low	Low to moderate
Startup time	2–4 weeks	2–4 months	<1 week	<2 weeks
Bioenergy recovery	No	Yes	No	Yes
Mode of treatment	Total	Essentially pretreatment	Total	Total pretreatment

Source: Lin et al. (2013); reproduced with permission from Elsevier.

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Table 25.3. Summary of the initiatives of hybrid AnMBR systems

Wastewater type	*Purpose of research*	*References*
Sewage and soybean-processing wastewater	Develop low-cost treatment processes utilizing bioreactors combined with membrane units	Kimura (1991)
low-strength wastewater and soybean-processing wastewater	Study the characteristics of highly concentrated anaerobic bacteria population	Kataoka et al. (1992)
Municipal sewage	Achieve high-performance separation to produce methane gas and to reclaim wastewater	Kiriyama et al. (1992)
Municipal sewage	Establish a methane gas generation system capable of obtaining certain level of conversion rate	Kiriyama et al. (1994)
Wheat starch wastewater	Enhance the efficiency of two-phase anaerobic degradation to treat wastewater containing high strength suspended solids	Yanagi et al. (1994)
Soybean processing wastewater	Improve the efficiency in gas production and treated water quality	Yushina and Hasegawa (1994)
Piggery wastewater	Increase the SRT of amidogens, enhance the solid separation and reduce the cake resistance of membranes in an anaerobic reactor	Lee et al. (2001)
Slaughterhouse wastewater	Overcome the VFA accumulation and mitigate acid inhibition	Saddoud and Sayadi (2007)
Municipal solid waste (Organic Fraction)	Promote stability and performance of a two-stage anaerobic membrane process	Trzcinski and Stuckey (2009)
Biodegradable municipal waste	Enhance the degradation of biodegradable municipal solid waste	Walker et al. (2009)
Sand-separated dairy manure	Evaluate the potential of the proposed AnMBR to treat agricultural waste	Wong et al. (2009)
Distillation residue or food waste	Stabilize methane fermentation	Kanai et al. (2010)
High strength molasses-based synthetic wastewater	Investigate the effects of the organic loading rate on VFA profile and biological activity of a two-stage thermophilic AnMBR system	Wijekoon et al. (2011)
Municipal wastewater primary-clarifier effluent	Evaluate effluent quality, biosolids production, energy requirements and production, and procedures for membrane fouling control	Yoo et al. (2012)

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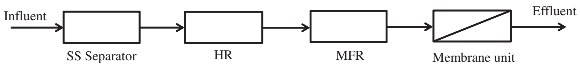
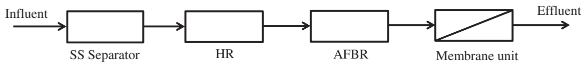
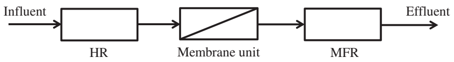
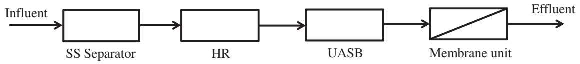
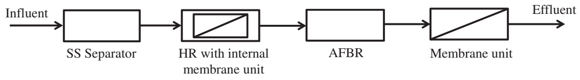
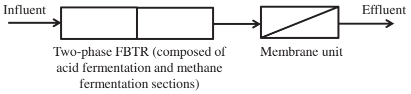
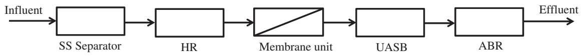
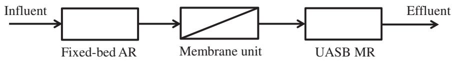
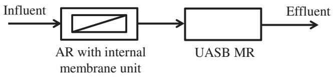
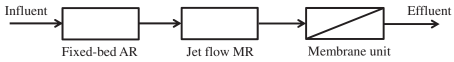
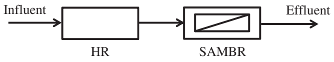
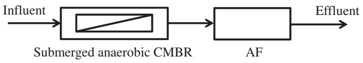
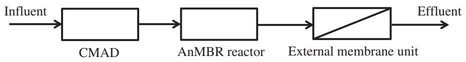
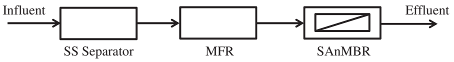
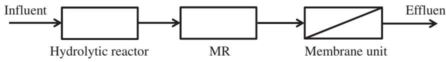
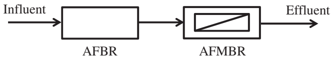
Table 25.4. Schematic diagrams of hybrid AnMBR systems

Schematics of hybrid AnMBRs	*References*
	Kimura (1991)
	Kimura (1991)
	Kimura (1991) and Yushina and Hasegawa (1994)
	Kataoka et al. (1992)
	Kataoka et al. (1992)
	Kataoka et al. (1992)
	Kiriyama et al. (1992, 1994)
	Yanagi et al. (1994)
	Lee et al. (2001)
	Saddoud and Sayadi (2007)
	Trzcinski and Stuckey (2009)
	Trzcinski and Stuckey (2009)
	Walker et al. (2009)

(Continued)

Table 25-4. Schematic diagrams of hybrid AnMBR systems (Continued)

Schematics of hybrid AnMBRs	*References*
	Wong et al. (2009)
	Kanai et al. (2010)
	Wijekoon et al. (2011)
	Yoo et al. (2012)

Notes: ABR: aerobic bioreactor; AF: anaerobic filters; AFBR: anaerobic fluidized-bed reactor; AFMBR: anaerobic fluidized-bed membrane bioreactor; AR: acidogenic reactor; CMAD: complete mix anaerobic digester; CMBR: coarse membrane bioreactor; FBTR: fixed-bed-type reactor; HR: hydrolyzation reactor; MFR: methane fermentation reactor; MR: methanogenic reactor; SAMBR: submerged aerobic membrane bioreactor; SAnMBR: submerged anaerobic membrane bioreactors; SS: suspended solids; UASB: upflow anaerobic sludge blanket

25.3 CURRENT STATUS OF ANMBRS IN WASTEWATER TREATMENT

25.3.1 Municipal Wastewater Treatment

The anaerobic treatment processes are known to have the inherent advantages over the aerobic counterparts, such as sludge minimization and energy savings. However, anaerobic processes have been historically less employed for municipal/ domestic wastewater treatment because of its low organic strength and high-suspended solids concentration (Liao et al. 2006; Lew et al. 2009). Furthermore, there have other two reasons causing the less popularity of anaerobic applications. Firstly, it is rare that anaerobic effluent can meet the discharge requirements, as anaerobic metabolism exist the kinetic limitations especially when the treatment processes experience the low temperatures. At low temperatures, the hydrolysis of suspended solids and colloidal fractions is the rate-limiting step, impeding anaerobic digestion of municipal wastewater. Secondly, it is difficult to retain the slow-growing anaerobic microbes with the short hydraulic retention time in association with low strength wastewater treatment. Therefore biomass concentrations are difficult to maintain, and can be mostly washed out from reactors (Uemura and Harada 2000; Lettinga et al. 2001; Martinez-Sosa et al. 2012; Lin et al. 2013).

However, the degradation efficiency can be enhanced by increasing the suspended solids retention time in an anaerobic reactor. Hence, AnMBR has been found extraordinarily attractive because it can maintain very high solids

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concentration as no particulates could be expelled from the membrane system (Lew et al. 2009). This means that the complete hydrolysis and decomposition of the retained particulate organics can be eventually accomplished due to the long SRT. Moreover, the anaerobic bacteria with relatively low growth rates can be allowed to fully grow without being washed out from the reactor. Additionally, comparing with aerobic MBRs, AnMBR can actually bring about a green approach to renewable sources of energy (methane production), lower sludge production and no extra energy consumption associated with aeration.

During municipal wastewater treatment, AnMBR is usually fed with primary treated effluent to protect membrane from the damage due to large particles and to maximize the longevity of membrane life. Thus, effective pretreatment such as screening and settling should be implemented to ensure the efficacy of AnMBR. Although the majority of AnMBR research in municipal wastewater treatment has been restricted to the external module (Lin et al. 2011), this configuration has its own inherent weaknesses as mentioned before. The submerged anaerobic membrane bioreactors have gained a great popularity among the research and industrial divisions in recent years. So far, researchers have been looking into the AnMBRs based on three areas (Lin et al. 2013): 1) the removal of common contaminants such as COD and total suspended solids (TSS); 2) the removal of nutrients such as total nitrogen (TN) and total phosphorus (TP); and 3) the removal of trace contaminants such as endocrine disrupting chemicals (EDCs) and pharmaceutically active compounds (PhACs).

According to the review of Lin et al. (2013), AnMBR systems can achieve more than 85% COD and 99% TSS removal at certain operational conditions, while Elmitwalli et al. (2001) have reported that the anaerobic biodegradation of domestic wastewater tended to be relatively low in terms of COD removal (71–74%). Hence, it is suggested to implement aerobic post-treatment to further enhance COD and nutrient removal (Chan et al. 2009). Nevertheless, the high removal efficiency of nutrients such as TN and TP is not expected in the AnMBR systems because the removal of TN and TP requires the anoxic or aerobic zone. As a result, it can be an advantage if the effluent is to be utilized directly to fulfill the irrigation or agricultural purpose. Nevertheless, in most cases, a further nutrient removal process is needed if the effluent is to be reused. Available nutrient removal technologies include conventional biological measures, partial nitritation/nitrification, forward osmosis (FO) processes, and physical/chemical nutrient removal processes (Lin et al. 2013).

With the growing environmental health concerns of the effects of the micropollutants, research has been focused on investigating the ways of removing micropollutants from the treated and untreated municipal wastewater. The anaerobic biodegradation of these trace contaminants was proved to be less effective, but the tactics of prolonging HRT (>30 d) and the adoption of bioaugmentation can serve as an effective countermeasure to enhance the removal efficiency, particularly for PhACs (Kujawa-Roeleveld 2008; Ifelebuegu 2011). Saravanane and Sundararaman (2009) applied bioaugmentation to a SAnMBR process in treating high-concentration antibiotic wastewater, and the treated

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effluent met the requirement for discharge with consistent quality. Saddoud et al. (2009) stated that if the domestic wastewater composition polluted by the toxic compounds originating from the industrial activities, the AnMBR process could be inefficient and likely to cause considerable variations in the biogas production rates and the methane levels present in the biogas. They also mentioned that the exposure to toxicity induced by industrial chemicals in the domestic influent could actually harm the biomass in reactors, which possibly led to the upset or even failure of the treatment system.

In terms of the economic attractiveness of AnMBR, many efforts have been made to observe whether the transition from conventional MBRs to anaerobic MBRs is an economically viable choice. The results show that under similar conditions, conventional ones and AnMBRs are able to produce similar soluble COD removal rates (Baek and Pagilla 2006). However, AnMBR can save all costs for aeration, which significantly elevates its economic efficiency. Nevertheless, operational temperature is a vital factor to determine the cost-effectiveness of AnMBRs, and this is due to the fact that the heating of anaerobic reactors requires heavy energy and capital expenditure. With respect to domestic wastewater treatment with a low organic content, operating under ambient temperature is favored because the low methane production cannot cover the heating requirements (Martinez-Sosa et al. 2011; Skouteris et al. 2012). Therefore, AnMBRs are usually suggested to operate under mesophilic (30–37°C) or thermophilic (50–55°C) temperature conditions so as to ensure the optimal biological activity, and maximize the economic efficiency (Du Preez et al. 2005; McKeown et al. 2011). On the other hand, Martinez-Sosa et al. (2011) has demonstrated an AnMBR for municipal wastewater treatment under psychrophilic temperature condition (20–28°C). The results have proven the feasibility of AnMBR in the low temperature region. Although aggravated membrane fouling was observed at psychrophilic temperatures that probably linked to an accumulation of TSS and soluble COD in the reactor, the AnMBR still had COD removal rate marked nearly 90% with effluent COD and BOD_5 lower than 80 and 25 mg/L, respectively.

25.3.2 Industrial Wastewater Treatment

The industrial sectors have been facing with the ever-stringent requirements on the effluent quality. The challenges are even more intensified when the significant amounts of discharged industrial wastewaters with extreme conditions are likely to occur more often in the future. The reduction in water consumption, water reuse and resource recovery are the three main goals that the cleaner industry has to achieve. Industrial wastewater is typically characterized by its high organic strength and extreme physical-chemical conditions in terms of pH, temperature and salinity. The presence of certain synthetic and natural toxic substances can be also found frequent in industrial wastewaters, and it could adversely influence the biological treatment processes. Each year, a large quantity of industrial wastewater is generated as a result of the ever-rapid industrialization, including effluents from food processing, pulp and paper, textile, chemical, pharmaceutical, petroleum, tannery, and manufacturing industries. To treat these wastewaters in a sustainable

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and efficient manner, the applications of AnMBR are advocated because of its intrinsic advantages. At present, AnMBRs have been widely used in food industrial wastewater treatment with both pilot- and full-scale applications. By contrast, the treatment of non-food processing effluents by AnMBRs applications is restricted mostly at lab- and pilot-scale (Liao et al. 2006; Dereli et al. 2012; Guo and Ngo 2012; Lin et al. 2013).

Wastewater from food industry is generally biodegradable and non-toxic, and it contains a high concentration of organics (1000–85000 COD mg/L) and suspended solids (50–17000 mg/L). In most cases, anaerobic digestion has been considered as a suitable method treating such wastewater. Since approximately 76% of all anaerobic reactor installations are in the food related industries, AnMBR applications have gained the most popularity in food processing wastewater treatment compared to other kinds of industrial wastewaters. Many AnMBR systems have been adopted in treating effluents from field crop processing (wheat starch, gluten and soybean), the dairy industry (whey), and the beverage industry (winery and distillery). Regarding the treatment performance of AnMBR, more than 90% COD usually could be removed when the applied organic loading rates (OLR) were between 2 and 15 kgCOD/m^3·d. This treatable OLR range was lower than the existing high-rate anaerobic reactors (HRARs) with 5–40 kgCOD/m^3·d, but was higher than the traditional CSTR digesters. Most AnMBR studies associated with food processing wastewater have used CSTR with external pressure-driven cross-flow membrane unit (Liao et al. 2006; Lin et al. 2012, 2013). There are also some cases that hybrid AnMBR systems were utilized in the studies to facilitate the biomass growth and enhance treatment efficiency (Tables 25.3 and 25.4).

Wastewaters from non-food industries are generated from a broad variety of industrial plants and manufacturing processes, and the features of these industrial wastewaters are sector specific. However, in general, they have similarities in terms of high organic strengths and embrace natural and synthetic chemicals, which can be hardly bio-degradable or non-degradable through anaerobic and/or aerobic processes. Conventionally, industrial wastewater treatment usually has to utilize various treatment processes, such as physical treatment (screening, sedimentation, filtration, skimming, water cooling and heating), chemical treatment (coagulation and flocculation, precipitation, chemical immobilization), and biological treatment (activated sludge processes, bioaugmentation, constructed wetlands and membrane bioreactors); no single type of treatment can accomplish the whole task (Liao et al. 2006; Guo and Ngo 2012).

There is a significant concern to the biological treatment of such wastewater as the presented toxicity can harm microorganisms, especially anaerobic ones. Anaerobic systems are complex and nonflexible, and have low capability of tolerating the toxins or inhibitory substances presented in substantial concentrations, which are the primary contributors to the upset or failure of the anaerobic digestion processes (Liao et al. 2006; Chen et al. 2008a). In particular, methanogenic microbes have higher possibility of being easily inhibited by toxic substances, resulting in the problems such as low methane yield and process instability (de Lemos Chernicharo 2007). However, AnMBRs have an obvious

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advantage over the conventional anaerobic systems because complete biomass retention can still be achieved even though inhibitors upset the system. As substances with high toxicity levels can hardly cause cell death, the treatment process may be temporarily impaired and eventually be recovered again (Liao et al. 2006). Moreover, the adverse impact can also be minimized if some feasible measures can be provided in place. The appropriate precautions include designing measures (e.g. prolonging the SRTs) and control methods (e.g. dilution below the toxicity level, pretreatment prior to AnMBR applications to remove toxic compounds, or acclimation of biomass by gradual increase of toxic levels) (Speece 1996; De Lemos Chernicharo 2007; Liao et al. 2010).

Some cases where AnMBRs were used in the treatment of such non-food processing wastewater are given in details:

Pulp and Paper Industry Wastewater. Paper and pulp industry wastes contain high COD concentrations because the produced pulp is equivalent to only 40–45% of the original weight of the wood (Ali and Sreekrishnan 2001). Furthermore, high temperature usually can be observed in the effluent, which is typically around 35°C. These two main characteristics make anaerobic digestion a promising treatment technique. According to Kleerebezem and Macarie (2003), anaerobic treatment of such wastewater has gained more and more popularity and roughly 9% of all anaerobic installations are for the pulp and paper industry. The number of the reported studies about AnMBRs' ability in treating pulp and paper industry wastewater has increased rapidly. Overall, more than 90% BOD could be eliminated in most cases, while the unsatisfactory absorbable organic halogens (AOX) removal (61%) was detrimental, implying the performance instability of AnMBRs. The system instability could be explained by the process inhibition, and the most common inhibitors to AnMBRs for treating pulp and paper industry wastewaters are sulfide, tannins acids, long chain fatty acids (LCFA) and halogenated compounds (Kimura 1991; Minami 1994; Okamura et al. 1994; Ali and Sreekrishnan 2001; Liao et al. 2006).

Evaporator condensate (EC) is one kind of the important wastewaters produced from the pulp and paper industry, and is of a major concern of the researchers, as it can be readily converted to methane during treatment (Xie et al. 2010). EC is typically characterized by its high soluble COD concentration (10–42 g/L due to methanol), high temperature, low suspended solids (<3 mg/L), and the presence of inhibitory substances including total reduced sulfur (TRS) compounds and terpene oils (Minami et al. 1991; Minami 1994). Thus, the pretreatment of condensate to remove the above mentioned toxic materials are highly recommended to maintain the system stability, and enhance the EC treatment performance. Minami (1994) operated a pilot-scale AnMBR to treat EC, and the condensate was pretreated through microfiltration and biogas stripping. pH was adjusted to neutral to ensure that the pretreated effluent was amenable to treatment in a thermophilic attached growth ultrafiltration AnMBR. More than 93% BOD removal efficiency was achieved with OLR of 35.5 kgCOD/m^3·d, which was more than doubled when compared with 15 kgCOD/m^3·d OLR without the membrane.

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Operating AnMBR under thermophilic temperatures may be favorable for EC treatment and reuse, because precooling and post-heating used in the mesophilic treatment can be avoided (Lin et al. 2012, 2013). Lin et al. (2009) have done a comparable study on two parallel SAnMBRs (mesophilic SAnMBR operated at 37°C and thermophilic SAnMBR operated at 55°C) treating kraft EC at a feed COD of 10,000 mg/L. Similar results in terms of COD removal (97–99%) and substantial methane production were reported in both SAnMBRs. The results showed that both mesophilic and thermophilic SAnMBRs have the potential of being promising processes for the treatment of kraft EC when considering the aspects of COD removal and biogas production. Nevertheless, the challenges of much-worsening membrane fouling were observed in thermophilic SAnMBR due to the fact that high temperature and relatively lower OLR could accelerate soluble microbial products (SMP) and disrupt sludge flocs. In addition, as sludge cake layers in the thermophilic SAnMBR were more compact and less porous, the filtration resistance in the thermophilic SAnMBR was about 5–10 times higher than that of the mesophilic SAnMBR when operated under similar hydrodynamic conditions. With regard to economic attractiveness of AnMBRs in treating paper and pulp industry wastewaters, it was concluded that the total capital cost using AnMBR to treat kraft mill effluent was remarkably lower than that of aerobic treatment, and only a bit higher than that of high rate anaerobic reactors (HRARs) such as UASB, whereas the effluent quality of AnMBR was the best (Kimura 1991; Minami 1994; Okamura et al. 1994).

Textile Industrial Wastewater. The wastewaters from the textile industry mainly originate from the washing or scouring, bleaching of natural fibers and the dyeing and finishing steps, and have great chemical complexity (Vandevivere et al. 1998; Chen et al. 2008a). Several lab-scale studies have demonstrated that methanogenic microorganisms could be easily inhibited by textile effluent due to the potential inhibitors such as dye, heavy metals and surfactants (Athanasopoulos 1992; Feitkenhauer 2004; Lee and Pavlostathis 2004). Hence, the potential of anaerobic treatment of such wastewater is considered low and it was found that only 1% of all industrial scale anaerobic installations are for the textile industry (Kleerebezem and Macarie 2003). There are some cases in the literature investigating the efficiency of the AnMBR technology for the treatment of textile industrial wastewater. Hogetsu et al. (1992) reported the anaerobic treatment of wool scouring wastewater using a fixed-bed anaerobic reactor combined with UF filter achieved good total oxygen demand (TOD), wool grease and SS removal efficiency of more than 89, 98 and 100%, respectively at the TOO loading rates of up to 20 kg/m^3·d. The recirculation of rejected liquid from the UF filter contributed to higher concentration of biomass (about two times than the process without recirculation) and 33% of organic solids decomposition.

Spagni et al. (2012) investigated Azo dye decolourisation of textile wastewater in a SAnMBR, and the reactive orange 16 was used as a model of an Azo dye. The results demonstrated that very high decolourisation (>99%) could be achieved by SAMBRs. Although decolourisation was not significantly influenced by the Azo dye concentrations up to 3.2 g/L, methane production was greatly inhibited (up to 80–85%) because of the accumulation of volatile fatty acids in the treatment

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system, suggesting methanogens seem to be the most sensitive microbial populations of the anaerobic ecological community. In another study, Baêta et al. (2012) conducted experiments to evaluate the performance of two SAnMBRs with and without the presence of powdered activated carbon (PAC) for genuine textile wastewater treatment. Both SAnMBRs were operated at 35°C with an HRT of 24 h and the textile effluent was diluted (1:10) with nutrient solution containing yeast extract as the source of the redox mediation riboflavin. Although both SAMBRs exhibited an excellent performance, the results indicated that the addition of PAC into SAnMBR could enhance reactor stability and improve the removal efficiency of COD and color (90 and 94% respectively), while 79 and 86% removal was obtained in the SAnMBR without PAC addition. In addition, the mean values of turbidity and VFA were 8 NTU and 8 mg/L for SAnMBR with PAC and 14 NTU and 26 mg/L for SAnMBR without PAC, suggesting that the presence of PAC inside SAnMBR led to the production of higher quality anaerobic effluent.

Petroleum Industry Wastewater. Petrochemical waste is generally characterized by its high BOD and COD concentrations, as well as high amounts of oil and total solids. Anaerobic digestion of high strength petrochemical refinery wastewater could also be a promising option. However, according to the review of Lin et al. (2013) on AnMBR's applications in industrial wastewater treatment, the cases of AnMBRs treating petroleum industrial effluents have only been reported twice in the last 6 years and neither of them was developed in an industrial scale (Van Zyl et al. 2008; Niekerk et al. 2009). The lab-scale SAnMBR was developed by Van Zyl et al. (2008) to treat high strength (18 gCOD/L) petrochemical wastewater from Sasol's coal to fuel synthesis process consisting mostly of C2 to C6 short chain fatty acids with a low pH. With OLR up to 25 kgCOD/m^3 reactor volume per day and HRT of 17 h, 98% of the COD was converted to methane (with effluent COD <500 mgCOD/L and ammonia <50 mg/L and no particulates >0.45 µm) and the submerged flat panel UF membranes could provide 100% solids-liquid separation. Besides, more than 30 g/L TSS in mixed liquor could be maintained without deterioration of membrane fluxes. On the other hand, the preliminary pilot-scale investigations undertaken by Niekerk et al. (2009) proved that anaerobic granules did not readily form with Fisher-Tropsch Reaction Water (FTRW) and there were effluent quality concerns with the system. Regarding process inhibition, the prolonged acclimation could eventually biodegrade acids, alcohols and esters into methane, whereas anaerobic digestion of petrochemical wastes would not contribute to energy savings over aerobic processes, and however the produced biogas could be used as a renewable source of energy (Chou et al. 1978).

Pharmaceutical Wastewater. The proper treatment of pharmaceutical wastewaters was often neglected worldwide and an estimation of half of the pharmaceutical wastewater produced all over the world is discarded (Lang 2006; Enick and Moore 2007). Presently, research and development, the conversion of organic and natural substances into bulk pharmaceutical substances or ingredients through fermentation, extraction, and/or chemical synthesis, as well as the formulation and assembly of the final pharmaceutical product all generate pharmaceutical wastewaters (Oktem et al. 2007). The disposal of pharmaceutical

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wastewater without appropriate treatment has led to an urgent water pollution problem as approximately 80–100 pharmaceuticals and their metabolites have been found in both effluent and surface waters in a number of countries (Ankley et al. 2005; Fent et al. 2006; Owen et al. 2007).

With the advantages in dealing with high strength wastewaters, anaerobic processes such as CSTR reactors, UASB reactors and anaerobic filters, have been attempted as an effective means to decrease the organic content of chemical synthesis-based pharmaceutical wastewater. The case of applying only AnMBR to treat pharmaceutical wastewater is very limited because anaerobic microbes alone cannot be able to biodegrade refractory contents in the wastewater. Moreover, owing to the different rates of acidogenesis and methanogenesis, and the subsequent occurrence of acid inhibition using single-stage anaerobic digester, hybrid anaerobic systems have to be introduced to reduce the competitions between different microorganisms and mitigate acid inhibition when treating pharmaceutical wastewater. Therefore, to meet the direct discharge requirement, the anaerobic unit combined with a subsequential aerobic process is often applied (Oz et al. 2002; Lin et al. 2013). For example, Chen et al. (2008b) have applied a pilot-scale integrated system, which consists of a two-phase anaerobic digestion and an aerobic MBR unit, for treating chemical synthesis-based pharmaceutical wastewater (5789–58792 mg/L COD and 4.3–7.2 pH) from a local pharmacy company. The TPAD system comprised a CSTR and an UASB-anaerobic filter, working as the acidogenic and methanogenic phases, respectively. With HRTs of 12, 55 and 5 h, the integrated system could remove almost all the COD, and the effluent from MBR had COD around 40 mg/L (>99% removal) and pH of 6.8–7.6, suggesting that the MBR effluent is qualified to be discharged into natural waters directly.

25.4 OPPORTUNITIES FOR ANMBR PROCESSES AND ENERGY RECOVERY

25.4.1 Biogas Production and Waste Minimization

Methane fermentation is a complex biological process, which mainly occurs in four steps: hydrolysis, acidogenesis, acetogenesis and methanogenesis. Hydrolysis acts as the first attack on the insoluble organic material and higher molecular mass compounds including polysaccharides, fat, protein, etc. The enzyme-mediated transformation is accomplished in this stage to convert such polymers into compounds suitable for the use as the source of energy and cell carbon such as monosaccharides, amino acids, acetate and varying amounts of VFAs. Acetate and hydrogen could also be produced as an ending product in the first stage, and they can be utilized by methanogens directly. In the second step, the biological process of acidogenesis takes place, and acidogenic bacteria further breaks down the simple monomers into VFAs, along with ammonia, carbon dioxide and hydrogen sulphide as well as other byproducts (Yadvika et al. 2004; Weiland 2010; Wikipedia 2013).

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In the step of acetogenesis, acetogens further digest the simple molecules created in the acidogenesis stage, and VFAs are converted into largely acetic acid as well as carbon dioxide and hydrogen by acetogenic bacteria. It is worth mentioning that the accumulation of hydrogen can inhibit the metabolism of the acetogenic microbes. Therefore, the maintenance of extremely low partial pressure of hydrogen is required for the well-being of the acetogenic and hydrogen-producing bacteria (Weiland 2010). Methanogenesis is the terminal step that contributes to the most methane production. The methanogenic bacteria usually use up intermediate products of the preceding stages including acetic acids, hydrogen and carbon dioxide, and convert them into methane, carbon dioxide and water. In this final phase, the availability of hydrogen is believed to be a limiting factor for hydrogenotrophic methanogens due to the fact that addition of the hydrogen-producing bacteria can increase the biogas yield (Bagi et al. 2007). As the final product of anaerobic digestion, biogas is mainly composed of methane and carbon dioxide, which can be considered as an alternative source of renewable energy.

A balanced methane fermentation process requires the individual degradation phases to be carried out by distinct consortia of bacteria, and these microorganisms are supposed to behavior in a syntrophic manner to perform efficiently (Angelidaki et al. 1993). For such a complex anaerobic microbial community, biogas formation depends on the activities of various groups of microorganisms of the anaerobic digestion (Gao et al. 2011). The detailed description of different types of microbes is shown in Table 25.5.

Wastewater has been regarded as a valuable energy source with the development of anaerobic digestion technology. The production of biogas offers significant advantages, including: 1) producing less biomass sludge compared to aerobic treatment technologies; 2) successfully treating wet wastes of <40% dry matter; 3) more effectively removing pathogens, especially for multi-stage digesters;

Table 25.5. Description of anaerobic microorganisms in each stage

Anaerobic Microorganisms	*Examples*
Hydrolytic and fermenting microorganisms	Strict anaerobes such as Bactericides, Clostridia and Bifidobacteria, and facultative bacteria such as Streptococci and Enterobacteriaceae
Obligate hydrogen-producing acetogenic bacteria	Homoacetogenic bacteria such as acetobacterium woodii and Clostridium aceticum
Methanogenic bacteria	Two types of strict anaerobes: i) Very few species degrade acetate into methane and carbon dioxide such as Methanosarcina barkeri, Methanococcus mazei and Methanothrix soehngenii ii) Most species use hydrogen to form methane

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4) minimizing odor emissions as 99% of volatile compounds are oxidatively decomposed upon combustion; 5) reducing the amount of biodegradable waste entering landfill; 6) The slurry produced being an improved fertilizer; and 7) producing a source of carbon neutral energy in the form of biogas. Additionally, the utilization of biogas can benefit the reduction of fossil fuel usage and greenhouse gas emissions (Ward et al. 2008; Weiland 2010).

AnMBR, which incorporates anaerobic digestion with membrane separation technology, can play a key role in transforming conventional processes to a more stable and more efficient future green process as well as improve the sustainability of this energy-intensive industry. It is capable of producing methane continuously through utilizing a large fraction of organics in the wastewater. Van Zyl et al. (2008) mentioned that AnMBR can convert approximately 98% of the influent COD into biogas. Lin et al. (2013) reported that although methane yield in AnMBR was generally less than the theoretical yield (0.382 LCH_4/gCOD removed at 25°C) because of high methane solubility, the value was quite considerable, ranging from 0.23–0.33 $LCH_4/gCOD_{removal}$. The biogas produced from AnMBRs is of much greater fuel quality and in some cases, having a composition of 80–90% methane content, and this value compares favorably with the 60–65% obtained from the conventional anaerobic digesters. The higher methane content is attributed to the shorter HRTs by applying membrane for sludge separation in AnMBR (Demirel et al. 2010; Skouteris et al. 2012).

Saddoud et al. (2007) have studied a two-phase anaerobic digestion process consisting of a stirred acidogenic reactor followed by a stirred methanogenic reactor, which was coupled with membrane filtration for cheese whey effluent treatment. Average removals of COD, BOD_5 and TSS in this system were 98.5, 99 and 100%, respectively. Combining the membrane system with the methanogenic reactor enhanced the daily biogas production, which exceeded 10 times the reactor volume at HRT of 4 days with the average rate of 0.3 LCH_4/gCOD removed. The biogas production increased steadily with the increase in OLR and the biogas methane content was greater than 70%. Xie et al. (2010) investigated the feasibility of employing a SAnMBR for kraft EC treatment at 37 ± 1°C over a 9-month period. The performance of the lab-scale SAnMBR was examined in terms of COD removal and biogas production (chemical composition and rate). The SAnMBR achieved an overall soluble COD removal efficiency of 93–99% with a feed COD concentration varying from 2600–10,000 mg/L. The effluent was colorless, had a very low soluble COD (50–200 mg/L) and zero solids concentration. Under tested OLRs of 1–24 $kgCOD/m^3 \cdot day$, the methane production rates ranged from 0.25–0.40 L CH_4/gCOD removed with the mean value of 0.35 ± 0.05 LCH_4/gCOD removed, which were very close to the theoretical yield of methane (0.397 L CH_4/g COD removed at 37°C). Moreover, an average of 80–90% methane was found in the biogas, indicating higher methane content as compared to conventional anaerobic digestion. In addition, the effective bubbling of recycled biogas could contribute to in-situ membrane cleaning, thereby mitigating membrane fouling. The membrane critical flux increased and the membrane fouling rate decreased with an increase in the biogas sparging rate.

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Lin et al. (2011) operated a lab-scale SAnMBR for municipal secondary wastewater treatment. The methane yield rate of this study was 0.26 L CH_4/gCOD removed with COD removal efficiency of approximately 90%. The high content of methane (75–85%) in the biogas was observed with 5–8% carbon dioxide and 5–15% nitrogen, which demonstrated that municipal wastewater is a great food source for energy recovery through the metabolism of anaerobic methanogens. A pilot-scale SAnMBR for municipal wastewater treatment under mesophilic and psychrophilic temperature conditions was operated by Martinez-Sosa et al. (2011) to measure biogas production and biogas composition. The average methane yields of 0.27 and 0.23 L CH_4/gCOD removed were obtained under mesophilic (35°C) and psychrophilic (20°C) conditions, which represent only 77% and 70% of the maximal theoretical value respectively. This was because not all organic wastes were properly degraded, but physically retained by the membrane in the reactor, and the real amount of degraded organics were supposed to be lower than that was used to calculate the methane yield. Besides, an accumulation of particulate organics in the reactor was observed when the temperature reduced from 28 to 20°C, which might lead to the decrease of methane yield under psychrophilic condition (Martinez-Sosa et al. 2011, 2012).

Apart from excellent effluent quality and energy production, the added benefit of sludge minimization is another highlight of the AnMBR applications. The low biosolids production is due to the fact that AnMBRs can permit a long SRT while maintain a short HRT. Using AnMBR, almost all the particulate and colloidal organics are supposed to be captured, and completely hydrolyzed and decomposed under the condition of the long SRT. Hence, the low sludge yield rate obtained during the treatment can contribute to a significantly reduced sludge handling and disposal cost. Lin et al. (2011) mentioned that the sludge yield of anaerobic digestion was normally less than that of aerobic processes. The SAnMBR they operated showed sludge yield coefficient of 0.032 kg MLSS/kgCOD removed, corresponding well with the value (0.0378 kg MLSS/kgCOD removal; MLVSS: mixed liquor volatile suspended solids) of the external AnMBR (Anderson et al. 1996). Yoo et al. (2012) also reported a low biosolids production when using a lab-scale staged anaerobic fluidized membrane bioreactor (SAF-MBR) system to treat a municipal wastewater primary-clarifier effluent. With the higher membrane flux of 9 $L/m^2 \cdot h$ and lower total system HRT of 2.3 h, total COD and BOD_5 removals of the two-stage system were 84% and 92% respectively. Furthermore, the secondary sludge production (0.031 g VSS/gCOD or 0.049 g VSS/gBOD_5 removed) was far less than the typical 0.42 g VSS/gBOD reported for aerobic secondary wastewater treatment.

25.4.2 Operational Parameter Affecting Biogas Production

There are several important operating parameters, which could influence the performance of AnMBR in terms of biogas yield, such as temperature, pH, HRT and SRT.

Temperature. Temperature is a vital parameter that has profound influences on the biogas production. Basically, anaerobic fermentation can be carried out in three different temperature ranges: psychrophilic (<30°C), mesophilic (30–40°C)

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and thermophilic (50–60°C). When the methane fermentation process is experienced under low-temperature conditions, the hydrolysis and solubilization of complex organic matter into soluble substrates will become a rate-limiting step (Lettinga et al. 2001; Lew et al. 2003, 2009). Psychrophilic temperature can also negatively affect methanogenic activities and slow down the methanogenic process. Besides, the loss of methane is another issue because the solubility of methane is much more enhanced when experiencing low temperatures (Souza et al. 2010).

Theoretically, an increase in operational temperature can accelerate the metabolic rate of the slow-growing anaerobic microorganisms, and benefit the maximum specific growth and substrate utilization rates, and thus increase biogas production. In particular, the growth rate of methanogenic bacteria is higher under thermophilic conditions, making the process faster and more efficient. Hence, a well-functioning thermophilic digester always can be loaded to a higher degree or operated at a lower HRT than at mesophilic conditions. For certain industrial wastewater streams, operating under thermophilic temperatures is of great interest because this kind of wastewater is usually high temperature, and precooling/post-heating used in the mesophilic treatment for the subsequent reclamation of treated effluent could be avoided (Chen and Hashimoto 1980; Yadvika et al. 2004; Chen et al. 2008a; Weiland 2010; Lin et al. 2013). However, higher temperatures do not necessarily always contribute to high biogas yields. In fact, the methane fermentation process can achieve the best results only when the optimal temperature range is adopted in the operation. Temperature higher than the optimal can result in an irreversible damage to proteins and other cellular components, and this will in turn lead to the performance loss of AnMBRs in terms of biogas production issue (Luostarinen 2005; Zhao 2011). Additionally, the temperature of thermophilic process is believed to cause ammonia toxicity problem, the frequent washout of microorganisms, inhibited digestion and unstable fermentation processes (Angelidaki and Ahring 1994; Weiland 2010).

Furthermore, it is crucial to maintain constant temperature during the fermentation processes as methanogens are likely to be affected by sudden temperature changes. Any temperature changes or fluctuations can adversely influence the biogas production. Thermophilic microbes are more sensitive to temperature fluctuations and require longer time to adapt to a new temperature, while mesophilic bacteria tolerate temperature fluctuations of ±3°C without significant reductions in methane production (Garba 1996; Weiland 2010).

Although the drop in temperature can result in the reduction of methane production, it may shift the proportion of methane in the biogas. Martinez-Sosa et al. (2011) mentioned that an increase in methane composite in the biogas was observed when the operational temperature of SAnMBR dropped from mesophilic (35°C) to transition condition (28°C), and this increase was more obvious when the temperature was further reduced to psychrophilic (from 28 to 20°C). This change in the biogas composition could be explained by the difference in gas solubility of two gases (CH_4 and CO_2). Based on Henry's Law, the solubility of methane in water is 11.4 times lower than that of CO_2 considering partial

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pressures of methane and CO_2 of 70 and 30 kPa, respectively, at 20°C. Thus, CO_2 was dissolved in a major proportion in the liquid phase of the reactor and left the reactor dissolved in the effluent. Nevertheless, the solubility of methane also increases with decreasing temperature, and in fact, the solubility of methane at 20°C is around 30% higher than that at 35°C. Therefore, a higher amount of methane could leave the anaerobic reactor in the form of dissolved gas in the effluent under psychrophilic conditions, which eventually cause decrease in overall methane production.

Gao et al. (2011) have also investigated the effects of temperature and temperature shock on the performance of a SAnMBR treating thermomechanical pulping pressate for 416 days. The results showed that the SAnMBR system was highly resilient to temperature variations in terms of COD removal. The residual COD in the treated effluent was slightly higher at 55°C than those at 37 and 45°C, but the removal efficiency was within the range of 76–83% in three cases. At 37, 45 and 55°C steady state, there were no significant changes in biogas production rate as well as biogas composition, and the biogas production rates were 0.21 ± 0.03, 0.20 ± 0.03 and 0.21 ± 0.02 $LCH_4/gCOD$ removed, respectively. On the other hand, temperature shocks led to a temporary increase in biogas generation rate. Although the SAnMBR could tolerate the 5 and 10°C temperature shocks at 37°C and the temperature variations from 37 to 45°C, the temperature shock of 5 and 10°C at 45°C led to slight and significant disturbance of the performance, respectively. Thus, larger magnitudes (10°C) of temperature shock had a more severe impact on the performance of the SAnMBR. In addition, Temperature shocks had little effect on the microbial community structure. However, increasing the operating temperature induced the deflocculation of the large sludge flocs, and the diversity and species richness could be affected by temperature variations.

pH. During anaerobic fermentation, pH variation has been reported to exert significant impact on the microbial metabolism, such as utilization of carbon and energy sources, efficiency of substrate degradation, synthesis of proteins and various types of storage materials, and release of metabolic products from cells. Moreover, pH variation can also affect cell morphology and structure, as well as flocculation and adhesion phenomena (Bailey and Ollis 1986; Gottschalk 1986; Yadvika et al. 2004). Weiland (2010) have stated that methane formation takes place from about 6.5 to 8.5 with an optimum interval between 7.0 and 8.0. The process is severely inhibited if the pH decreases below 6.0 or rises above 8.5. Nevertheless, Ward et al. (2008) have had little different opinion and indicated that the optimum pH for anaerobic digestion appears to be 6–8. The ideal pH range for anaerobic digestion is very narrow, which ranges between 6.8 and 7.2 by feeding at an optimum loading rate. The growth rate of methanogens is severely inhibited when pH falls below 6.6, while an excessively alkaline pH (above 8.5) can lead to disintegration of microbial granules and subsequent failure of the process. Although the optimal pH of methanogenesis is around pH 7.0, the optimum pH for hydrolysis and acidogenesis has been reported between pH 5.5 and 6.5. This is an important reason why some designers prefer the separation of the hydrolysis/acidification and acetogenesis/methanogenesis processes in two-stage processes.

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Till now, AnMBRs have been operated at the pH range of 5.5–8.2 according to different treatment purposes and characteristics of the wastewaters. Most AnMBR systems operate at near neutral pH, and such a pH range is usually maintained through neutralization, which could require the excessive use of chemicals. Normally, as hydrolysis and acidogenesis phases decrease pH values, equalization at a desired pH appears to be a prospective solution although related research was very limited in AnMBR systems. Moreover, the extreme pH conditions in some streams (e.g. industrial wastewaters) not only damage biologic performance, but also affect membrane permeability and lifespan (Lin et al. 2013).

Commonly, the pH value increases by ammonia accumulation during degradation of proteins while the accumulation of VFA decreases the pH value. However, the accumulation of VFA will not always contribute to a pH drop because of the buffer capacity of the substrate. For example, animal manure has a surplus of alkalinity, which stabilizes the pH value at VFA accumulation. Although acetic acid is usually present in higher concentrations than other fatty acids, but propionic and butyric acids have a more inhibitory effect on methanogens. As a result, as a key intermediate in the process, VFA are capable of inhibiting methanogenesis in high concentrations, and the inhibiting effect of VFAs is much higher in AnMBR operating at low pH value (Weiland 2010)

Jane Gao et al. (2010) carried out a 120-day study to investigate the impact of elevated pH shocks (pH 8.0, 9.1 and 10.0) on a SAnMBR for thermomechanical whitewater treatment. The results showed that a pH 8.0 shock had a minor impact, whereas pH 9.1 and 10 shocks had significantly long-lasting negative effects on COD removal, biogas production and membrane performance of the SAnMBR. During pH 9.1 and 10.0 shocks, the COD removal efficiency was dramatically decreased from almost 90% to <75% and from 90% to <30%, respectively. Regarding the biogas production rates, the methane generation was slightly reduced from 0.41 ± 0.04 to 0.38 ± 0.07 LCH_4/gCOD removed when the pH increased from 7.0 to 8.0. However, the biogas production rates were sharply decreased to almost 0 as a response to the pH 9.1 and 10.0 shocks. The gas composition was also remarkably affected by pH shocks. At pH 7.0, the gas phase was composed of about 68% CH_4 and 25% CO_2 with N_2 as the main remainder gas. After the reactor had received a pH 8.0 shock, the CH_4/CO_2 ratio was slightly reduced from 2.7 to 2.1, and recovered within 2 days. Further increased pH shocks resulted in a significant reduction of CH_4/CO_2 and a longer recovery period. When the normal pH (7.0) was resumed, it took approximately 1, 6, and 30 days for the performance of AnMBR to recover for pH 8.0, 9.1 and 10.0 shocks, respectively. Moreover, with the pH 10.0 shock, it exhibited a lower biogas yield (0.35 ± 0.02 vs 0.41 ± 0.01 LCH_4/gCOD removed before the pH 10.0 shock) after the process ran stably. Chemical analysis showed that the ammonia concentration in the mixed liquor (36.5 mg/L) was significantly higher than that (21.8 mg/L) in the feed, implying the accumulation of ammonia in the mixed liquor was caused by biomass death or decay after the pH 10.0 shock. In addition, the elevated pH shocks induced the dispersion of sludge flocs and resulted in the accumulation of colloids and solutes or biopolymers in the sludge suspension, and thus

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deteriorated membrane performance. Statistical analysis showed that the lower ratio of proteins (PN) to polysaccharides (PS) in extracellular polymeric substances (EPS) had a strongly negative effect on the membrane fouling rate. There were smaller size particles deposited on the membrane surface and a more compact and denser cake layer was formed after being exposed to an alkaline shock at pH 10, resulting in higher membrane fouling rates.

HRT and SRT. As two key operational parameters, HRT and SRT are controllable and make contributions to different treatment performance and biomass characteristics. For example, lower HRTs mean smaller reactor, and lower cost, while longer SRTs potentially result in higher soluble COD removal, lower sludge yields for disposal and more methane production (Stuckey 2012). For the conventional anaerobic digestion processes which do not decouple SRT from HRT, long SRTs are necessary to retain slow-growth anaerobic microorganisms, and thus reduce their competitiveness. In contrast, SRT is independent of HRT in AnMBRs, thereby providing easy control of SRT (Van Haandel and Lettinga 1994; Liao et al. 2006; Trzcinski and Stuckey 2010; Stuckey 2012).

In principle, AnMBRs operation with relatively long HRTs and SRTs are favorable, in order to enhance methane recovery and reduce sludge production. However, prolonged HRT may only be able to improve pollutants removal with a limited extent. On one hand, although HRTs of AnMBR (generally >8 h) are longer than those of aerobic MBR (generally 4–8 h), they are compared favorably with conventional anaerobic systems. According to review of Lin et al. (2013), the applied HRTs in AnMBR varied from 2.6 h to 14 d, while the typical HRTs for high strength wastewater treatment and dilute wastewater treatment were 1–10 d and 0.25–2 d, respectively. However, for treating the high-solid-content streams, the applied HRT range of AnMBR is usually higher than the range applied in industrial or municipal wastewater treatment, which ranges at 1.5–11.8 d. This indicated that for particulate stream treatment, a relatively long HRT may be necessary to ensure significant hydrolysis of solid matters. On the other hand, although SRT can determine both treatment performance and membrane fouling of AnMBR, the relationship between SRT and treatment performance or membrane fouling is complex, and highly depends on the applied HRT and the feed characteristics. Normally, since hydrolysis or solubilization stage represents the rate-limiting step in the anaerobic degradation of most solid organic materials, long SRTs are required for hydrolysis proceeds completely at optimal conditions. The applied SRTs in AnMBR, however, are significantly higher than the applied HRTs. In case of municipal wastewater treatment, SRTs have ranged from 19 to 217 d, while for high-solid-content wastes, the SRTs have been employed with a range of 20–335 d (Liao et al. 2006; Lin et al. 2013).

Ho and Sung (2009) studied a lab-scale external AnMBR to treat synthetic municipal wastewater (OLR: 1–2 kgCOD/m^3·d) at different HRTs (6, 8 and 12 h) for 280 d. They concluded that AnMBR operation with relatively long SRTs (90–360 d) and low crossflow velocity (0.1–0.2 m/s) could reduce sludge production. The effluent quality was excellent regardless of HRT variation and COD concentration was always lower than 40 mg/L (>90% removal). However, the fraction of

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methane recovered from the synthetic wastewater decreased from 48 to 35% with the decrease of HRT from 12 to 6 h, which was attributed to the increase of mixed liquor soluble COD accumulated in the AnMBR. Maximum possible methane recovery (0.22 L 0.22 L CH_4/gCOD removed), considering methane solubility, sulfate reduction and cell synthesis, was approximately 50 to 60% at the longest HRT of 12 h.

Huang et al. (2011) evaluated the effects of different SRTs (30, 60 and infinite d) and HRTs (12, 10 and 8 h) on the performance of three SAnMBRs for synthetic low-strength wastewater treatment. Total COD removals higher than 97% were achieved at all operating conditions. Maximum biogas production rate was 0.056 L CH_4/gMLVSS·d at the infinite SRT. The results also elucidated that shorter HRT or longer SRT could promote biogas production due to increased OLR or improved dominance of methanogens. However, shorter HRT enhanced biomass growth and SMP accumulation, which accelerated membrane fouling. In spite of higher carbohydrate and protein concentrations in SMP at longer SRT can lead to higher membrane fouling rate, the effect of SRT on biomass concentration in SAnMBRs was negligible and membrane fouling was controlled at the longest HRT (12 h). Nevertheless, at 8 and 10-h HRTs, infinite SRT in SAnMBR caused highest MLSS and SMP concentrations, which accelerated particle deposition and biofouling development. Additionally, lower bounded EPS at longer SRT reduced flocculation of particulates and particle sizes, further aggravated membrane fouling.

25.5 FUTURE PERSPECTIVES AND RESEARCH NEEDS FOR ANMBR TECHNOLOGY

The review of literature has revealed that much progress has been made in the research and applications of AnMBRs as a future green technology. The key competitive advantages of AnMBRs over conventional aerobic and anaerobic processes have been well documented as follows: 1) total biomass retention; 2) excellent effluent quality; 3) sludge and waste minimization; 4) bioenergy recovery; 5) smaller footprint; 6) lower energy consumption; 7) high efficiency of wastewater treatment; 8) high OLR treatment capacity; 9) strong ability of handling fluctuation in influent quality; 10) high flexibility of treatment mode (either total or pretreatment); and 11) sustainable waste management (Liao et al. 2006; Skouteris et al. 2012; Lin et al. 2013).

Biogas recovery represents one of the key green features of AnMBR technology, particularly for SAnMBR. The compact configure of SAnMBR allows to collect biogas more conveniently. Through a cost analysis, Lin et al. (2011) revealed a benefit value of US$ 341640/year from energy recovery from a full-scale AnMBR, which was about 1.5 times of the annual operational costs. This indicated that it was possible to operate a SAnMBR not only at low costs, but also to create benefit of biogas recovery. However, how to control the system to achieve optimized biogas production is an immediate goal for AnMBR. Till now, the

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process control systems available for monitoring both hydrolysis and fermentation processes have not been successfully applied at the commercial scale due to the complexity for the consortia of organisms. To develop better spectroscopic sensors, gas sensors, the software sensor approach and generic process model are needed to conduct real time measurements, as well as predict important parameters (e.g. pH, temperature or VFA) that incorporate optimal biogas production (Ward et al. 2008; Lin et al. 2013).

Moreover, the results of recent research have demonstrated that strong variations in the community structures occur during the ongoing fermentation process, which influences the process efficiency. Recent molecular analyses have also illustrated the presence of numerous unknown bacteria that may have an important impact on the degradation process (Weiland 2010). Therefore, research on microbial community structure and the influence of the microbial community structure on process stability are also of significance to accomplish kinetic perspective-based improvement of biogas production.

In addition, the development of effective and economical methane recovery process (i.e. reactor design, applying co-digestion, pretreatment of substrates, addition of micronutrients and improving mixing characteristics) also needs attention in order to further improve economic feasibility of AnMBR for real wastewater treatment. Importantly, a study on development multi-stage hybrid AnMBR systems will be promising for future wastewater treatment. Such a process would combine the benefits of anaerobic digestion (i.e. biogas production), aerobic degradation (i.e. nutrient removal) and membrane separation (i.e. pathogen and micropollutants removal). As an increased methane yield and reduced HRT can be fulfilled by increasing the microbial density by immobilization, AnMBR combined with the attached-growth (biofilm) process seems to have great potential advantages of improving process efficiency and reducing fermentation failure.

So far, most literature has been focused on the research on bench-scale AnMBRs; further research of larger scale AnMBRs is needed for their wide implementation for municipal or industrial sectors. Nevertheless, AnMBR has always been facing another crucial challenge of membrane fouling and its consequences, which are not discussed in this chapter due to extensively existing reviews. In spite of the obvious key advantages, membrane fouling of AnMBR remains as a main challenge for its worldwide applications, especially associated with its economic consequences in terms of plant maintenance and operation costs (Lin et al. 2013). Although the comprehensive investigations on membrane fouling mechanisms and fouling control in AnMBRs have been undertaken with intensive efforts, further research is still needed to look for more feasible and easier fouling mitigation measures. High membrane cost is also a critical issue hindering the faster commercialization of AnMBRs, even though the cost of MF and UF membranes used in the majority of projects has been dramatically reduced in recent years. Skouteris et al. (2012) reported that the cost of membranes appear to be up to 10 times higher than the energy consumption cost per m^3 of treated water, and thus can significantly reduce economic affordability and attractiveness. Moreover, Lin et al. (2011) stated that cost analysis of the full-scale SAnMBR

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system indicated that membrane costs and gas scouring energy accounted for the largest fraction of total life cycle capital costs and operational costs, respectively. Although the operational costs can be totally offset by the benefits from biogas recovery, sensitive analysis showed that membrane parameters including flux, price and lifetime play decisive roles in determining the total life cycle costs of the SAnMBR. Therefore, efforts aiming at developing low costs and better performance membranes for AnMBRs are greatly appreciated so as to increase their economic sustainability.

25.6 CONCLUSION

The critical analysis in this chapter provides detailed information about the state-of-the-art development and applications of the AnMBR technology in wastewater treatment. In general, AnMBRs have great potential to efficiently treat a rich variety of wastewaters, producing high-quality effluent ready for recycling or reuse. As a promising future green technology, the biogas recovery in AnMBR not only promote the reduction of greenhouse gases emission but also can fulfill the heating requirements of wastewater treatment plant instead of using fossil fuel. The complex digestion occurring in AnMBR is significantly influenced by many factors such as wastewater characteristics, temperature, pH, HRT, SRT, OLR, nutritional requirements and so on. Among these factors, temperature, pH, HRT and SRT play important roles in biogas production and process stability. In addition, the opportunity of applying such green technology at large- or commercial-scale needs prospective studies to conquered many research challenges such as biogas recovery, better process control, process efficiency, membrane cost, membrane fouling as well as economic issues.

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CHAPTER 26

Composting Toilet for Sustainable Water Management

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26.1 INTRODUCTION

26.1.1 Onsite Wastewater Differentiable Treatment System (OWDTS) for Sustainable Water Management

Centralized water-borne sewage systems leading to multistage sewage treatment plants seem to be unsuitable as a blanket solution for developing countries, particularly in aridzones, due to their enormous investment, operating and maintenance costs, their high water consumption and other drawbacks. These centralized systems are also running into criticism in developed countries because of economic and ecological issues. However, conventional individual disposal systems also make poor alternatives, especially in view of increasing population densities and the substantial groundwater contamination they cause (Werner 2000). With these considerations, the Onsite Wastewater Differential Treatment System (OWDTS), a new approach for improvement of onsite wastewater treatment systems, is proposed based on differential management and treatment of householdwastewater effluents by López Zavala et al. (2002a).

The wastewater effluent from a household or group of households is made up of contributions from various appliances, such as WC, kitchen sink, washbasin, bath, shower, and washing machine as shown in Table 26.1. The WC represents the highest contribution to the wastewater interms of volume and load for five out of the six determinants, the exception being nitrate. The kitchen sink is the most important appliance for nitrate production and second in production of COD, TSS and PO4-P (Almeida et al. 1999).Traditionally, wastewater effluent from a household has been divided into two fractions, blackwater (toilet wastes) and graywater (kitchen sink, wash basin, bath, shower, and washing machine). Elimination of blackwater from the residential wastewater stream by using a non-water carriage toilet will reduce the mass of COD, TSS, nitrogen and

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Table 26.1. Contribution of each appliance to the daily total discharge volumes and pollutants loads (% of totalvolume or mass per capita)

Appliance	*Type of water*	*Volume*	*COD*	*NH_3-N*	*NO_3-N*	*PO_4-P*	*TS*
WC	Black Water	31	44	97	3.8	80	77
Kitchen sink	Higher-load graywater	13	23	0.3	38	9.4	10
Washing machine		16	22	1.2	7.6	4.3	4.0
Wash basin	Lower-load graywater	13	1.7	0.1	11	1.3	2.1
Bath	—	16	2.5	0.6	15	1.1	1.3
Shower	—	12	6.4	0.7	25	4.1	5.1
Total	—	0.1 m^3	110 g	2.4 g	0.37 g	6.7 g	56 g

Source: Made by authors based on the data from Almeida et al. (1999)

phosphorus in the remaining wastewater stream (graywater), thus allowing smaller treatment units(Ayres Associates 1998).

Figure 26.1 shows a hypothetical model for an onsite wastewater differential treatment system proposed by López and Funamizu (2002). In this system, the fractioning of household wastewater into three types is essential. Thus, reduced-volume blackwater, higher-load and lower-loadgraywater are new concepts that are introduced in this model. Here, the treatment of blackwater conceives a change in the traditional way of using the WC. In other words, the use of water in the WC is just to clean the toilet, not to transport the toilet wastes; this is a crucial change that is possible by using a composting toilet. The essential and new concept in the OWDTS is to treat separately the three fractions ofhousehold wastewater. The importance of conceiving differential treatment for each fraction is indicated by the fact that:

1. *Blackwater* is practically eliminated from the household effluent by using the composting toilet. It means approximately 31% of fresh water will be saved

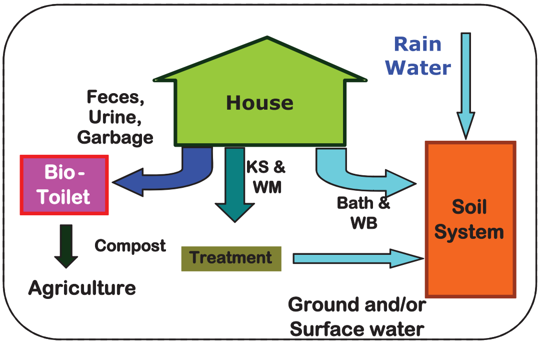

Figure 26.1. The concept of OWDTS

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and 44% of organic load, 97% of NH_3-N, 80% of PO_4-P, and 77.4% of TS will be eliminated from the householdeffluent. Composting toilet is a non-water carriage toilet that uses natural biological decomposition to transformwastes (feces, urine and toilet paper) into a relatively dry, nutrient-rich humus material called compost.

2. *Lower-load graywater* could be treated by utilizing the natural capacity of soil microorganisms as its pollution concentration was found to be 210 to 501 mg-COD/L(Almeida et al. 1999). Regarding the capacity of microorganisms for degrading surfactants in solution, it is expected that soil microorganisms display the same capacity for reduction of COD and denitrification.
3. *Higher-load graywater* with a pollution concentration of 1,079 to 1,815 mg-COD/L represents 29% of household effluent that needs any conventional treatment process forreaching acceptable quality (Almeida et al. 1999). Candidate technologies for higher-load graywater treatment must be robust to contamination from all likely sources. Several researchers around the world have shown interest in graywater treatment, some of them applying technologies developed initially for wastewater treatment.

The benefits of using an onsite wastewater differential treatment system (OWDTS) may be analyzed from the viewpoints of water and soil contamination prevention, conservation of resources, reduction of health risk for population, and economics. Such benefits may be the following:

1. The sources of pathogens, mainly toilet wastes, are eliminated from the wastewaterstream; therefore, the groundwater contamination risk is reduced considerably.
2. The toilet wastes are converted into a stable organic matter source, probably free ofpathogens, that may be recycled into the household when a garden area is available or be disposed in external systems such as urban green areas or agricultural land.

26.1.2 Composting Toilet as a Key Green Technology in OWDTS

Bio-toilet is the name of dry closet or composting toilet using sawdust as an artificial soil matrix for bioconversion of human excreta into compost which can be used either as organic fertilizer rich in N, P and K, or as a soil conditioner (Del Porto and Steinfeld 1998; Kitsui and Terazawa 1999). The bio-toilet consists mainly of a toilet bowl, composting reactor, as well as ventilation and mixing systems. The composting reactor is filled with sawdust, and a button activates the mixer after using the toilet. The human excreta, including toilet paper, are incorporated quietly and odorless into the sawdust matrix where the aerobic biodegradation occurs. Kitsui and Terazawa (1999) reported that sawdust creates an environment for bacteria thriving since high porosity, high void volume ratio, high water and air retention, and high drainage characterize the matrix. The high bacterial tolerance of the woody materials allows the long-time use of sawdust. The

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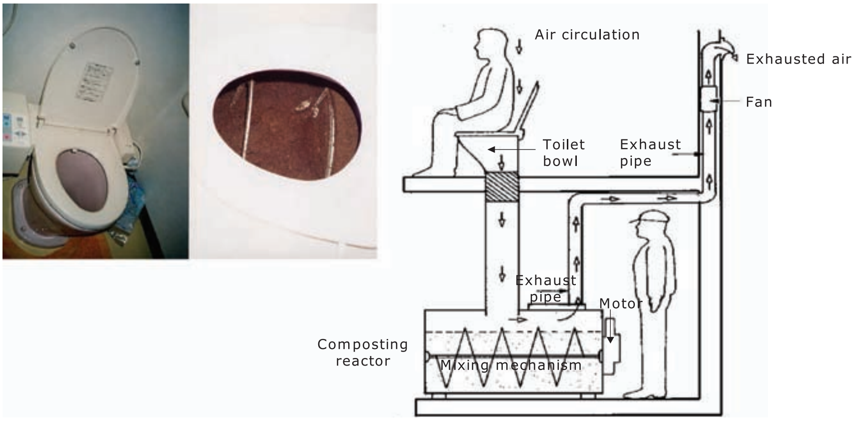

Figure 26.2. Composting toilet
Source: Photo by Funamizu; adapted from López Zavala et al. (2005a); reproduced with permission from Elsevier

low apparent density of sawdust mass saves energy when mixing is performed. However, the key characteristic is the essential biodegradability of sawdust that makes it be an excellent soil conditioner (Kitsui and Terazawa 1999).

The composting toilet considered here (Figure 26.2) differs from conventional composting systems in several ways: 1) sawdust is used as an artificial soil matrix for biological reactions; 2) the composting reactor is provided with heating and mixing systems that ensure a continuous thermophilic-aerobic biodegradation process and a uniform temperature distribution; 3) the moisture content in the reactor is kept in the range of 50–60% by heating and ventilation; and 4) traditional composting systems have batch configuration; whereas the composting toilet here is a continuous feed system with rather constant reaction conditions in terms of temperature and moisture content of sawdust matrix.

Black water contains: 1) organic matter; 2) water; 3) nutrients; 4) pathogenic microorganisms; and 5) micro-pollutants such as hormones and pharmaceuticals. Therefore, evaluating and analyzing functions of the composting toilet from different point of view contributes to the proper planning, design, installation, operation and maintenance of OWDTS, when the bio-toilet is used to eliminate blackwater and nutrients, especially nitrogen and phosphorus, from the household wastewater stream.

26.2 CHARACTERISTICS OF FECES

Performance of the bio-toilet system, and more specifically biodegradation rates, is affected by several factors, including the substrate bio-availability that is mainly associated with the biodegradability of organic matter contained in feces.

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There is a wide range of variability in the content of feces from person to person and place to place. Factors such as nutrition, climate, health, age, and lifestyle are responsible for that variability. In this respect, from the analysis of 26 feces samples, Table 26.2 shows average values for some bulk parameters that indicate in a certain way the organic load and nutrient availability of feces. Data of moisture content, TS and COD are in accordance with those reported by other researchers (Almeida et al. 1999). As seen, approximately 82% of water and 18% of solids constitute feces. 84% of solids are volatile solids (organic material), and 16% are fixed solids (inorganic material). Fixed solids and non-biodegradable VS remainedin the experimental reactor without any transformation.

Characterization of feces has been traditionally carried out regarding the concentration of different constituents or values of several parameters that indicate in certain way the organic load and nutrient availability, as shown in Table 26.2. However, this way of characterizing feces does not allow judging the biodegradability of organic matter contained in feces. Thus, biodegradability of feces should be assessed attending its biodegradable character, non-biodegradable and biodegradable organic matter. This fractioning can be determined through the performance of simple batch tests; measuring the chemical oxygen demand (COD); monitoring the oxygen utilization rate (OUR) and simulating OUR profiles. Additionally, biodegradability may be assessed in terms of mass units by measuring simple physical parameters such as total solids (TS) and volatile solids (VS).

26.2.1 Characterization Based on COD

COD is undoubtedly the superior measure of the concentration of organic material because it alone provides a link between electron equivalents in the

Table 26.2. Pollution load of excreta

Parameter	*Unit*	*Average*	*Almaeida et al. (1999)*
Moisture	%	81.8	79.2
TS	%	18.2	20.8
VS	%	84.4	—
pH	—	7.5	—
EC	µS/cm	115.9	—
COD	mg/mg	1.45	1.38
NH_3-N	mg/g	3.4	7.2
T-N	mg/g	60.1	—
NO_3-N	mg/g	0.03	0.14
Cl	mg/g	4.2	—
SO_4	mg/g	1.1	—
PO_4-P	mg/g	4.5	27.9

Units in mass/mass are expressed on dry basis

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organic substrate, the biomass and oxygen utilized. Furthermore, mass balance can be made in terms of COD (Henze et al. 1987). When characterization is thought for modeling purposes, it is important to note that there is a close relationship between characterization of feces and the model and constants used. The quality of characterization may be evaluated based on biological response (oxygen consumption) during biodegradation, so that, the level of fractioning will be given by modeling and simulating the oxygen utilization rate. Thus, the most proper characterization will be the one that allows better model predictions.

The total organic matter contained in feces can be measured as COD, which can be divided depending on the complexity and the use of the model. López Zavala et al. (2002b) found that feces were constituted by slowly biodegradable particulate organic matter (X_S) and non-biodegradable (inert) particulate matter (X_I). Thus, the total COD of feces includes the following components:

$$TCOD = X_I + X_S \tag{Eq. 26.1}$$

During biodegradation, X_S is transformed into readily biodegradable organic matter (S_S) by hydrolysis; growth of heterotrophic biomass (X_H) occurs at expense of S_S associated with oxygen utilization; under the death-regeneration approach (Henze et al. 1987), decaying biomass is split into two fractions: inert matter (X_{IP}) and slowly biodegradable matter (X_S); the latter is subsequently hydrolyzed into readily biodegradable substrate. The death-regeneration model implies that, even when all the substrate originating from the feces has been oxidized, there remains an oxygen consumption associated with the growth on substrate released from decay. The amount of new biomass formed from the released substrate is always less than the amount of biomass lost (Henze et al. 1987). If the oxygen consumption rate at this stage is quite low, approximating toward to the initial level, it might be able to assume that the fraction associated with biomass is negligible and only two fractions of inert material remain at the end of the biological reaction, X_I and X_{IP}.

The total biological inert material remaining at the end of the biological reaction (X_{IT}) can be expressed as follows:

$$X_{IT} = X_I + X_{IP} = X_I + Y_H(X_S)f_{XI} \tag{Eq. 26.2}$$

where, X_{IT} = total biologically inert material that remains in the experimental reactor, g COD; Y_H = yield coefficient for heterotrophic biomass, g COD $(\text{g COD})^{-1}$; f_{XI} = inert COD production coefficient in endogenous respiration, g COD $(\text{g COD})^{-1}$; and $Y_H(X_S)$ = quantity of biodegradable organic matter that is converted into biomass, g COD. Substituting Eq. 26.1 in Eq. 26.2 and rearranging terms yields:

$$X_S = \frac{TCOD - X_{IT}}{1 - Y_H f_{XI}} \tag{Eq. 26.3}$$

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Estimation of X_S requires the prior determination of stoichiometric parameters such as biomass yield coefficient Y_H and the inert COD production coefficient in endogenous respiration f_{XI}. Estimation of them constitutes a real challenge due to the difficulty of measuring directly the biomass growth in the sawdust matrix; so that, conservative values of these parameters are adopted from those reported in the literature of activated sludge systems, mainly determined at 20°C. Regarding the uncertainty associated with the impact of temperature on yield coefficient, most engineers assume it to be independent of temperature (Grady et al. 1999). Thus, Y_H and f_{XI}, were set as 0.63 g COD $(\mathrm{g\,COD})^{-1}$ and 0.10 g COD $(\mathrm{g\,COD})^{-1}$, respectively (Kappeler and Gujer 1992; Spanjers et al. 1995; Vanrolleghem et al. 1999).

Based on COD reductions observed during batch tests performance, the fraction of total biologically inert material (X_{IT}) remaining in the experimental reactor is estimated. Thus, substituting this known term and values of Y_H and f_{XI} in Eq. 26.3, fractions X_S, X_I and X_{IP} are determined from Eqs. 26.3, 26.1 and 26.2, respectively.

For easier comparisons, all values of fractions shown below are expressed in decimal fractions (relative values respect to TCOD). López Zavala et al. (2001) evaluated the effect of organic loading on the aerobic biodegradation of feces using sawdust as a matrix; they found that the fraction of total biologically inert material (X_{IT}) remaining in the experimental reactor after biodegradation was 25%. Substituting this value and those adopted for stoichiometric parameters in Eq. 26.3 yields:

$$\frac{X_S}{TCOD} = \frac{1 - X_{IT}/TCOD}{1 - Y_H f_{XI}} = \frac{1 - 0.25}{1 - 0.63 * 0.10} = 0.80$$

Therefore, from Eqs. 26.1 and 26.2, the values of following fractions were obtained:

$$\frac{X_I}{TCOD} = 0.20$$

and

$$\frac{X_{IP}}{TCOD} = 0.05$$

26.2.2 Characterization in Terms of Mass Units

Knowledge of the amount and character of the compost produced during the aerobic biodegradation of feces allows proper design and operation of the bio-toilet system, since quantity of remaining residue is increasing with the time and the composition of such residue determine the quality of the compost generated.

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Characterization of feces based on mass units may be an affordable way for evaluating the quantity and composition of the residue accumulated in the composting reactor. Hypothetical composition of feces regarding mass units (g) assumes that feces are composed by fixed solids (X_{FS}) that are biologically inert, non-biodegradable volatile solids (X_{NB}) that are also biologically inert and biodegradable volatile solids (X_B) which are used by heterotrophic biomass to growth, fixed solids (X_{FS}), and non-biodegradable volatile solids (X_{NB}) remain in the composting reactor without any transformation. During biodegradation, fixed solids production (X_{FSP}) occurs since some chemical species (S, P) contained in feces change to their oxidized form trapping oxygen in their molecular structure (Kaiser 1996). Biologically inert volatile solids (X_{BIP}) are produced in endogenous respiration and, besides X_{FSP}, remain in the composting chamber. Thus, the total mass of feces solids (TS) includes the following components:

$$TS = X_{FS} + (X_{NB} + X_B) \qquad \text{(Eq. 26.4)}$$

The total mass of solids remaining in the experimental reactor encompasses:

$$TS_R = (X_{FS} + X_{FSP}) + (X_{NB} + X_{BIP}) \qquad \text{(Eq. 26.5)}$$

X_{FS} is estimated gravimetrically on the base of total solids and volatile solids measurements as follows:

$$X_{FS} = TS - VS \qquad \text{(Eq. 26.6)}$$

where TS and VS are expressed in mass units (g).

On the other hand, the total mass of remaining volatile solids (VS_R) may be expressed as follows:

$$VS_R = X_{NB} + X_{BIP} = X_{NB} + Y'_H(X_B)f'_{XI} \qquad \text{(Eq. 26.7)}$$

where, $Y'_H = Y_H$ expressed in g VS $(\text{g VS})^{-1}$; $f'_{XI} = f_{XI}$ expressed in g VS $(\text{g VS})^{-1}$; and $Y'_H(X_B)$ = quantity of biodegradable volatile solids that is converted into biomass, g VS. Substituting $VS = X_{NB} + X_B$ in Eq. 26.7 yields:

$$X_B = \frac{VS - VS_{\mathrm{R}}}{1 - Y'_H f'_{XI}} \qquad \text{(Eq. 26.8)}$$

Then, X_{NB} and X_{BIP} are computed from Eq. 26.7.

Estimation of X_B requires the prior determination of the stoichiometric parameters Y'_H and f'_{XI}. Those values adopted in COD characterization may be used but expressing them in mass units, g VS $(\text{g VS})^{-1}$. Conversion factors are used for that purpose.

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As seen, it is not required to know X_{FSP} for estimating the fractions that constitute feces; however, it can be determined as follows:

$$X_{FSP} = TS_R - VS_R - X_{FS} \qquad \text{(Eq. 26.9)}$$

For easier comparisons, all values of fractions shown below are expressed in decimal fractions (relative values respect to TS). As shown in Table 26.2, volatile solids constitute approximately 84% of feces; therefore, from Eq. 26.6 the fraction (X_{FS}) was computed as 16%.

The conversion factor VS to biomass was estimated as 0.76 g VS $(\text{g COD})^{-1}$ from activated sludge literature (Gujer et al. 1999). Based on VS and COD measurements, the conversion factor VS to substrate was approximately 0.58 g VS $(\text{g COD})^{-1}$ and adopting the same ratio for VS to X_{BIP}, the stoichiometric parameters expressed in mass units yields:

$$Y'_H = 0.48 \text{ g VS}(\text{g VS})^{-1} \quad \text{and} \quad f'_{XI} = 0.13 \text{ g VS}(\text{g VS})^{-1}$$

On the other hand, López Zavala et al. (2001) found that approximately 70% of feces VS was depleted during batch test performance. Substituting this value and those for stoichiometric parameters in Eq. 26.8 yields:

$$\frac{\mathrm{X_B}}{\mathrm{TS}} = \frac{(\mathrm{VS} - \mathrm{VS_R})/\mathrm{TS}}{1 - \mathrm{Y'_H f'_{XI}}} = \frac{0.84 \times 0.70}{1 - 0.48 \times 0.13} = 0.63$$

Hence, from Eq. 26.7 the values of following fractions were computed:

$$\frac{\mathrm{X_{BIP}}}{\mathrm{TS}} = 0.48 \times 0.63 \times 0.13 = 0.04 \quad \text{and} \quad \frac{\mathrm{X_{NB}}}{\mathrm{TS}} = 0.84 \times 0.30 - 0.04 = 0.21$$

López Zavala et al. (2001) also found that total solids remaining in the experimental bioreactor (TS_R) counted approximately 44%; thus, substituting these values in Eq. 26.9 yields:

$$\frac{X_{\mathrm{FSP}}}{TS} = 0.44 - 0.84 * 0.30 - 0.16 = 0.03$$

Figure 26.3 summaries schematically the results obtained by applying the two methods of characterizing feces. Characterization based on mass units may be useful for assessing the quantity and character of residue that accumulates in the composting reactor of bio-toilet systems, whereas characterization of feces based

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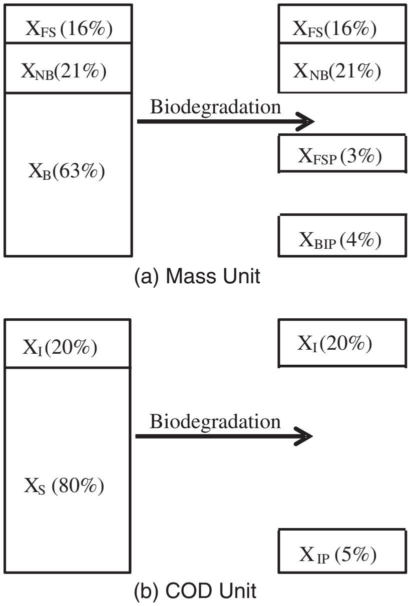

Figure 26.3. Theoretical composition of feces and its transformation during biodegradation
Source: López Zavala et al. (2002b)

on COD measurements is convenient for modeling purposes, technique that allows the establishment of criteria for the proper design and operation of bio-toilet systems.

26.3 BIODEGRADATION OF ORGANIC MATTER DURING COMPOSTING PROCESS AND ITS MATHEMATICAL MODEL

Knowledge of the amount and character of the compost produced during the aerobic biodegradation of feces allows proper design and operation of the bio-toilet system, since quantity of remaining residue is increasing with the time, and the composition of such residue determines the quality of the compost generated (López Zavala et al. 2002b). On the other hand, biodegradability of feces can be assessed by conducting mass balances of simple physical and chemical parameters such as total solids (TS), volatile solids (VS), and chemical oxygen demand (COD). Reduction and stabilization of organic matter are a result of microorganisms' activity. Thus, biological activity in the biotoilet system is assessed by quantification of reductions in TS, VS, and COD, i.e., based on the quantity of the residue accumulated in the composting reactor and its chemical oxygen demand.

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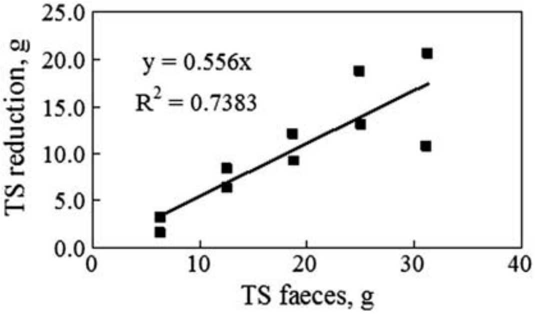

Figure 26.4. Total solids (TS) reduction during the aerobic biodegradation of feces
Source: López Zavala et al. (2005a); reproduced with permission from Elsevier

Figure 26.4 shows the TS reductions observed on experiments where five organic loads were evaluated. TS reduction is correlated to the TS of feces used in each organic loading, for instance, 6.5 g TS feces for F/S = 5%. As seen, there is a clear linear correlation between TS reduction and organic loading. Furthermore, the TS reduction was approximately 56% irrespective of the organic loading. It means that about 44% of TS of feces remained in the composting reactor.

Similarly, the VS reductions determined for the five organic loads were correlated to the organic loading expressed in terms of VS of feces, as depicted in Figure 26.5. Like TS, a clear linear correlation between VS reduction and organic loading was observed; however, the VS reduction was nearly 70% irrespective of the organic loading regarded. Thus, 30% VS remained in the composting reactor after biodegradation.

Results of mass balance made in terms of COD for the two whole experiments and for the five organic loads are plotted in Figure 26.6; like TS and VS, COD reduction showed a linear correlation to feces COD. However, the COD reduction totalized 75% irrespective of the organic loading. It means that 25% of biological inert material remained in the composting reactor.

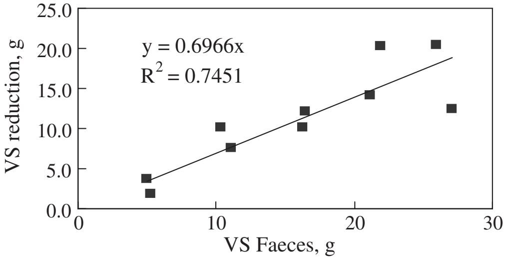

Figure 26.5. Volatile solids (VS) reduction during the aerobic biodegradation of feces
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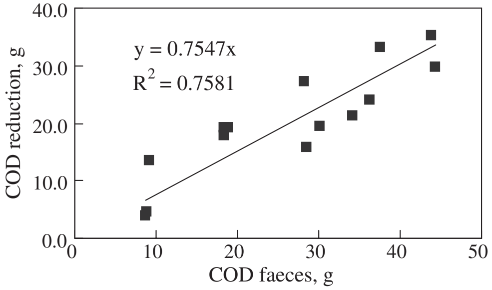

Figure 26.6. Chemical oxygen demand (COD) reduction during the aerobic biodegradation of feces

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It is important to mention that biodegradation occurred only on feces as shown by the experimental tests conducted only with sawdust, under the same conditions, and with addition of essential nutrients for microorganisms such N, P, and K. As seen, decomposition (COD reductions) of sawdust was not observed (Figure 26.7). This is in agreement with results reported by other researchers. For instance, Kaiser (1996) mentions that microorganisms are responsible for degrading sawdust such as actinomycetes and fungi stop growing at thermophilic temperatures, conditions prevailed during the batch tests. Kitsui and Terazawa (1999) found that even though bacteria are the microorganisms responsible for biodegradation of feces in the composting reactor of the biotoilet system, sawdust showed high bacterial tolerance. Furthermore, these results denote that organic loads and F/S ratio were not influenced by the existence of organics in the sawdust. Indeed, they existed but they are already biologically inert materials.

Thus, above results show that biodegradation of feces (in terms of TS, VS, and COD reductions), under thermophilic conditions, is kept constant irrespective of the organic loading in the range of loadings used in the experiments. Thus, limitations to increase organic loading beyond the F/S = 25% will be imposed by constraints related to high moisture content levels rather than the organic loading itself, because increases in the quantity of feces to be degraded imply necessarily high levels of moisture content in the sawdust matrix.

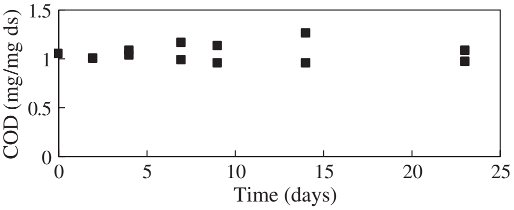

Figure 26.7. Tolerance of sawdust to bacterial decomposition

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The practical implication of above results can be visualized as follows. The feces production rate per adult per day is approximately 130 g (wet basis) (Almeida et al. 1999), and feces are constituted by 82% of water (López Zavala et al. 2002b). Therefore, approximately 23.5 g TS are excreted per adult per day. As shown above, 44% of TS remains in the composting reactor after biodegradation, so that, it is expected that every day 10.3 g of TS are becoming part of the sawdust matrix of the composting reactor. Regarding that sawdust can be used as a matrix for long time (6 months, 1 year, or longer) (Terazawa 1997), and a household integrated by four members uses the bio-toilet, the amount of TS accumulated in the composting reactor of the bio-toilet yields approximately 7.6 and 15 kg for 6 months and 1 year, respectively. This mass occupies a volume of the composting reactor that must be considered during the process of design and operation of the bio-toilet.

26.3.1 Reaction Kinetics

The models developed for conventional composting processes include simple formulations of biodegradation kinetics and deal mainly with energy and water balances. Therefore, formulation of kinetics that can reasonably describe the biodegradation process in the bio-toilet system is required for better modeling predictions. In this work, a bio-kinetic model is introduced to describe the aerobic biodegradation of feces in the bio-toilet system. This model includes three processes for carbonaceous material degradation and is prepared by using the activated sludge modeling techniques and formulations. Stoichiometric parameters were adopted from the literature in activated sludge processes. Kinetic parameters are estimated by conducting batch tests for several organic loadings and by using respirometry, curvefitting techniques, and sensitivity analysis. Feasibility and applicability of these parameters are assessed by conducting feces intermittent-feeding tests and by simulating the experimental respiration rates. Model, stoichiometric and kinetic parameters proved to be affordable for describing the biodegradation of feces in the bio-toilet system.

The activated sludge models in their different versions (Henze et al. 1987; Gujer and Henze 1991; Henze et al. 1995, 1999)include all or some processes associated with carbonaceous material biodegradation, nitrogen and phosphorous transformations. Some of them occur under aerobic, anoxic or anaerobic conditions. Regarding carbonaceous material biodegradation, three transformation processes are considered. One describes the hydrolysis process, in which complex organic materials become available for biodegradation in the form of simpler molecules; the second relates to the growth of heterotrophic biomass, and the third one represents thedecay of biomass. Nitrogen transformations are mainly associated with ammonification, nitrification and denitrification where processes such as hydrolysis, growth and decay of nitrifying, and denitrifying biomass are involved. Phosphorous transformations generally consider cell internal storage of product, growth and decay of phosphorus-accumulating organisms.

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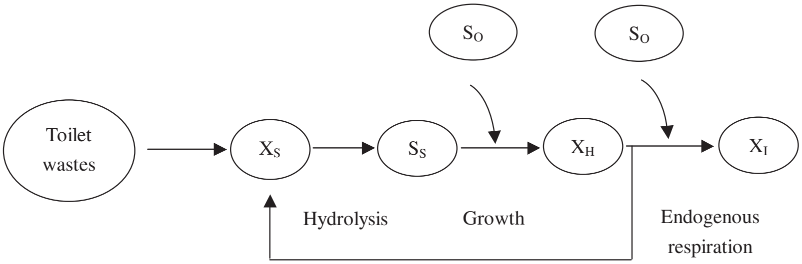

Figure 26.8. Modeling approach for the aerobic biodegradation of toilet wastes
Source: López Zavala et al. (2004a); reproduced with permission from Elsevier

Our interest concentrates on describing the kinetics of aerobic biodegradation of carbonaceous material contained in feces (not included toilet paper); therefore, as shown in Figure 26.8, three processes are selected for preparing the bio-kinetic model: hydrolysis, growth, and endogenous respiration. We adopted the concepts and notation of the activated sludge models; where, slowly biodegradable substrates (X_S) are high molecular weight, colloidal and particulate substrates, which must undergo cell external hydrolysis before they are available for degradation. It is assumed that a product of hydrolysis is readily biodegradable (S_S) material, a soluble fraction directly available for biodegradation by heterotrophic organisms (Henze et al. 1987; Gujer and Henze 1991; Henze et al. 1995; Henze et al. 1999). By following these concepts and notation, López Zavala et al. (2002b) conducted the characterization of feces. They found that biodegradable fraction of feces was constituted by slowly biodegradable organic matter (X_S). This material is transformed into readily biodegradable organic matter (S_S) by hydrolysis and used by heterotrophic biomass (X_H). One portion of the consumed S_S is oxidized to provide energy, and the remainder of the substrate molecules is reorganized into new cell mass. Under the death-regeneration approach (Henze et al. 1987), decaying biomass is split into two fractions: inert matter (X_I) and slowly biodegradable matter (X_S); the latter is subsequently hydrolyzed into readily biodegradable substrate (Figure 26.8).

The processes incorporated into the model are listed in Table 26.3, adopting matrix notation that appears to be the most efficient method to overview the complex transformations among the components (Gujer and Henze 1991). Hydrolysis and aerobic growth according to Monod kinetics and endogenous respiration according to first-order kinetics are the three processes of the model. They are listed in the first column as processes j: five components (i) are considered; four of them are associated with carbonaceous material biodegradation (S_S; X_H; X_S; X_I) and the other one with oxygen (S_O). Short definitions with units are included in the bottom of Table 26.3. The center of Table 26.3 contains the stoichiometric coefficients for the different processes in the form of a stoichiometric matrix. The stoichiometry of the three transformation processes considers conservation principles for chemical oxygen demand (COD).

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Table 26.3. Bio-kinetic model for aerobic biodegradation of feces by using sawdust as a matrix

	Components (i)					
Processes (j)	S_O O_2	S_S *COD*	X_H *COD*	X_S *COD*	X_I *COD*	*Process Rate Equation*
Hydrolysis		1.0		−1.0		$k_H \frac{X_S/X_H}{K_X+X_S/X_H} X_H$
Heterotrophic organisms						
Aerobic growth		$-\frac{1}{Y_H}$	1.0			$\mu_H \frac{S_S}{K_S+S_S} \frac{S_O}{K_O+S_O} X_H$
Aerobic endogenous respiration	$-(1-f_{XI})$		−1.0		f_{XI}	$b_H X_H$

Definition of terms

Y_H: Yield coefficient for heterotrophic biomass, g COD $(\mathrm{g\,COD})^{-1}$.
f_{XI}: Inert COD production in endogenous respiration, g COD $(\mathrm{g\,COD})^{-1}$.
S_O: Oxygen concentration in the bioreactor, g O_2.
S_S: Readily biodegradable organic matter, g COD.
X_H: Heterotrophic organisms, g COD.
X_S: Slowly biodegradable organic matter, g COD.
X_I: Inert organic material, g COD.
μ_H: Heterotrophic maximum growth rate, d^{-1}.
b_H: Coefficient for endogenous respiration, d^{-1}.
k_H: Hydrolysis rate constant, g COD $(\mathrm{g\,COD} * \mathrm{d})^{-1}$.
K_X: Hydrolysis saturation constant, g COD $(\mathrm{g\,COD})^{-1}$.
K_S: Saturation constant for substrate S_S, g COD.
K_O: Saturation constant for S_O, g O_2.

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26.3.2 Numerical Solution of Process Rate Equations

Regarding isothermal, uniform and thoroughly mixed conditions based on the assumptions stated above, the numerical solution of process rate equations, included in Table 26.3, is performed by solving the mass balance Eqs. 26.10 to 26.14 for every component (i)

For oxygen

$$\frac{dS_O}{dt} = \frac{Q_a}{V}(S_{Oi} - S_O) + \left[\left(1 - \frac{1}{Y_H}\right)\mu_H \frac{S_S}{K_S + S_S}\frac{S_O}{K_O + S_O}X_H - (1 - f_{XI})b_H X_H\right] \quad \text{(Eq. 26.10)}$$

where Qa = input air flow rate ($\mathrm{l\,d^{-1}}$); S_{O_i} = oxygen concentration of input air ($\mathrm{g\,O_2}$); and V = volume of the bioreactor (l).

For readily biodegradable organic matter

$$\frac{dS_S}{dt} = k_H \frac{X_S/X_H}{K_X + X_S/X_H}X_H - \frac{1}{Y_H}\mu_H \frac{S_S}{K_S + S_S}\frac{S_O}{K_O + S_O}X_H \quad \text{(Eq. 26.11)}$$

For heterotrophic organisms

$$\frac{dX_H}{dt} = \mu_H \frac{S_S}{K_S + S_S}\frac{S_O}{K_O + S_O}X_H - b_H X_H \quad \text{(Eq. 26.12)}$$

For slowly biodegradable organic matter

$$\frac{dX_S}{dt} = -k_H \frac{X_S/X_H}{K_X + X_S/X_H}X_H \quad \text{(Eq. 26.13)}$$

For inert material

$$\frac{dX_I}{dt} = f_{XI} b_H X_H \quad \text{(Eq. 26.14)}$$

Integration of differential expressions of mass balance equations for each component can be implemented by means of a simulation program that uses a numerical method, for instance the Runge-Kutta method. The simulation program might have inputs such as stoichiometric and kinetic parameters; initial conditions (S_O, S_S, X_H, X_S, X_I); as well as S_{Oi}, Qa, V, time interval, and simulation time.

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26.3.3 Determination of Initial Concentration of Components (I) of Bio-Kinetic Model

Components S_S, X_S and X_I of the bio-kineticmodel are determined through the evaluation of biodegradability of organic matter contained in feces. Characterization of feces for bio-toilet systems using sawdust as a matrix was conducted by López Zavala et al. (2002b)attending the biodegradability of organic matter contained in feces. They characterized feces on COD basis into two fractions, biologically inert material (X_I) 20% and slowly biodegradable organic matter (X_S) 80%. Readily biodegradable organic matter (S_S) was not considered as a constituent of feces, i.e. $S_S = 0\%$.

Initial concentrations of heterotrophic microorganisms (X_H) can hardly be found experimentally (Kaiser 1996). For engineering applications, biomass has been defined as a calculated biomass, based on measurement of the oxygen utilization rate (OUR), i.e. an activity-based biomass determination (Bjerre et al. 1995). Thus, the concentration of heterotrophic biomass is calculated based on the initial OUR value. This value is associated exclusively to the heterotrophic biomass contained in the sawdust since i) sawdust used in the experimental bioreactor was taken from a bio-toilet under operation where biological activity had occurred, ii) biomass contained in feces grows under anaerobic conditions in the human intestine, therefore, it is expected a negligible contribution to the initial OUR value.

The oxygen concentration in the bioreactor S_O is estimated based on oxygen measurements in the outlet of the experimental bioreactor assuming that the oxygen concentration in the exhausted air is the same as the homogeneous reactor concentration, and that O_2 can only be consumed by the oxidation of organic matter.

26.3.4 Estimation of Stoichiometric Parameters, Y_H and F_{XI}

Estimation of stoichiometric parameters in the bio-toilet system constitutes a real challenge due to the difficulty to measure directly the biomass growth in the sawdust matrix. Kaiser (1996) considers that in composting processes, only indirect information of stoichiometric parameters can be obtained on the progress of matter conversion; thus, only limited precision of derivative parameters can be achieved. He used a yield coefficient of 0.2 kg/kg for simulating composting processes; however, he did not describe the procedure for the parameter estimation.

On the other hand, in activated sludge models, procedures and techniques have been developed for estimating the yield coefficient for heterotrophic biomass (Y_H) and the coefficient for inert COD production in endogenous respiration (f_{XI}) (Henze et al. 1987; Sollfrank and Gujer 1991; Brands et al. 1994). However, they cannot be applied to our system because the techniques employed were developed for a liquid medium.

Human excrement is an important contributor of organic matter in domestic wastewaters. Almeida et al. (1999) reported COD contributions of approximately 44% of the total COD in wastewater. Thus, organic matter in the composting

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reactor of the bio-toilet system is assumed to be not so different from that found in sewage systems. In addition, regarding the uncertainty associated with the impact of temperature on yield coefficient, most engineers assume it to be independent of temperature (Grady et al. 1999). Hence, average values of Y_H and f_{XI} may be adopted from those reported in the literature of activated sludge systems, mainly determined at 20°C. Thus, Y_H and f_{XI}, were set as 0.63 g COD $(\mathrm{g\,COD})^{-1}$ and 0.10 g COD $(\mathrm{g\,COD})^{-1}$, respectively (Henze et al. 1987, 1995, 1999; Gujer and Henze 1991; Sollfrank and Gujer 1991; Kappeler and Gujer 1992; Brands et al. 1994; Spanjers and Vanrolleghem 1995; Gujer et al. 1999; Vanrolleghem et al. 1999). The validity of such assumed values should be confirmed by comparison of model predictions and experimental data.

26.3.5 Estimation of Kinetic Parameters: k_H, K_X, K_S, and b_H

Respirometry (measurements of the oxygen utilization rates in simple batch tests), curve-fitting techniques and sensitivity analysis are common tools used for estimating such parameters in activated sludge systems (Kappeler and Gujer 1992; Spanjers and Vanrolleghem 1995; Vanrolleghem et al. 1999). The parameter estimation is performed as a systematic parameter variation in response to feedback from simulation results. This method succeeds because each parameter is almost uniquely responsible for the shape or certain parts of the OUR profile, the parameters can thus be almost completed separated (Kaiser 1996).

These techniques and a simulation program can be used to determine the kinetic parameters as follows:

a) A trial is selected, for instance a feces-sawdust ratio (F/S) 5%, and then the simulation program is fed with the input data shown in Table 26.4 and average values of kinetic parameters reported in the literature of activated sludge and composting processes, for a temperature condition similar to that fixed in experimental batch tests.

b) One kinetic parameter, for instance k_H, is selected to conduct systematic variations meanwhile the rest of kinetic parameters are kept constant. Then, its contribution is observed for the shape or certain parts of the OUR profile and a sensitivity analysis is conducted to determine the parameter influence on the respiration rate. A sensitivity of all parameters is regarded to be 15% of deviation respect to the parameter value with the best curve-fitting. However, in case of those parameters with low sensitivity, a higher deviation is considered, for instance 50%. Thus, the best-fitting value in response to the feedback from simulation results is chosen.

c) The simulation program is run for the next scenario, where another kinetic parameter is varied systematically keeping constant the rest of parameters including the best-fitting value already determined.

d) The last step is repeated until the best-fitting value for all kinetic parameters is determined and the experimental OUR profile is properly fitted by the simulated one.

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Table 26.4. Input data used for estimating kinetic parameters

	F/S ratio (%)			
Input data	*5*	*10*	*15*	*25*
Air flow Q_a (l/d)	72.0	72.0	72.0	144.0
Reactor volume V (l)	1.77	1.77	1.77	1.77
S_{Oi} (g O_2)	0.5	0.5	0.5	0.5
S_S (g COD)	0.0	0.0	0.0	0.0
X_H (g COD)	0.4	1.3	0.4	1.3
X_S (g COD)	7.2	15.0	23.4	35.5
X_I (g COD)	1.8	3.7	5.9	8.9
Y_H (g COD/g COD)	0.63	0.63	0.63	0.63
f_{XI} (g COD/g COD)	0.10	0.10	0.10	0.10

e) The already estimated kinetic parameters are used to feed the simulation program for the next trials and the steps b) to d) are repeated. Thus, best-fitting kinetic parameters for each trial are determined.

Table 26.4 shows the input data used during simulations; the initial concentration of components X_S and X_I corresponds to 80% and 20% of total COD of feces, respectively, as described above.

26.3.6 Batch Tests

Batch tests for four different feces/sawdust ratios (F/S: 5%, 10%, 15% and 25%, on dry basis) were conducted at 55°C and under the conditions described in Table 26.5. The composting bioreactor of bio-toilet systems is in practice operated under organic loadings near to the F/S 10%, however, in this case a wider range was covered. Feces were properly mixed with the sawdust for ensuring uniform and thoroughly mixed conditions, and initial moisture content of the mixtures

Table 26.5. Experimental conditions set up for batch tests

F/S¹ (%)	*TS feces² (g)*	*TS sawdust² (g)*	*Moisture content of feces (%)*	*Initial moisture content (%)*	*Air flow rate (ml/min)*
5	6.3	125.0	80.4	60.0	50.0
10	12.5	125.0	84.7	60.0	50.0
15	18.8	125.0	73.4	60.0	50.0
25	31.2	125.0	83.8	60.0	100.0

Note: 1. F/S ratios (on dry basis) were fixed based on experimental results reported by Terazawa (1997); 2. TS: Total solids expressed on dry basis

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Table 26.6. Kinetic parameters obtained from batch tests

Kinetic parameters	*F/S ratio (%)* 5	10	15	25	*Adopted*[1]
μ_H (d^{-1})	68.0	68.0	68.0	68.0	68.0
b_H (d^{-1})	0.2	0.2	0.2	0.2	0.2
k_H (g COD $(\text{g COD} * \text{d})^{-1}$)	18.5	18.5	18.5	18.5	18.5
K_X (g COD $(\text{g COD})^{-1}$)	8.9	3.3	7.9	2.8	5.7
K_S (g COD)	4.0	4.0	4.0	4.0	4.0

Note: 1: Values adopted after confirmation of kinetic parameters by simulating experimental OUR profiles obtained from feces intermittent-feeding tests

was adjusted to 60%. Enough air was supplied in each trial for keeping aerobic conditions. Input and output oxygen concentrations were monitored every 20 minutes, and the corresponding COD and moisture content of feces, sawdust, and composted material were measured in all trials.

Based on results of batch tests and sensitivity analysis conducted by using a simulation program described above, kinetic parameters were estimated. Table 26.6 summarizes the results.

26.3.7 Feces Intermittent-Feeding Tests

Tests were conducted to confirm the kinetic parameters estimated in batch tests. Four different feces intermittent-feeding tests were conducted at 55°C and under the conditions described in Table 26.7. Four feedings of feces were performed for every trial regarding several feces- sawdust ratios within the range regarded in

Table 26.7. Experimental conditions set up for feces intermittent-feeding tests

		Feces feeding (on dry basis)							
		1st		*2nd*		*3rd*		*4th*	
Trial	*Air flow rate (ml/min)*	*TS (g)*	*F/S (%)*	*TS (g)*	*F/S (%)*	*TS (g)*	*F/S (%)*	*TS (g)*	*F/S (%)*
1	50.0	10	10	8.4	8.4	12.2	12.2	8.1	8.1
2	50.0	10	10	6.3	6.3	11.9	11.9	8.1	8.1
3	75.0	10	10	6.3	6.3	14.1	14.1	12.7	12.7
4	100.0	20	20	5.8	5.8	16.8	16.8	15.9	15.9
Frequency of feces feeding (d)		0		3		6		9	

TS: Total solids expressed on dry basis

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batch tests (5–25%). Frequency of feeding was approximately every 3 days. Similarly to batch tests, feces were thoroughly mixed with the sawdust for ensuring uniformity and enough air was supplied in each trial for keeping aerobic conditions. Input and output oxygen concentration was monitored every 20 minutes and the corresponding COD and moisture content of feces, sawdust, and composted material were measured in all trials.

Using the kinetic parameters already estimated, simulation of experimental OUR profiles obtained from feces intermittent-feeding tests was performed. Table 26.8 shows the input data for simulation. Initial X_H value was calculated based on the initial OUR value observed, and the initial concentration of

Table 26.8. Input data for simulating the OUR profiles of feces intermittent-feeding tests

	Stoichiometric parameters					
Y_H (g COD/g COD)			0.63			
f_{XI} (g COD/g COD)			0.10			
	Input					
	Q_a (l/d)	V (l)	S_S (g COD)	X_H (g COD)	X_S (g COD)	X_I (g COD)
Trial 1						
1	72.0	1.77	0.0	4.6	11.0	2.8
2			0.0		9.5	2.4
3			0.0		14.4	3.6
4			0.0		10.3	2.6
Trial 2						
1	72.0	1.77	0.0	3.6	10.6	2.6
2			0.0		7.1	1.8
3			0.0		13.4	3.3
4			0.0		10.3	2.6
Trial 3						
1	108.0	1.77	0.0	2.7	11.8	2.9
2			0.0		7.1	1.8
3			0.0		15.9	4.0
4			0.0		14.1	3.5
Trial 4						
1	144.0	1.77	0.0	5.3	23.2	5.8
2			0.0		6.7	1.7
3			0.0		20.0	5.0
4			0.0		17.7	4.4

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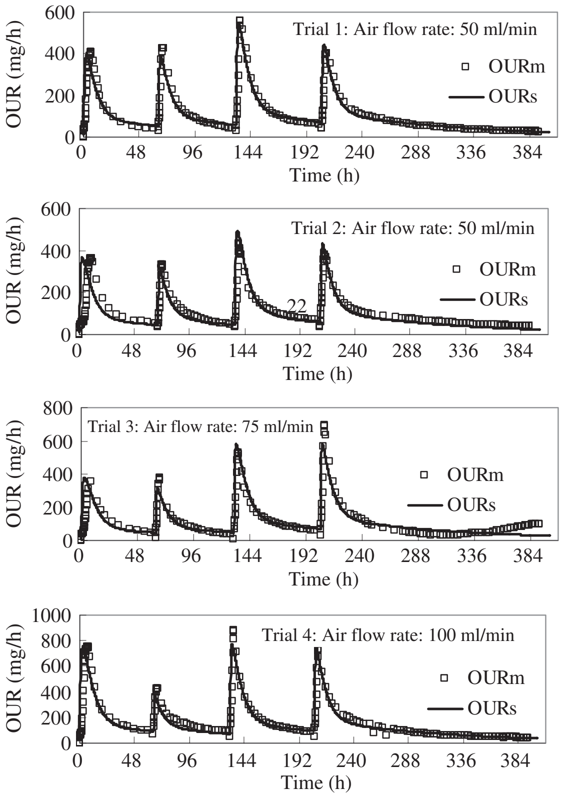

Figure 26.9. Simulation of the OUR profile for four different feces intermittent-feeding tests

Source: López Zavala et al. (2004a); reproduced with permission from Elsevier

components X_S and X_I corresponds to 80% and 20% of total COD of feces, respectively.

Simulation results of feces intermittent-feeding tests are depicted in Figure 26.9. As shown, the simulated OUR profiles follows properly the trend defined by the experimental data, except in the first reaching peak where the deviation of simulated OUR profile is a little higher. A small deviation is also observed between the peaks of the experimental data and simulated OUR. The first deviation is caused probably by the initial and boundary conditions; whereas the second one is introduced by the adoption of an average value for K_X, which seems to be affected by the moisture content of feces, as explained above. In spite of these deficiencies, the simulated results are quite acceptable; therefore, the assumed stoichiometric and estimated kinetic parameters are affordable for describing the aerobic biodegradation of feces. The kinetic parameters adopted after confirmation are presented in Table 26.6.

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Simulation of feces intermittent-feeding is quite important because the bio-toilet system operates in this way and criteria for the proper design and operation can be set by using this tool. The key parameters in these criteria are the frequency of feces feeding and organic loading.

26.4 FACTORS AFFECTING COMPOSTING PROCESS IN TOILET

Since composting of toilet wastes in the bio-toilet system is a biological process, kinetics of biodegradation are affected by several factors such as type and quantity of microorganisms, availability, and degradability of substrate; availability of nutrients (N, P, K and others), and environmental conditions (temperature, moisture content, oxygen availability and pH).

26.4.1 Temperature

Temperature is one of the most important factors affecting microbial growth and biological reactions. Temperature can exert an effect on biological reactions in two ways: by influencing the rates of enzymatically-catalyzed reactions and by affecting the rate of diffusion of the substrate to the cells (Grady et al. 1999).

Although microorganisms have been found in extreme environments, most of them exhibit a relatively narrow temperature range over which they can be active. Within that range, most reaction rate coefficients increase as the temperature is increased, but then eventually decrease as the heat begins to inactivate cellular enzymes. Microorganisms are grouped into three categories depending on that temperature range. Of main concern in biological processes are mesophilic organisms, which grow well over the range of 10–35°C (Grady et al. 1999); they can even grow up to 45°C (Del Porto and Steinfeld 1998). The optimum temperature for the mesophilic bacteria is around 35°C, they die at 40 to 45°C (Mckinney 1962). The microorganisms that grow best at elevated temperature range between 55 and 65°C are called thermophilic microorganisms (Mckinney 1962); they can grow even at higher temperatures, up to 71°C (Del Porto and Steinfeld 1998).

In conventional composting, growth of organisms is restricted to the temperature range of 0 to 80°C. Only some bacteria remain active up to 80°C, other microorganisms stop growing at about 60°C (Kaiser 1996). In most composting toilet systems, mesophilic bacteria are dominant (Del Porto and Steinfeld 1998). However, in the composting reactor of the bio-toilet the temperature distribution can vary widely from 20°C to 70°C, and thermophilic temperatures between 50°C and 60°C are dominant in 44.5% of the reactor volume (Nakata et al. 2003). Therefore, it is expected that mesophilic and thermophilic microorganisms interact simultaneously in the system. Temperature distribution in the composting reactor is critical because: i) mesophilic and thermophilic microorganisms respond differently to temperature, and therefore, biodegradation rates of feces are affected; and ii) destruction and/or inactivation of pathogens and parasites is a

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thermophilic process, and consequently, the non-uniform temperature distribution would reduce the over-all inactivation rate.

Knowledge of how the temperature affects the biological processes is essential to ensure better performance of the bio-toilet, set heating necessities and devices, and take decisions during operation of the system. Therefore, the effect of temperature on aerobic biodegradation of feces, covering a wide range of temperatures that characterize mainly mesophilic and thermophilic processes, is described through the comparison and analysis of experimental oxygen utilization rates (OUR) for those ranges of temperature. Additionally, the temperature effect on aerobic biodegradation of feces was incorporated into the bio-kinetic model introduced by López Zavala et al. (2004b) and simulation of experimental OUR profiles. Main findings are summarized as follows:

a) Three stages were characteristically observed in the experimental OUR profiles obtained from the batch tests: *rapid increase*, *rapid decrease* and *steady stages*. Mesophilic and thermophilic microorganisms showed different response to the temperature. Additionally, results suggest that the optimum temperature from the viewpoint of feces biodegradability is within the thermophilic range, nearly to 60°C. At 70°C the activity of biomass was very low; even, after 24 hours of having started the batch tests the oxygen consumption was negligible. It was clear that enzymatic activity of microorganisms diminished remarkable at this high temperature (see Figure 26.10).

b) In the mesophilic range, the slowly biodegradable organic matter, which constitutes the feces, was fractionated for higher quality bio-kinetic model predictions into easily hydrolysable organic matter (X_{Se}) and slowly hydrolysable organic matter (X_{Ss}). The first fraction is associated with the *rapid increase* and *rapid decrease stages* of OUR profiles, and the second is linked to the steady stage of OUR profiles (see Figure 26.11).

c) In the thermophilic range, temperature affects the maximum growth rate more remarkable than others kinetic parameters. Whereas in the mesophilic range, μ_H, k_{He}, and K_{Xe} are sensitive to temperature. The effect of temperature on maximum growth rate is acceptably described by using the Arrhenius equation within the mesophilic and thermophilic ranges of temperature (see Figure 26.12).

d) Predictions of the bio-kinetic model introduced by López Zavala et al. (2004a) were improved by incorporating the effect of temperature and by fractioning the slowly biodegradable organic matter in the mesophilic range; predictions with the improved model fitted properly to the experimental data (see Figure 26.13).

26.4.2 Moisture Content

Moisture content is another important factor in microbial growth and biological reactions. The moisture content in the composting reactor of the bio-toilet system is kept in the range 50–60% by heating and ventilation. Horisawa et al. (2000)

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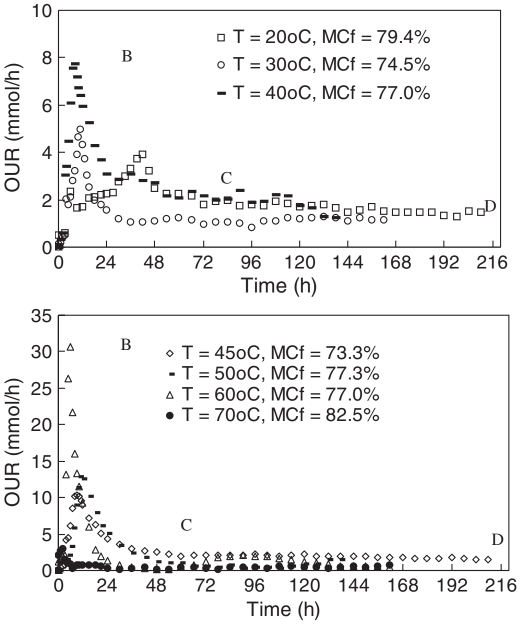


Figure 26.10. Effect of temperature on oxygen utilization rates. MCf = moisture content of feces

Source: López Zavala et al. (2004b); reproduced with permission from Elsevier

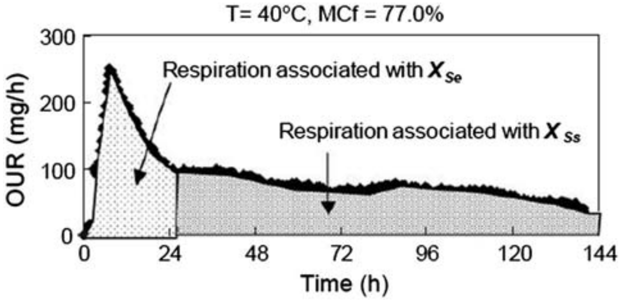
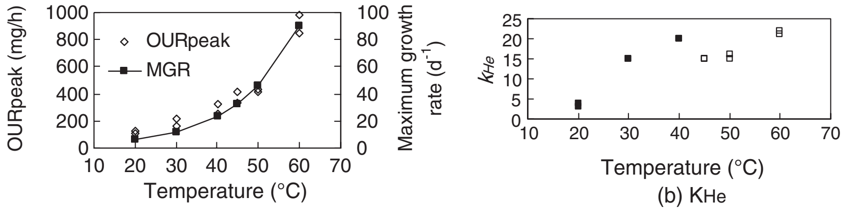


Figure 26.11. Fractioning of slowly biodegradable organic matter into easily hydrolysable (X_{Se}) and slowly hydrolysable (X_{Ss}) (mesophilic range)

Source: López Zavala et al. (2004b); reproduced with permission from Elsevier

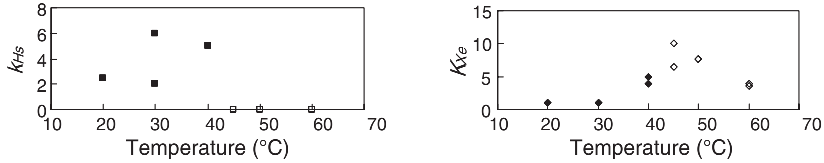
conducted an experiment to evaluate the effect of moisture content of a sawdust matrix on small-scale biodegradation system for organic solid waste and they found that the highest microbial growth occurred at 60% moisture content.

"Forced" convection (driven by mechanical means) and diffusion are the two mechanisms by which oxygen moves from the ambient air into the sawdust matrix and ultimately to the microorganisms themselves. Oxygen transport is closely



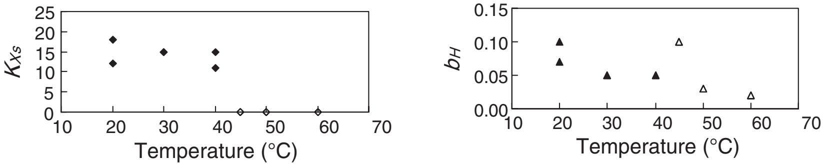
(a) Maximum growth rate

(b) KHe



(c) KHe

(d) KXe



(e) KXs

(f) bH

Figure 26.12. Effect of temperature on kinetic parameters

Source: López Zavala et al. (2004b); reproduced with permission from Elsevier

related to the moisture content of the sawdust matrix. As moisture content increases beyond 60%, the pores of the sawdust matrix will be rapidly filled and resulted in anaerobic condition (Richard 1997).

Biodegradation rates are affected by moisture through changes in oxygen diffusion, water potential and microbial growth rates (Richard et al. 2002). Several studies have taken the challenge of setting optimum moisture contents and their relationships in conventional composting systems (Suler and Finstein 1977; Kaneko and Fujita 1986; U.S. EPA 1994, 1995; Madejon et al. 2002; Richard et al. 2002).

The optimum moisture content represents a trade-off between moisture requirements of microorganisms and their simultaneous need for adequate oxygen supply (Madejon et al. 2002). Water is the key ingredient that transports substances within the composting matrix and makes the nutrients physically and chemically accessible to the microbes. If the moisture levels drop below about 40 to 50%, the nutrients are no longer in an aqueous medium and not easy available to the microorganisms. Their microbial activity decreases and the composting process slows. Below 20% moisture, very little microbial activity occurs (U.S. EPA 1994). Optimum moisture content for biodegradation can vary widely for different compost mixtures and composting times, ranging from near 50 to over 70% on a wet basis (Richard et al. 2002). Other researchers have reported optimum moisture content in the range of 50 to 60% for different compost

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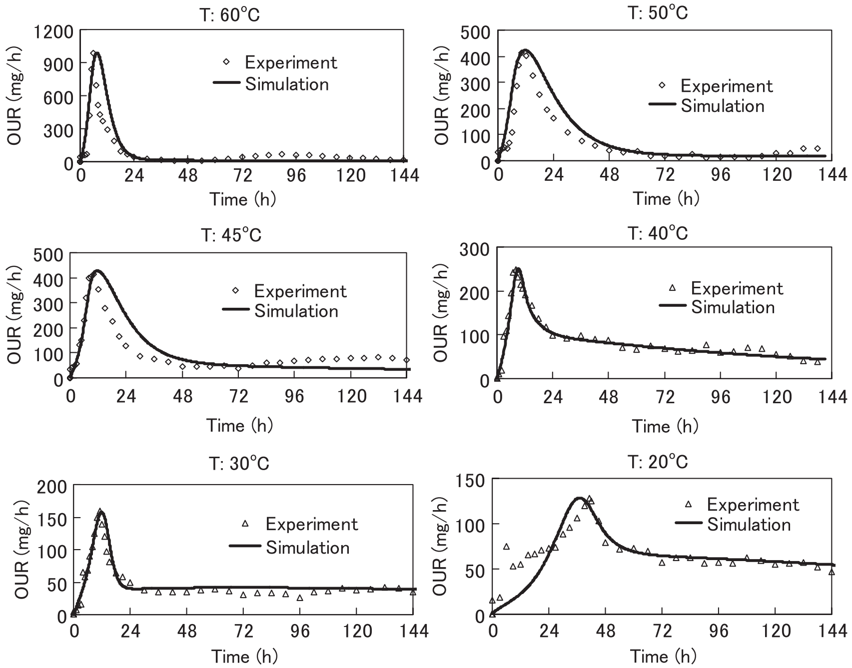

Figure 26.13. Simulation of experimental OUR profiles. Simulation improved in the mesophilic range

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mixtures (Suler and Finstein 1977; Kaneko and Fujita 1986; U.S. EPA 1995), even others in the range 25, 30 to 80% moisture (Horisawa et al. 2000; Madejon et al. 2002). This wide range of optimum moisture content indicates *i)* the complex dynamic nature of the composting process, with changes in particle size and structure occurring over the time, and *ii)* the necessity of more fundamental and inclusive parameters for understanding the physical and biological interactions controlling the composting process (Madejon et al. 2002; Richard et al. 2002).

The composting process in the bio-toilet system differs from that in conventional composting systems. Understanding how the moisture content affects the rates of aerobic biodegradation of feces in the bio-toilet composting reactor is a key factor in setting criteria for the proper design and operation, and for achieving the aims of the system. Only a few studies have been conducted on systems similar to the bio-toilet (Horisawa et al. 2000), but no research has been conducted to describe the effect of moisture content on the composting process in the bio-toilet system.

Because optimum moisture management is a critical factor in the composting process and consequently in the design and operation of the bio-toilet system, the effect of moisture content on the thermophilic aerobic biodegradation of feces was assessed through the quantification of reductions in total solids (TS),

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volatile solids (VS), and chemical oxygen demand (COD); the production of anaerobic products (volatile fatty acids) and odors; the changes in concentration of nitrification products and sulfates; and the analysis of oxygen utilization rates (OUR) and CO_2 production rates in batch tests conducted in laboratory-scale composting reactors under several moisture content levels. The main findings of the moisture content evaluation were:

a) Composting in the bio-toilet system is characterized by thedifferent biological response of microorganisms depending on the moisture content under which the process is conducted. Low moisture contents (<65%) ensured aerobic degradation of feces, whereas high moisture levels (≥65%) caused both aerobic and anaerobic decomposition (Figure 26.14).

b) Aerobic and anaerobic decomposition, during the experimental batch tests, occurred under the unbound moisture conditions, i.e., unbound waterwas a synonym of anaerobic conditions. Unlike, bacteria conducted aerobic decomposition of feces under the bound moisture conditions (Figure 26.14).

c) Because anaerobic conditions occurred at high moisture contents (≥65%), microorganisms activity generated odor and VFA emissions. In addition, simultaneous aerobic and anaerobic processes at high moisture levels caused the increase of sulfate concentrations and formation of nitrites in the sawdust matrix, even though the composting process was conducted at thermophilic temperatures. At low moisture contents, anaerobic emissions, nitrification products and increase of sulfate concentrations were not detected (Figure 26.15).

d) Higher reductions in parameters such as TS, VS, and COD, and higher oxygen utilization rates were determined at moisture content nearly to

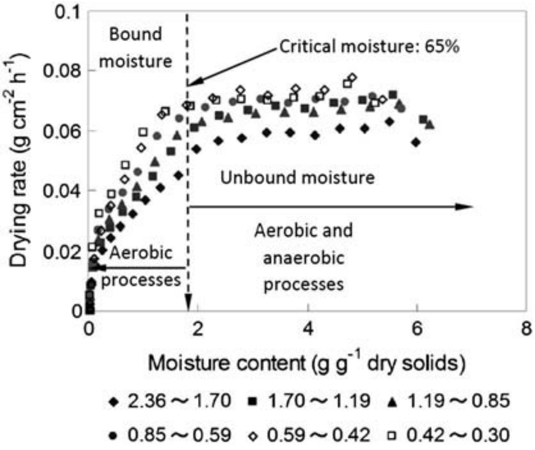

Figure 26.14. Types of moisture and their link with the biological response of microorganisms in the composting process of the bio-toilet system. Size of sawdust particles is in mm

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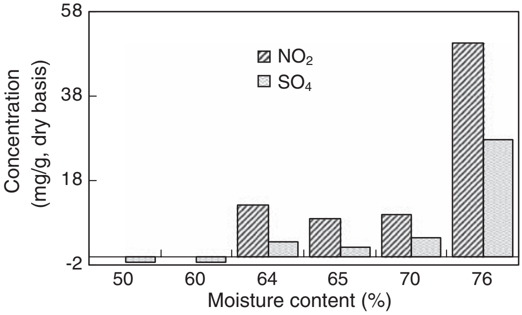

Figure 26.15. Nitrites formation and increase of sulfates concentration for several moisture contents

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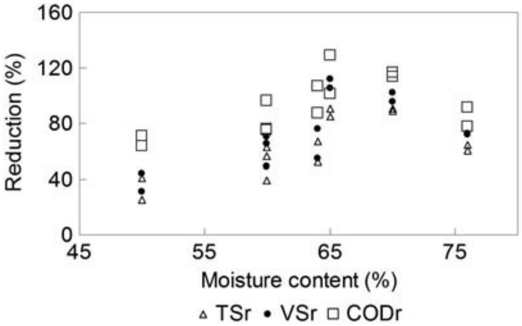

Figure 26.16. TS, VS, and COD reductions obtained in batch tests

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65%. This moisture level was the critical moisture estimated during drying tests on sawdust. Thus, critical moisture was the frontier moisture content which defined either the highest degradation rates or the beginning of odor and anaerobic emissions, increases of sulfate concentrations, and the nitrification process under thermophilic conditions. Reasonable degradation rates were obtained at 60% (Figure 26.16). Even at moisture levels of 65 and 70%, the reduction of VS and COD was higher than 100%. According to the characterization of feces conducted by López Zavala et al. (2002b), volatile solids (organic material) constitute approximately 84% of feces, whereas fixed solids (inorganic fraction) represent the rest l6%; therefore, VS reductions higher than 84% and COD reductions higher than 100% imply that not only feces were biodegraded but also the sawdust matrix was partially decomposed. This partial decomposition of sawdust may be associated to the growth and activity of actinomycetes and fungi, which are capable of degrading hemi-cellulose and cellulose and lignin, respectively (Kaiser 1996). Indeed, white-rot fungi were observed during

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experimental batch tests. Sawdust has high bacterial-activity tolerance (Terazawa et al. 1995), so that, it is assumed that these microorganisms were only involved on the feces degradation.

e) Optimum moisture control and management in the composting reactor of the bio-toilet system should take into account not only high performance on biodegradation of feces, but also problems of odor and anaerobic emissions, and necessities of maintenance and services, associated with frequency of sawdust replacement. These requirements could be achieved by keeping moisture contents at 60% or little higher, but avoiding levels near or higher than 65%, i.e., moisture levels near, but lower than the critical moisture. Very low moisture contents, less than 50%, should also be avoided to ensure aproper environment for microorganisms and consequently faster and complete stabilization of organic matter contained in feces.

f) At high moisture contents, nitrites formation and increase of sulfate concentrations contributed importantly to the respiration rate; however, the oxygen utilization rates decreased as moisture content increased. At low moisture levels, carbonaceous material biodegradation was the only contributor to the respiration rate. Higher OUR at lower high moisture contents was a result of aerobic heterotrophic bacteria activity and oxidation of anaerobic products. The existence of a second peak may denote the aerobic oxygen consumption of actinomycetes and fungi when they acted on the sawdust matrix after feces degradation, as explained above. It is clear that the second peak contributed importantly to obtain higher biodegradation rates at these moisture contents, as shown above. Because actinomycetes and fungi are aerobic microorganisms (Smith and Scott 2002), much higher moisture content, such as 76%, could limit their growth and activity over the sawdust when more severe anaerobic conditions prevailed in the matrix, consequently a second peak in the OUR profile was not observed and lower reductions on TS, VS, and COD were obtained (Figure 26.17).

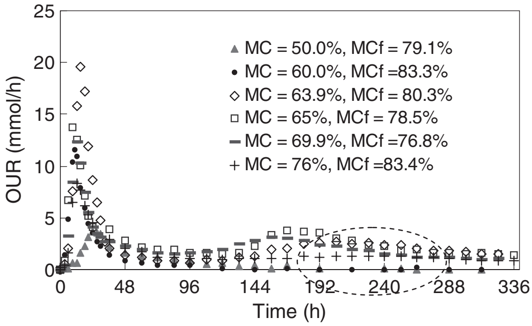

Figure 26.17. Effect of moisture content on oxygen utilization rates. MCf: moisture content of feces

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g) Carbonaceous material biodegradation is not the only process that consumes oxygen; other bacterial processes such as nitrification and oxidation of reduced-sulfur compounds also consume oxygen. Like nitrifiers, the autotrophic sulfur bacteria utilize inorganic compounds instead of organic matter to obtain energy, and use carbon dioxide or carbonate as a carbon source. Sulfur bacteria are able to oxidize hydrogen sulfide (or other reduced-sulfur compounds) to sulfuric acid (Spanjers et al. 1998). However, thecontribution of each process to the observed total respiration rate of the biomass is difficult to distinguish in many cases. On the other hand, carbonaceous material biodegradation is a CO_2 generating process, so that, OUR is linked to the CO_2 production rate (CPR). If OUR and CPR profiles are expressed in (mmol/h), it is expected that, when plotted, both show almost same magnitude. However, when OUR is higher than CPR, the difference between them should be assumed as the contribution of nitrification and oxidation of reduced-sulfur compounds. Thus, the oxygen consumption associated with these processes can be quantified through the formation of nitrites and nitrates and the increase of SO_4 concentration in the sawdust matrix (Figure 26.18).

h) Contributions of non-carbonaceous material biodegradation processes to the respiration rate were more remarkable at much higher moisture levels, as seen in Figure 26.18, where differences between OUR and CPR were more visible. These differences are a good indication and support the occurrence of nitrification process and aerobic oxidation of hydrogen sulfide (or other reduced-sulfur compounds).

26.5 COMPOST SAFETY

26.5.1 Health Risk Assessment

Destruction of pathogenic microorganisms in the bio-toilet system is an important process of public health concern. Thermal disinfection is a process for inactivation and/or destruction of pathogens. It is well known that temperatures higher than 50°C do kill pathogens in a short time. The United States Environmental Protection Agency (U.S. EPA 1985) has set a minimum time-temperature requirement for in-vessel, aerated and static pile composting method's on control of pathogens in biosolids and says that the material must keep a minimum temperature of 55°C for at least three consecutive days. For turned windrow composting, at least 55°C must be maintained for 15 consecutive days with the material turned at least 5 times (Wu and Smith 1999).

Among several opportunities to contact sawdust and feces mixture in the bio-toilet system, withdrawing the compost from the system gives a direct contact occasion to users. It may be a crucial question how long reaction time is required to handle compost safely. The second purpose of this section is to assess infection risk in withdrawing the compost from the system.

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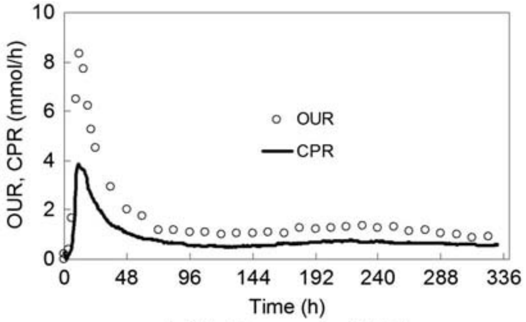
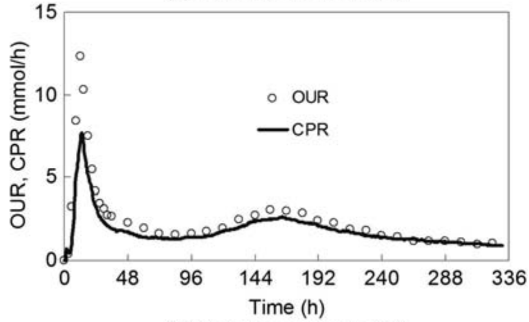
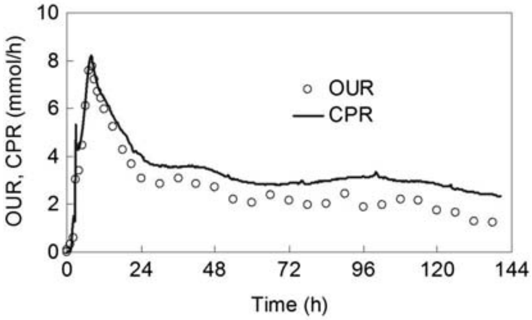


(a) Moisture content: 76%



(b) Moisture content: 70%



(c) Moisture content: 60%

Figure 26.18. Oxygen utilization and CO_2 production rates

Source: López Zavala et al. (2005b); reproduced with permission from Taylor and Francis

Batch Tests for Measuring Pathogen Decline Processes. Nakata et al. (2003) showed their experimental results on pathogens decline at several temperature conditions. They measured the decay process of pathogens measured through the inhibition on coliforms colony formation and bacteriaphages plaque-formation during the aerobic biodegradation of feces. Figure 26.19 shows their experimental device. Bioreactors were placed into water baths and air was supplied into the bioreactor continuously. At the batch tests, 10 (g-dry base) of feces and 100 (g-dry base) of sawdust were mixed. RNA bacteriophages Qß was spiked to the feces and

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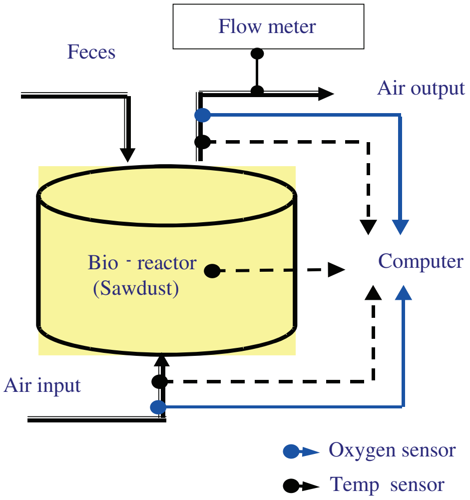

Figure 26.19. Experimental equipment
Source: López Zavala et al. (2004a); reproduced with permission from Elsevier

sawdust mixture. All mixtures were set up at 60% of initial moisture content by adding distilled water. OUR and time course of total coliform group count and bacteriophages plaque-formation count then were monitored at several temperatures (20, 30, 35, 40, 45, 50 and 60°C). In this study, indicator organisms were used to assess the temperature effect on pathogens decline during aerobic biodegradation of feces using sawdust as an artificial soil matrix. Initially, total and fecal coliforms were thought as candidate alternatives. However, similar values of coliform counts were obtained for total and fecal coliform group from the experiment at 20 °C. Hence, total coliform was adopted as an indicator of bacteria. Bacteriophages Qß was measured by the double agar layer method with *E.coli* K12 $F^{+}(A/\lambda)$ as the host bacterium (Otaki et al. 1998).

Figure 26.20 is the time courses of Colony Formation Unit (CFU) of total coliform and OUR at 60°C, showing that there is not a clear correlation between the decline of bacteria and biodegradation rates of organic matter. The OUR profiles in Figure 26.20 shows the peak value at 12–48 hours, but the values of CFU decrease monotonically. Similar behavior was observed for the rest of temperatures evaluated.

Figures 26.21 (a) and (b) show the relationships between log (C/C_o) and time obtained from batch tests under several temperatures. As seen in Figure 26.21(a), temperatures higher than 45°C degrees were very effective to inactivate coliform bacteria in the experimental bioreactor. Coliform bacteria colony formation at 60°C was inhibited in only 1.17 h after the beginning of the batch test, whereas at 50 and 45°C the inactivation occurred after 8 and 24 hours, respectively, of the batch tests start. On the other hand, at temperatures lower than 45°C, it took much longer time to obtain 6-log reduction of CFU. The decay process of bacteriophage in Figure 26.21(b) also shows the same profile. The batch tests using mixture of

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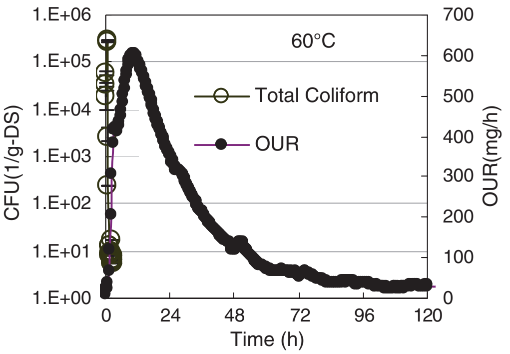
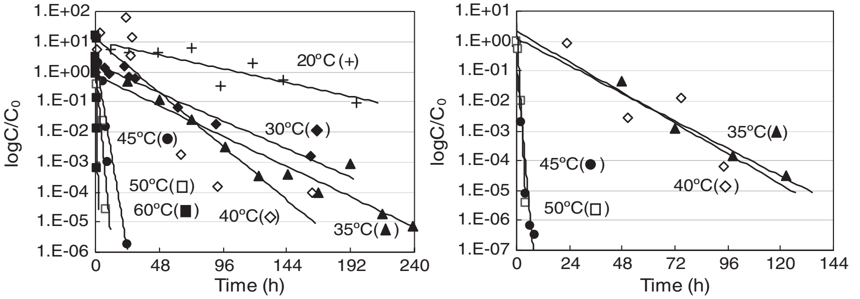


Figure 26.20. Total coliform density and oxygen utilization rate profile at 60°C
Source: Nakata et al. (2003)



(a) Total Coliform (b) bacteriophage

Figure 26.21. Time courses of total coliform and bacteriophage count at several temperatures
Source: Nakata et al. (2003)

feces and 4% (w/v) - solution of KH_2PO showed that temperatures higher than 45°C were quite effective to inactive bacteria coliform, but at temperature lower than 40°C, activation of coliform colony formation was observed rather than an inhibitory effect. This pattern differs from that observed in the sawdust matrix where an inactivation effect occurred. However, this inhibition effect in solid phase seems to be associated to the moisture content decrease rather than to the direct temperature effect. Turner (2002) reported that inactivation of *E. coli* at 50°C may depend on the moisture content and the nature of the material. Therefore, care should be taken when composting is conducted at mesophilic temperatures because the results indicate that the inactivation is not a merely temperature dependent. Since the moisture content effect on the decline of pathogens has not been evaluated, further study is required to explore the reason why the decay of coliform and bacteriophage count was observed at a temperature lower than 40°C.

Table 26.9. Required infection risk for one withdrawal of compost to meet annual risk 10^{-4}

Number of withdrawal (year^{-1})	*Allowable infection risk for one withdrawal*	*Level*
2 (every half year)	5.00×10^{-5}	
3 (every quarter year)	3.33×10^{-5}	I
6 (every two month)	1.67×10^{-5}	
12 (every month)	8.33×10^{-6}	
24 (every half month)	4.17×10^{-6}	II
52 (every week)	1.92×10^{-6}	
121 (every three days)	8.26×10^{-7}	
182 (every two days)	5.49×10^{-7}	III
365 (everyday)	2.74×10^{-7}	

Risk Assessment. Bacteria and virus infection risk of withdrawing the compost from the bio-toilet was assessed by Nakata et al. (2003). They applied the risk assessment protocols listed by the National Research Council (NRC 1983, 1994). In this work, *Salmonella* and *rotavirus* were used as indicators of bacteria and virus risk, respectively. The value of 10^{-4} was used as an acceptable annual infection risk, and calculated allowable infection risk of one withdrawal to meet this annual risk as shown in Table 26.9. The values of allowable infection risk in Table 26.9 depend on the number of withdrawals, and three control levels were set corresponding to the order of allowable risk: Level I is the order of 10^{-5}; Level II is 10^{-6}; and Level III is 10^{-7}. The beta-Poisson model (Sakaji and Funamizu 1998) was used as their dose-response model, and parameter values were adapted in the model reported by Rose and Gerba (1991).

The following scenario was used for estimating the dose and pathogen counts, resulting from one withdrawal of compost from bio-toilet:

- Four members of a house are infected with *Salmonella* or *Rotavirus*, and they release pathogen to toilet along with 150 g of feces per person.
- Pathogen count in one gram of feces is 10^6 that is reported by Suzuki et al. (1999).
- The ingestion rate of compost is 800 mg/day. 150–800 mg/day is used in the risk assessment of dioxin for soil ingestion rate (Theelen 1991; U.S. EPA 1994). In this study 800 mg/day is adopted.
- Inactivation process of thepathogen can be modeled by the first order kineticsmodel.
- It is assumed that sawdust and feces are mixed thoroughly and uniformly in the reactor during mixing operation.
- There is a temperature distribution in the composting reactor. Figure 26.22 is the volume fractions of each temperature zone in the bio-toilet reactor

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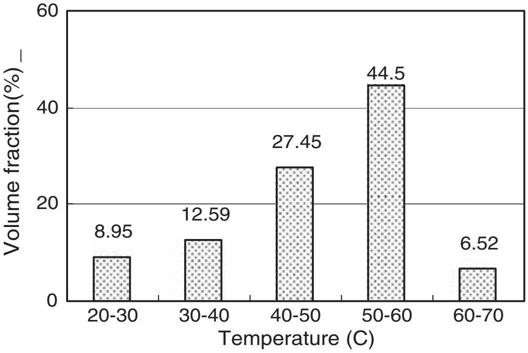

Figure 26.22. Temperature distribution of bioreactor
Source: Nakata et al. (2003)

measured by Nakata et al. (2003), showing that there is a significant temperature difference inside the reactor. The zones having a high temperature were located near the bottom where plate heaters were set. The lowest temperature zone was found near the top surface of sawdust. The volume weighted average temperature of the reactor was 42.7°C.

Taking account of temperature distribution inside the reactor into risk estimation gives results in Figures 26.23(a) and (b). In the normal operation of bio-toilet, mixing frequency is expected around 5–10 times per day because the mixing is added by the users just after their use. The estimated results in Figures 26.23(a) and (b) show that the reduction of compost withdrawal infection risk to an acceptable level is achieved by mixing 20 times per day for 2 days or 15 times per day during 3 days after the last using-event of the bio-toilet.

26.5.2 Toxicity Assessment

The black water contains several chemicals such as pharmaceutical residues and endocrine disruptors; some of them might be non-biodegradable or partially biodegradable, and non-biodegradable organicmatter might be produced during bioconversion process. Since the compost as a final product of toilet contains residual chemicals, it may be possible that those chemicals accumulate in soil systems and leads to soil and/or groundwater pollution when the compost is applied to farmland. Among several methods for characterizing residual chemicals in compost, toxicity assessment by bio-assay is one of the effective techniques to characterize mixture of unknown chemicals (Kunimoto et al. 1992). The bio-assay method of using a cultured human cell and mammalian cell lines is an effective method to assess the effect for thehuman system (Kunimoto et al. 1996; Fukushima et al. 2002).

Kakimoto et al. (2006) applied the bio-assay method to three compost samples from three kinds of composting toilet (Bio-Toilet A, K and T)operating in Japan. Along with compost samples, in order to assess the original toxicity of fresh sawdust and feces, fresh sawdust used for toilet and fresh feces were also

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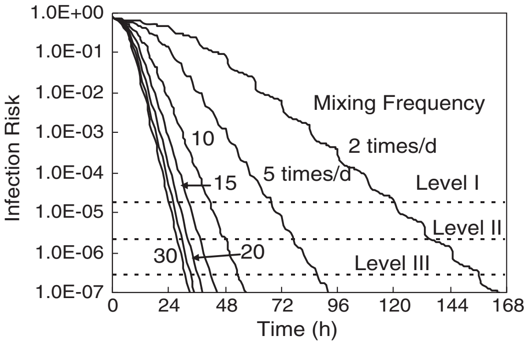
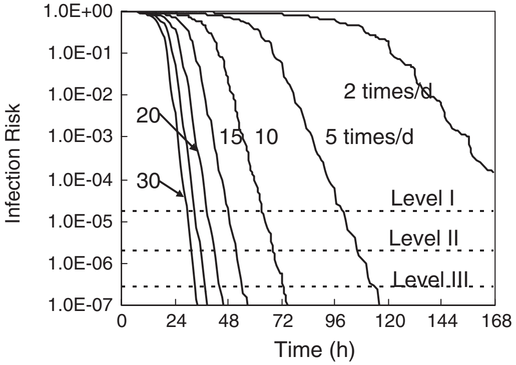


(a) Salmonella



(b) Rotavirus

Figure 26.23. Effect of mixing frequency on infection risk
Source: Nakata et al. (2003)

examined. Feces used in the assay were provided by a healthy man who did not take any medicines. For the bio-assay, one liter of distilled water was used as a solvent and mixed with 100 g of sample. The mixture was left at rest for 30 minutes, and the supernatant was filtered through 0.45 μm membrane filter. This filtrate was used for bio-assay and analytical test. Some samples are concentrated by a rotary evaporator to obtain enough response data in a bio-assay. Cultured human neuroblastoma cell lineNB-1 was used for the assay. This cell was inoculated in 96-well plates and incubated for 48 h in the CO_2 incubator before and after the sample exposure (Kunimoto et al. 1992).

Figure 26.24 is the bio-assay results from an experiment using the extract of feces given by a healthy man. This figure shows the dose-response relationship, the vertical axis is the viability percentage of NB-1 cell and the horizontal axis is DOC concentration of the sample in log-scale. It is seen from Figure 26.24 that there is no evidence to show the toxicity since the viability remains nearly 100% at any DOC concentration. Figure 26.25(a) is the dose-response relationship obtained from the extract of unused sawdust used in Bio-Toilet A, showing that the unused sawdust in Bio-Toilet A does not have any toxicity. Figure 26.25(b) shows the

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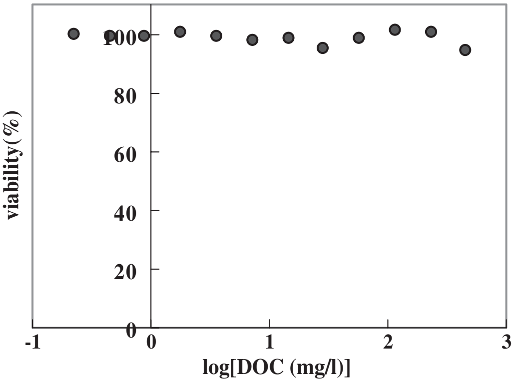

Figure 26.24. Bio-assay result from experiment with feces
Source: Kakimoto et al. (2006); reproduced with permission from IWA Publishing

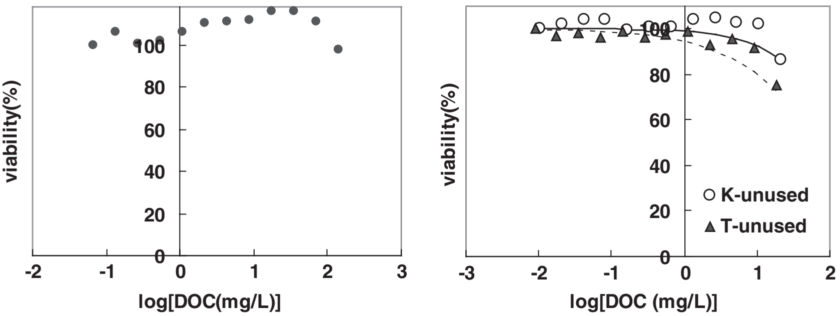

Figure 26.25. (a) Bio-assay result from experiment with fresh sawdust from Bio-Toilet A; (b) Bio-assay result from experiment with fresh sawdust from Bio-Toilet K and T
Source: Kakimoto et al. (2006); reproduced with permission from IWA Publishing

results of bio-assay from experiments with unused sawdust used in Bio-Toilets K and T. Unlike the results from Bio-Toilet A shown in Figure 26.25(a), the unused sawdust show stoxicity. This difference in the dose-response relationship may be due to material of sawdust. The sawdust used in Bio-Toilet A is Japanese red pine, and on the other hand, Japanese cedar is used in Bio-Toilets K and T.

Figure 26.26 is the dose-response relationship obtained from bioassay with the extract of compost from Bio-Toilet A, showing that the extract of compost has toxicity. In order to compare the strength of toxicity, the dose-response relationships with 100 mM $CdCl_2$ solution and 1MNaCl solution are also plotted in Figure 26.26. It is seen from Figure 26.26 that 1) the toxicity of the extract may be comparable to 100 mM $CdCl_2$ solution, and (2) high concentration of NaCl gives low viability of cell, and this effect must be examined for the extract of compost.

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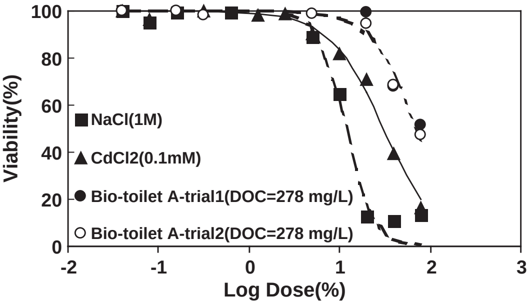

Figure 26.26. Bio-assay results from experiment with compost from Bio-Toilet A
Source: Kakimoto et al. (2006); reproduced with permission from IWA Publishing

The above-mentioned assay results show that (i) the extract of feces showed no toxicity, and the extracts of unused sawdust had no or low-level toxicity, and (ii) the extracts of composts had heavier toxicity than unused sawdust. These results implied that some chemicals that have toxicity were generated by biological reactions or accumulated in the toilet system.

26.6 OPERATION AND DESIGN OF COMPOSTING TOILET

Proper design of the bio-toilet implies that the system fulfills criteria such as safety, functionality, economy, aesthetics, and social and environmental affordability. Attending the criteria of functionality and social and environmental affordability, the bio-toilet must be designed with the aim of accelerating decomposition of human excreta, optimizing efficiency, and minimizing any potential environmental or nuisance problems (odor). These objectives must be coupled safety, low-manufacturing and operational costs, and aesthetics, to become an affordable option for the users. Thus, the design process of bio-toilet will consist of determining the size of the composting reactor that ensures the achievement of the criteria mentioned previously.

There are five important factors or aspects with which we must deal at the time of establishing criteria for the proper design and operation of the bio-toilet, these are degradation of organic matter, water balance, nutrients (mainly nitrogen processes), pathogens inactivation, and fate of micropollutants.

Based on the results achieved in previous studies on such issues, an establishment of criteria for the proper design and operation is the aim of this section. Micropollutants degradation is not discussed in this section. Because bio-toilet deals with the evaporation of the water contained in human excreta, theory and concepts of drying of solids are used in the design process; however, results of drying tests, conducted in a laboratory-scale drying device designed by us.

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26.6.1 Considerations for the Operation

As mentioned above, the bio-toilet system is managed with the aim of accelerating decomposition, optimizing efficiency, and minimizing any potential environmental or nuisance problems (odor). The conditions under which the composting reactor must be operated to meet these goals are given by the results of the research presented in previous chapters, especially related to moisture content and temperature. Thus, criteria for the proper operation of the system under the current configuration are summarized as follows:

a) Continuous thermophilic aerobic conditions and organic loading are not limiting factors for the composting process in the bio-toilet system. However, constraints associated with high moisture contents may affect the performance of the composting process if organic loads beyond the $F/S = 25\%$ are planned to be used.

b) Optimum moisture control and management in the composting reactor of the bio-toilet system should take into account not only high performance on biodegradation of feces, but also problems of odor and anaerobic emissions, and necessities of maintenance and services, associated with frequency of sawdust replacement. These requirements could be achieved by keeping moisture contents at 60% or slightly higher, but avoiding levels near or higher than 65%, i.e., moisture levels near, but lower than the critical moisture. Very low moisture contents, less than 50%, should also be avoided to ensure aproper environment for microorganisms and consequently faster and complete stabilization of organic matter contained in feces.

c) Composting in the bio-toilet system is characterized by different biological responses of microorganisms depending on the moisture content under which the process is conducted. Low moisture contents (<65%) ensured aerobic degradation of feces, whereas high moisture levels ($\geq$65%) caused both aerobic and anaerobic decomposition.

d) Because anaerobic conditions occurred at high moisture contents ($\geq$65%), microorganisms' activity generated odor and VFA emissions. In addition, simultaneous aerobic and anaerobic processes at high moisture levels caused the increase of sulfate concentrations and formation of nitrites in the sawdust matrix, even though the composting process was conducted at thermophilic temperatures. At low moisture contents, anaerobic emissions, nitrification products and increase of sulfate concentrations were not detected.

e) Critical moisture was the frontier moisture content which defined either the highest degradation rates or the beginning of odor and anaerobic emissions, increases of sulfate concentrations, and the nitrification process under thermophilic conditions. Thus, critical moisture may be adopted as a simple physical operation parameter.

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f) Mesophilic and thermophilic microorganisms showed different response to the temperature; additionally, results suggest that the optimum temperature from the viewpoint of feces biodegradability is within the thermophilic range, nearly to 60°C.

g) At 70°C, the activity of biomass was very low. It was clear that theenzymatic activity of microorganisms diminished remarkable at this high temperature. At temperatures lower than 60°C, biodegradation rates of feces slowed following a pattern described by Arrhenius equation. In the mesophilic range, hydrolyzability of organic matter was remarkably dependent on the temperature at which the composting process was conducted.

h) Temperatures over than 45°C (the thermophilic range) were more effective in inhibiting the coliforms colony-formation and bacteriophages plaque-formation, consequently for pathogens inactivation.

i) Coliform bacteria colony formation at 60°C was inhibited in only 1.17 h, whereas at 50 and 45°C the inactivation occurred after 8 and 24 hours, respectively. On the other hand, at temperatures lower than 45°C, it took much longer time to obtain 6-log reduction of CFU. The decay process of bacteriophage also showed the same profile.

j) Temperature distribution in the bio-toilet system was not uniform, even just after mixing the sawdust matrix. The non-uniformity in temperature distribution causes reducing theoverall performance of destruction of pathogens. Results of risk assessment showed that the reduction of compost withdrawal infection risk to an acceptable level (1×10^{-4} per year) is achieved i) by mixing the sawdust mixing 20 times per day during 2 days or ii) by mixing 15 times per day for 3 days after the last using-event of the bio-toilet in current operating bio-toilet. Eliminating low-temperature zone is more effective to reduce reaction time to obtain affordable infection risk especially in low mixing frequency such as 2 times per day than increasing high temperature volume.

k) Low pH (6–7) should be kept in the composting reactor of the bio-toilet system to ameliorate the high nitrogen losses observed. During feces degradation conducted at 55°C, T-N losses in the form of NH_3 were on the order of 94%, regardless of the organic loading. Experiments with urine confirmed that ammonification of organic nitrogen occurred in the composting reactors at high and low temperatures. At 40 and 60°C,lower T-N reductions were observed, but the ammonia releases from the composting reactors were approximately 97.5% of T-N reductions. Unlike, at 20 and 30°C, T-N reductions were approximately 81.5% and 89.1%, respectively, whereas ammonia losses resulted to be about 57% of T-N reductions.

l) Nitrification products were not detected in all range of temperatures evaluated, except when high moisture content were kept. High salinity, especially high concentrations of Cl, seems to be the main inhibitory factor

> for the nitrification process in the composting reactor. Therefore, alternative methods to conserve nitrogen in the sawdust matrix, for instance mineralization of NH_4 in the form of struvite crystals, should be evaluated to enhance the agricultural quality of the compost generated, and to reduce the human health risk and air pollution problems due to ammonia emissions.

In practice, the aforementioned optimum temperature and moisture conditions in the composting reactor can be achieved by i) monitoring continuously the composting process; and ii) manipulating the temperature controller of the system, the mixing frequency, and the water amount for cleaning purposes. pH control is more difficult to achieve, but the addition of sulfates containing for instance magnesium may help to reduce pH or enhance the formation of struvite crystals at higher pH.

Based on above considerations, an operation scheme for the bio-toilet was prepared (Figure 26.27). In this scheme, three parameters were considered, temperature, moisture content, and mixing frequency. The effect of mixing frequency on human health risk was studied by Nakata et al. (2003). However, the effect on moisture content reduction due to drying process and on biodegradation rates has not been studied yet; therefore, the operation zones associated with mixing frequency are not conclusive, so that they are delimited by dashed lines. The *white dotted zone (green zone)* denotes the conditions where the best performance of the bio-toilet is expected. In the *shadow-dotted zone (yellow zone),* the composting process can be conducted, but performance is not the most efficient. Out of these two zones, operation of the bio-toilet is not recommended

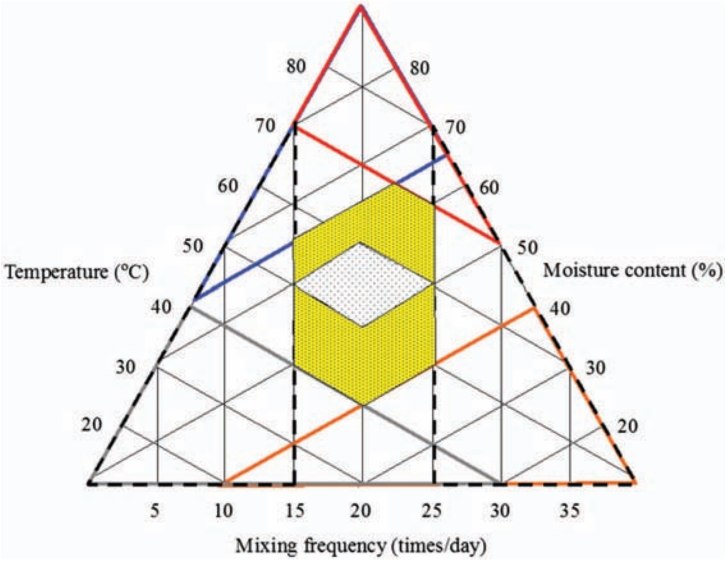

Figure 26.27. Criteria for proper operation of the bio-toilet system
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because odor problems and human health risk will come, high operation cost for concept of excessive mixing, or in the worst case, biodegradation of feces will not occur because microorganisms will die due to adverse environmental conditions.

26.6.2 Design Considerations

Under the current configuration of the bio-toilet system, the size of the composting reactor is determined by conditions such as:

a) Water loading rate due to daily contributions of urine, water contained in feces, and water for cleaning the toilet bowl.

b) Drying rate, i.e. evaporation rate of water contained in urine and feces and cleaning water.

c) Organic loading rate due to daily feeding of feces and toilet paper; i.e. feces–sawdust ratio (F/S).

d) Operating conditions described above.

e) Mixing frequency.

The water loading affects the water balance in the bio-toilet system. The average daily feces and urine production rates per capita per day found in the literature are approximately 130 g (wet basis) for feces and 1200 mL for urine (Almeida et al. 1999; Del Porto and Steinfeld 2000). The water content of feces is approximately 82% (López Zavala et al. 2002b). Thus, the daily water-loading rate of human excreta totaled 1,307 mL per capita per day (or 1,325 g per capita per day if the density of urine is 1.015 g/cm^3). Because no studies have been conducted to evaluate the amount of water needed for cleaning the bio-toilet, but regarding that the quantity used for that purpose is relatively small, cleaning water may be considered negligible for design purposes. On the other hand, the design of the composting reactor must ensure the evaporation of the water loaded in one day, in such a way the bio-toilet is capable of receiving the next day water loading. If the water content of feces is 82%, the daily organic loading in dry basis due to feces is 23.5 g per capita per day. Compared with the water-loading rate, the organic loading rate is very low. Therefore, as mentioned previously, the size of the composting reactor will be mainly determined by the water-loading rate.

Even though toilet paper is biodegradable organic material, its decomposition is quite slow compared with feces biodegradation. This is because toilet paper is a cellulosic material that is degraded by actinomycetes and/or fungi, microorganisms, which are not dominant in the composting reactor of the bio-toilet system. Therefore, for design purposes, toilet paper may be considered as a part of the bulking matrix (sawdust).

Mixing in the bio-toilet enhances the incorporation of toilet wastes and air into the sawdust matrix, and the homogenization of the sawdust matrix in terms of organic matter, microorganisms, water content and temperature distribution. Thus, the direct benefits of mixing are: acceleration of toilet wastes decomposition, increase of drying rates that will lead to smaller size of the composting reactor,

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enhancement of pathogens inactivation, and reduction of odors and possible anaerobic emissions. In general, mixing will improve the performance of the bio-toilet system. Nakata et al. (2003) evaluated the mixing frequency effect on the reduction of health risk when compost is withdrawn from the composting reactor. However, an evaluation of mixing frequency on drying rates has not been conducted yet, therefore, for design purposes, mixing may be considered as a "safety factor". Thus, the size of the composting the reactor may be estimated regarding no mixing conditions.

Drying in the composting reactor is an important process to maintain proper water balance in the sawdust matrix and, consequently, for the design of the system. The drying process was evaluated in the bio-toilet system (López Zavala and Funamizu 2006).

The procedure adopted for conducting the drying tests, and their results are not reported here. In their design procedure, the surface area required to evaporate the water loads was estimated by using concepts of the drying theory; these concepts were also initially applied to determine the mass and volume of sawdust requirements. However, these parameters were then revised to consider the accumulation of stabilized solids. This accumulation process finally governed the estimation of mass and volume of sawdust required.

Mixing will enhance the drying process; consequently, it may be thought that dimensions of the composting reactor may be reduced. However, because the effect of mixing in the drying process is difficult to evaluate with precision, mixing may result as being more important for operation rather than for design purposes. Thus, the mixing effect was not regarded in the design procedure.

In addition, in this study, the shape of the composting reactor is considered to be parallelepiped. However, the current configuration is a semicircle in the bottom due to the shape of the mixing mechanism utilized. The dimensions determined here correspond to non-mixing conditions; therefore these may change depending on the type and shape of the mixing mechanism.

It was established that the composting process in the bio-toilet should be conducted at 60°C and a 60% moisture content for good performance. Based on these recommendations and regarding the results of the drying tests the size of the composting reactor may be determined as follows.

Estimation of the Drying Surface of the Bio-toilet Reactor (A). The drying surface A can be expressed as follows:

$$A = \frac{M_s(W_1 - W_2)}{tDR_m} \quad \text{and} \quad DR_m = \frac{DR_1 - DR_2}{\ln\left(\frac{DR_1}{DR_2}\right)} \qquad \text{(Eq. 26.15)}$$

where DR_m = the logarithmic average of the rate DR_1, at moisture content W_1, and DR_2 at W_2. W_1 and W_2 are the initial and final moisture contents, respectively. t is time interval while the moisture content changes from its initial value W_1 to its

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final value W_2. The water content is, by definition, the mass of water divided by the mass of dry solids:

$$W = \frac{Mw}{Ms} \tag{Eq. 26.16}$$

Thus, Eq. (26.15) can be transformed into:

$$A = \frac{(Mw_1 - Mw_2)}{tDR_m} \tag{Eq. 26.17}$$

The moisture content in the composting reactor should not be lower than 50% to ensure proper environmental conditions for microorganisms responsible for feces degradation, as discussed above. Thus, the moisture content of the sawdust matrix should change from 60 to 50% when drying occurs and from 50 to 60% due to contributions of human excreta. This 10% of moisture content variation must ensure the evaporation of total water contained in excreta. Thus,

$$\mathrm{Mw}_1 = \text{Mass of urine} + \text{mass of water in feces} + \text{mass of water for cleaning}$$

It was established above that the daily water-loading rate of human excreta totalized 1,307 ml per capita per day (or 1,325 g per capita per day, if density of urine is 1.015 g/cm^3). Neglecting the contribution of water for cleaning would result in:

$$Mw_1 = 1{,}325 \text{ g per capita}$$

Because all water contained in excreta must be evaporated during the drying period:

$$\mathrm{Mw}_2 = 0 \text{ g}$$

In order to receive the water contribution of the next day, the composting reactor must evaporate the daily water contribution in 1 day; thus, time of drying will be:

$$t = 24 \text{ h}$$

From Figure 26.28, the drying rates at 60 (DR_1) and 50% (DR_2) moisture contents are:

$$DR_1 = 0.123 \text{ g/cm}^2\text{/h}$$

$$DR_2 = 0.088 \text{ g/cm}^2\text{/h}$$

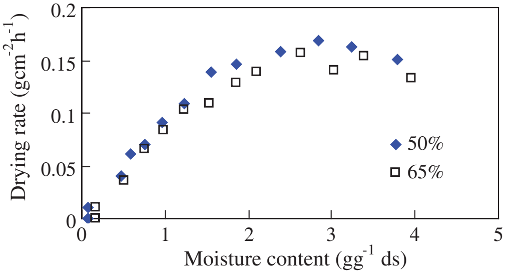

Figure 26.28. Experimental drying rate profiles

Figure 26.28 shows the results of drying tests conducted. Two drying periods were observed, as described in the drying theory, the constant- and falling-rate periods, and the average critical moisture was approximately 65% (or 1.85 $g\,g^{-1}$ ds) and the corresponding drying rate was about 0.137 $g/cm^2/h$. As seen in the falling rate period, the drying rate is almost linear to the moisture content. This result is important because ease the calculations during the design process due to the operation of the composting reactor of the bio-toilet should be conducted in this drying period, nearly to the 60% moisture content. The drying rate at this moisture content was approximately 0.123 $g/cm^2/h$. Substituting values, the logarithmic average DR_m yields:

$$DR_m = \frac{0.123 - 0.088}{\ln\left(\frac{0.123}{0.088}\right)} = 0.1045\ g/cm^2/h$$

Thus, the drying surface is estimated substituting all these values in Eq. (26.17)

$$A = \frac{(1325 - 0)}{24(0.1045)} = 528.2\ cm^{-2}\ \text{per capita}$$

Estimation of the Sawdust Matrix Volume. For design purposes, the volume of the sawdust matrix must ensure that: i) moisture content becomes approximately 60% when excreta is totally added to the system in only one even; and ii) water contained in excreta is totally evaporated in 24 hours, i.e., the moisture content of the sawdust matrix becomes approximately 50% one day after the excreta is fed.

Rearranging the Eq. (26.16) and regarding that M_s is the mass of dry sawdust (M_{ds}) plus the mass of dry feces (M_{df}) yields:

$$M_s = \frac{Mw}{W} = M_{ds} + M_{df} \qquad \text{(Eq. 26.18)}$$

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The mass of dry feces generated per person per day was determined above as 23.5 g; therefore, the mass of dry sawdust required to have a W of 60% (or 1.5 $\mathrm{g\,g^{-1}}$) is estimated as follows:

$$M_{ds} = \frac{Mw}{W} - M_{df} = \frac{1325}{1.5} - 23.5 = 859.8 \text{ g per capita}$$

With these results, the F/S ratio at which the composting reactor of the bio-toilet will work is estimated:

$$\frac{F}{S} = \frac{23.5}{859.8} 100 = 2.7\%$$

As seen, the F/S ratio is very low; consequently, it does not govern the design of the composting reactor.

The average density of the sawdust used in the bio-toilet under operation is about 0.19 $\mathrm{g/cm^3}$ (Terazawa et al. 1995; Horisawa et al. 2000), therefore the volume of dry sawdust is:

$$\begin{aligned} V = \frac{M_{ds}}{\delta_s} &= \frac{859.8}{0.17} \\ &= 5{,}057.6 \text{ cm}^3 \text{ per capita (or 5.11 per capita, approximately)} \end{aligned}$$

The daily use of the bio-toilet causes the accumulation of biologically inert material in the composting reactor. This material occupies volume in the reactor that must be considered during the design process. It was mentioned above that 44% of solids remain in the composting reactor after degradation. Thus, the mass of solids that will accumulate in 6 months and in 1 year is:

In six months:

$$\begin{aligned} Ms_{ac} &= (M_{df})(0.44)(182.5 \text{ days}) = (23.5)(0.44)(182.5) \\ &= 1{,}887.0 \text{ g per capita} \end{aligned}$$

In one year:

$$Ms_{ac} = (M_{df})(0.44)(365 \text{ days}) = (23.5)(0.44)(365) = 3{,}774.1 \text{ g per capita}$$

Because the high porosity of the sawdust (78% approximately; Horisawa et al. 2000), the stabilized solids will fill up partially the pores of sawdust. When it

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happens, physical properties of the sawdust matrix such as density, porosity, air and water retention, and water storage capacity will also change affecting the performance of the composting process. To avoid this, additional volume for remaining solids should be considered. The density of stabilized organic solids is unknown; however, studies of physical properties conducted on fine-texture mull soils report bulk densities of 0.74 $\mathrm{g\,cm^{-3}}$ (Wall and Heiskanen 2003). Adopting this value as the density of the remaining solids in the composting reactor, the additional volume to be considered in the design is:

a) If the compost is withdrawn every six months:

$$Vs_{ac} = \frac{Ms_{ac}}{\delta s_{ac}} = \frac{1887.0}{0.74} = 2{,}550.0\ \mathrm{cm^{-3}}\ \text{per capita}$$

b) If the compost is withdrawn annually:

$$Vs_{ac} = \frac{Ms_{ac}}{\delta s_{ac}} = \frac{3774.1}{0.74} = 5{,}100.1\ \mathrm{cm^{-3}}\ \text{per capita}$$

As seen, if the compost is withdrawn every six months, the volume of solids accumulated in the reactor will be almost the half of that of sawdust. But, if the accumulation of sawdust is during one year the volume of solids accumulated equals that of sawdust. Thus, the total volumefor composting matrix will be:

a) If the compost is withdrawn every six months:

$$\begin{aligned} V_T &= V + Vs_{ac} = 5057.6 + 2550.0 \\ &= 7{,}607.6\ \mathrm{cm^{-3}}\ (\text{or } 7.6\ \mathrm{l})\ \text{per capita} \end{aligned}$$

b) If the compost is withdrawn annually:

$$\begin{aligned} V_T &= V + Vs_{ac} = 5057.6 + 5100.1 \\ &= 10{,}157.7\ \mathrm{cm^{-3}}\ (\text{or } 10.2\ \mathrm{l})\ \text{per capita} \end{aligned}$$

Using these values and the drying surface determined above, the thickness of the composting matrix (regarding a rectangular reactor) at the time of withdrawing the compost (H_s) is:

a) If the compost is withdrawn every six months:

$$H_s = \frac{V_T}{A} = \frac{7607.6}{528.2} = 14.4\ \mathrm{cm}$$

b) If the compost is withdrawn annually:

$$H_s = \frac{V_T}{A} = \frac{10157.7}{528.2} = 19.2\ \mathrm{cm}$$

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These dimensions were estimated regarding that no mixing was conducted. Therefore, the shape of the mixing mechanism or the mixing system may affect such dimensions. In addition, free space for air circulation will also contribute to the total depth of the composting reactor. 10 cm may be reasonable. Thus, the total depth of the reactor could be:

a) If the compost is withdrawn every six months:

$$H_T = H_s + H_f = 14.4. + 10 = 24.4 \text{ cm}$$

b) If the compost is withdrawn annually:

$$H_T = H_s + H_f = 19.2. + 10 = 29.2 \text{ cm}$$

Mixing will enhance the drying process; consequently, it may be thought that dimensions of the composting reactor may be reduced. However, because the effect of mixing in the drying process is difficult to evaluate with precision, mixing may become more important for operation rather than for design purposes. Thus, mixing effect was not regarded in the design procedure.

The dimensions of a rectangular composting reactor required for 1 to 20 users are summarized in Table 26.10. The thickness of the sawdust matrix at the time of withdrawing the compost is expected to be 10 cm lower than the high of the

Table 26.10. Dimensions of the composting reactor of the bio-toilet system for 1 to 20 users

	Dimension							
Number of users	*Area (dm^2)*	*Width (cm)*	*Length (cm)*	*Hight[1] (cm)*	*Volume[1] (l)*	*Hight[2] (cm)*	*Volume[2] (l)*	*M_{ds} (kg)*
1	5.3	18.8	28.1	24.4	12.9	29.2	15.4	0.86
2	10.6	26.5	39.8	24.4	25.8	29.2	30.0	1.72
3	15.8	32.5	48.8	24.4	38.7	29.2	46.3	2.58
4	21.1	37.5	56.3	24.4	51.6	29.2	61.7	3.44
5	26.4	42.0	62.9	24.4	64.4	29.2	77.1	4.30
6	31.7	26.0	68.9	24.4	77.3	29.2	92.5	5.16
7	37.0	49.6	74.5	24.4	90.2	29.2	108.2	6.02
8	42.3	53.1	79.6	24.4	103.1	29.2	123.4	6.88
9	47.5	56.3	84.4	24.4	116.0	29.2	138.8	7.74
10	52.8	59.3	89.0	24.4	128.9	29.2	154.2	8.60
15	79.2	72.7	109.0	24.4	193.2	29.2	231.4	12.90
20	105.6	83.9	125.9	24.4	257.8	29.2	308.5	17.20

1) Sawdust withdrawn every six months; 2) Sawdust withdrawn every year; L: 1.5 W; M_{ds}: Mass of dry sawdust

reactor, i.e., 14.4 and 19.2 cm for two and one compost withdraws per year, respectively. In addition, in this study the shape of the composting reactor is considered to be parallelepiped. However, the current configuration is a semicircle in the bottom due to the shape of the mixing mechanism utilized. The dimensions here determined correspond to non-mixing conditions; therefore these may change depending on the type and shape of the mixing mechanism.

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CHAPTER 27

Sustainable Wastewater Management in Palm Oil Mills

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27.1 INTRODUCTION

Palm oil is one of the most productive edible oils with a potential production of about 7.0 ton of oil per hectare/year. At present, the average productivity of palm oil is about 4.0 ton of oil per hectare/year. Good agricultural practices are needed to increase and maintain a higher level of productivity (Basiron 2007). Recycling biomass waste from palm oil mills and plantations is one valuable way to develop a sustainable oil palm plantation by maintaining the soil quality in the plantation.

Indonesia has been the biggest palm oil producer in the world since 2007. Palm oil industries have contributed significantly to Indonesia's economic development. Having sustainable oil palm plantations is a key issue in the development of palm oil industries in Indonesia. Besides crude palm oil (CPO), which is the main product, a palm oil mill also produces shell, fiber, empty fruit bunches, boiler ash, solid decanter, and *Palm Oil Mill Effluent* (POME) as by-products or waste. Due to the fact that the yield of CPO is typically not more than 25% of the fresh fruit bunches (FFB), it is important to consider how to minimize the environmental impact of palm oil mills. The major environmental impact of palm oil mills is from POME. POME is the effluent from the final stage of palm oil production in a mill. It is a colloidal suspension containing 95–96% water, 0.6–0.7% oil and 4–5% total solids including 2–4% suspended solids (Mohammad et al. 2008). Each ton of CPO production generates about 2.5–3.0 m^3 of POME (Saidu et al. 2013). The high concentration of organic content and the vast amount of POME can cause environmental pollution if they are not treated properly. On the contrary, POMEutilization can produce some valuable materials or energy that contribute to the sustainability of oil palm plantations and the mills (Hasanudin 2008).

Sustainable POME management is crucial to developing a sustainable palm oil industry (MPOB 2013a). Appropriate technologiesfor sustainable POME management at each palm oil mill is dependent on the condition of the palm oil mill and plantation, such as energy supply and utilization, soil characteristics of the oil palm plantations, and how much management pays attention toreducing

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greenhouse gas emissions. This chapter discussed sustainable POME management systems fordifferent conditions of palm oil mills in Indonesia.

27.2 PALM OIL INDUSTRIES

27.2.1 The Development of Palm Oil Industries in the World

The two main palm oil producers in the world are Indonesia and Malaysia. Together, they contribute about 85.3% of the world's production. Indonesia, as the biggest CPO producer with a share of about 46.6%, produced 23,500,000 ton CPO in 2011.Its projected production was about 26,703,000 ton CPO in 2013. Total global demand for palm oil was about 53.9 million ton in 2011 and is predicted to increase to 64.5 million ton in 2015 (Widjaya et al. 2013) and 95.7 million ton in 2025 (Oil World 2013). This situation indicates that palm oil industries will continuously grow to meet global demand.The growth of CPO production in Indonesia is 7.8% per year, which is higher than in Malaysia (only 4.2% per year) (MP3EI 2011).

Oil palm is one of the important plantation crops in Indonesia. Palm oil industries grow very quickly, supported by the growth of oil palm plantations. The total area of oil palm plantations is about 7.5 million hectares. About 60% of oil palm plantations are owned by companies, and the other 40% are owned by smallholder farmers. The growth of palm oil industries has created new jobs and increased farmers' income. Currently, about 700 palm oil millsare being operated to process FFBs from the plantations (http://www.jpnn.com/index.php?mib=berita.detail&id=142890).

The development of palm oil industries worldwide currently focuses on increasing the productivity of the land and efficiency of CPO processing in the mill. Expanding the planting area is not an attractive choice due to problems with land-use change. Environmental impact is also considered one important issue. With increased awareness about the impacts of uncontrolled economic development on the environment, especially in relation to global warming and climate change, there is mounting pressure to ensure that future development is sustainable and environmentally friendly. The oil palm industry, with its rapid expansion over the last few decades, is also not spared from such pressure.

Oil palm is a perennial crop which starts yielding palm fruit for oil about three years after planting and has a continuous productive lifespan of 25–30 years. Furthermore, with total yield of about 4.26 ton of oil/hectare-year, it is the most productive oil crop in the world, 10 times more productive than soybean, which produces only about 0.45 ton of oil/hectare-year (MPOB 2013b). This means that to produce the same volume of oil, oil palm only requires one-tenth of the area required by soybean (Basiron 2007). This is an important characteristic when considering land expansion for oilseeds cultivationto feed the increasing world population, namely production efficiency and consistent supply of edible oils.

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The increase in palm oil production worldhas had direct consequences the handling of co-products and waste. Enhancing the sustainability of its production process will give the palm oil industry many opportunities to increase its shareholder value. Improving the efficiency of power generation and its use is one important way to improve the sustainability of the palm oil industry. Implementing *Programmable Logic Controller* (PLC) in boiler and sterilizer units is known to improve the efficiency of energy and water consumption in palm oil mills.

Currently, RSPO (Roundtable of Sustainable Palm Oil) and ISPO (Indonesian Sustainable Palm Oil) have been promoting sustainable palm oil industries. RSPO has been promoting sustainable palm oil industry through voluntary involvement. On the contrary, ISPO has been promoting sustainable palm oil industry in Indonesia on a mandatory basis.

27.2.2 Palm Oil Processing

The primary objective of palm oil processing is to produce CPO and crude palm kernel oil (CPKO) through physical oil extraction of FFBs. The main steps in palm oil processing are as follows:

1. **Sterilization of the FFBs**: The fruit bunches are steamed in pressurized vessels at 135–150°C and 2.5–3 Bar for 90 min to prevent the formation of free fatty acids, destroy oil-splitting enzymes, remove mucus and prepare the fruits for subsequent processes.
2. **Threshing in a rotating drum thresher:** the steamed fruit bunches are conveyedto a drum thresher to separate the fruitlets and empty fruit bunches.The fruitlets are conveyed to the press digester, while the empty bunches are collected and transferred to the plantation as mulching or composted together with POME.
3. **Digestion and pressing:** In the digesters, the fruits are heated at 85–95°C and continuously stirred to loosen the oil-bearing mesocarp from the nuts as well as to break open the oil cells present in the mesocarp. The digested mash is then pressed using a screw press at 50 kg/cm^2 and 85–90°C for about 6–10 min to extract the oil. The press cake is then sent to a palm kernel processing unit.
4. **Clarification, purifying and drying:**Crude oil from the pressing unit containing crude palm oil (35–45%), water (45–55%), and others (cell debris, fibrous materials and non-oily solids) is then pumped to clarifier tanks to separate the oil from its entrained impurities. The temperature of the crude oil is maintained at about 90°C to get a maximum CPO yield. Clarified oil movesout from the surface part of the clarifier and is fed to centrifuge units to remove dirt and moisture before being dried further in the drying unit (vacuum dryers). The clean and dry CPO withmoisture and impurities content not more than 0.1% is ready for storage and dispatch. The sludge from the clarifier is centrifuged for further oil recovery. The water and

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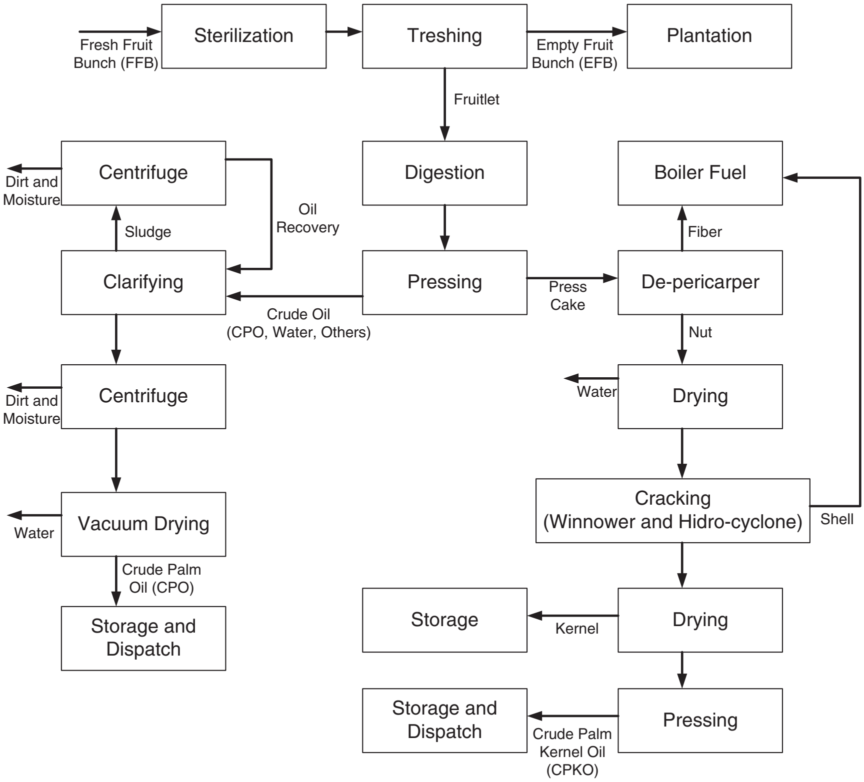

Figure 27.1. Palm Oil Processing Diagram

sludge mixture coming out of the centrifugation unit is treated in a POME treatment plant.

5. **Palm kernel processing:** The process begins with the separation of fiber and nuts in a depericarper unit. The mixed nutsare then fed to a drying unit to remove water. The nuts are cracked, and the shell and kernel are separated using a winnower and hydro-cyclone. The clean kernels are dried prior to storage or fed to a pressing unit to produce crude kernel oil.

Figure 27.1 shows the schematic diagram of crude palm oil processing in a palm oil mill, while Figure 27.2 shows the mass balance for a mill with a capacity of 40 ton FFB per hour.

The yield of CPO is only about 21.8% of FFB. The wastes generated from palm oil processing are also described in Figure 27.2. Based on the calculation, palm oil processing produces almost 40%solid waste from total FFB in theform of empty fruit bunch (EFB), fiber, boiler ash, decanter solids, and shells. Palm oil mills have used biomass waste (fiber and shells) to generate energy and steam for palm oil processing. Diesel oil is only used to generate electricity in the start-up stage. After start-up is achieved, steam is generated from fiber and shells. Figure 27.3 shows a schematic diagram of energy sources in a palm oil mill.

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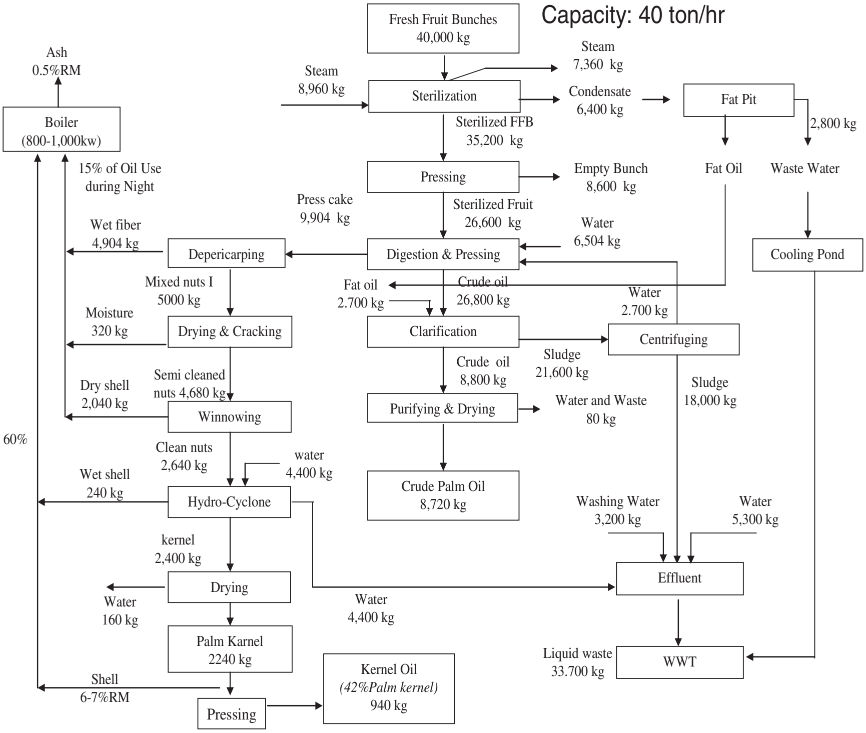

Figure 27.2. Mass balance in Palm Oil Processing

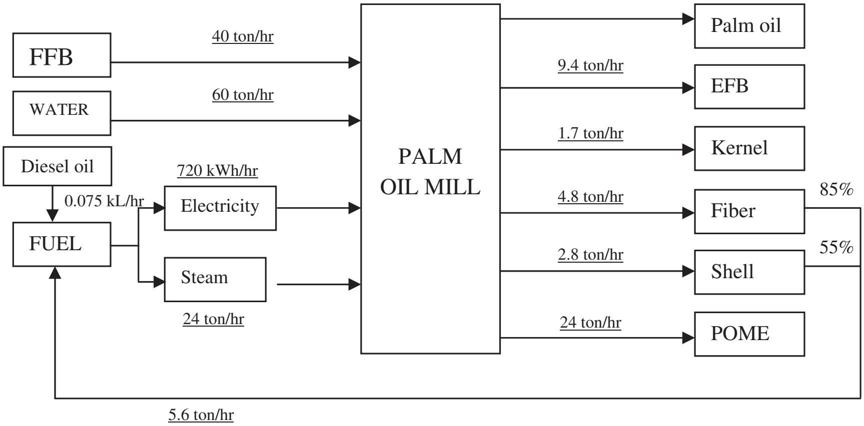

Figure 27.3. Schematic diagram of energy sources in a palm oil mill

Figure 27.3 shows that almost all mesocarp fibers are utilized.However, palm kernel shells are only 55% utilized. Therefore, a typical palm oil mill can fulfill the energy demand from mesocarp fibers and palm kernel shells. Utilizing all themesocarp fibers and palm kernel shells will produce more electricity than

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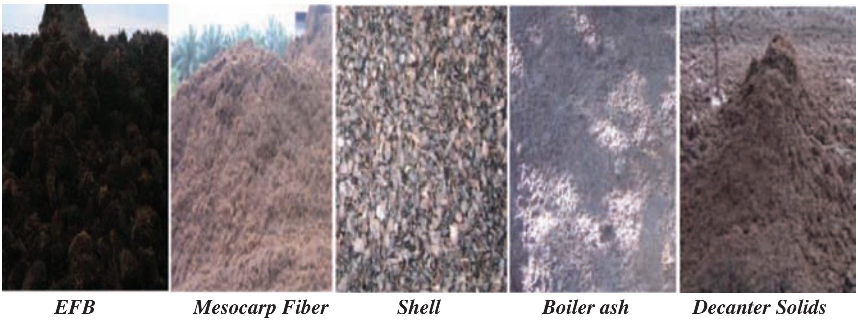

Figure 27.4. Types of solid waste from a palm oil mill

that needed by a palm oil mill. The excess energy can eventually be utilized for domestic consumption in the areas surrounding the palm oil mill.

27.2.3 Palm Oil Waste and Wastewater

Palm oil industries generate solid and liquid waste. Solid waste from the palm oil mill consists ofEFB, mesocarp fiber, kernel shell, solid decanter, and boiler ash (Figure 27.4). The amounts of each type of solid waste from a palm oil millare described in Table 27.1. Mesocarp fiber and kernel shell are utilized as a fuel to generate steam and electricity which are utilized in the palm oil processing plant. The heating values of mesocarp fiber and kernel shell are shown in Table 27.2. Incineration of mesocarp fiber and kernel shell in a boiler unit will

Table 27.1. Types and amount of solid waste from a palm oil mill

Type	*Unit*	*Amount*
EFB (wet)	ton/ton FFB	0.23$^{2)}$
Mesocarp Fiber (dry)	ton /ton FFB	0.13$^{1)}$
Kernel Shell (dry)	ton /ton FFB	0.05$^{1)}$
Solid Decanter (from millswhich use decanters)	ton /ton FFB	0.035$^{2)}$
Boiler ash	ton /ton FFB	0.025$^{2)}$

Sources: $^{1)}$KLH (2009) and $^{2)}$Schuchardt et al. (2008)

Table 27.2. Heating value of mesocarp fiber and shells of oil palm fruit

Type	*Unit*	*Amount*	*Heating value*
Mesocarp fiber (dry)	ton/ton FFB	0.13	19.055 MJ/ton
Shell (dry)	ton/ton FFB	0.05	20.093 MJ/ton

Sources: calculated from Isroi dan Mohajoeno (2007)

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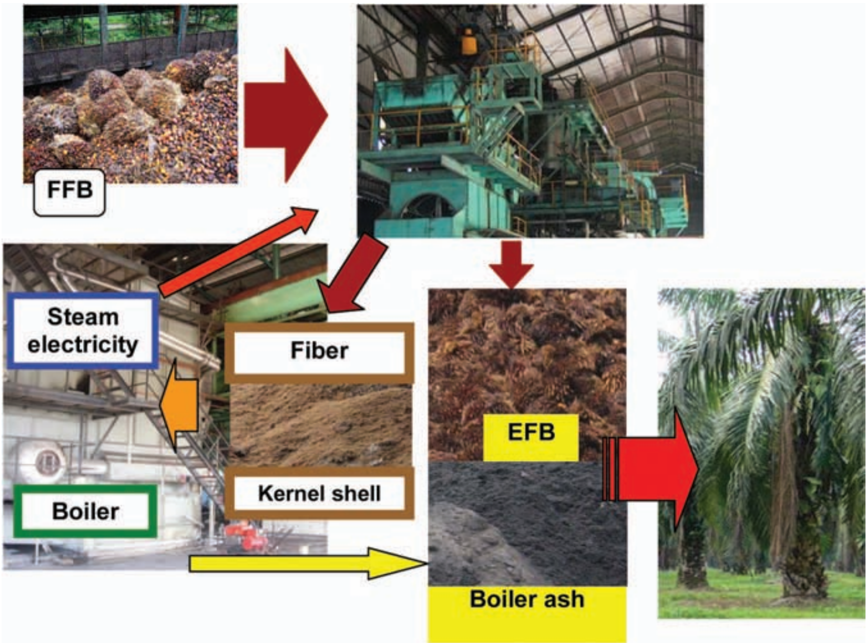

Figure 27.5. Typical utilization of solid biomass waste in palm oil mills and plantations

produce boiler ash with ahigh concentration of potassium. The boiler ash is utilized together with EFB compost or mulch and decanter solids as a fertilizer in the oil palm plantation. Figure 27.5 shows a typical system of solid biomass waste utilization in palm oil industries.

Figure 27.6 shows the application of EFB for mulchingin oil palm plantations. The application of EFB as mulching in oil palm plantations will increase organic-C and some nutrient content in the soil, which is critical to maintaining soil quality in the plantation. Even though it can provide energy by direct burning, EFB is not utilized for fuel due to its high moisture content and low heating value (otherwise, pre-treatment would be needed to reduce moisture).

Co-composting of EFB together with POME is another possibility for EFB utilization. POME is used to maintain the moisture atan optimum level during composting. Co-composting EFB with POME will unify the nutrients of both in one product and reduce the cost of EFB transport and utilization. Applying EFB-POME compost will also increase the productivity ofland to produce FFBs of oil palm (Schuchardt et al. 2008). Figures 27.7 and 27.8 show compost production from EFB and its application in an oil palm plantation.

The amount of POME produced depends on the efficiency of water consumption in the mill. It varies from 25 to 100% of FFB processed. Implementing

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Figure 27.6. Different methods of EFB for mulchapplication in an oil palm plantation

Figure 27.7. Co-compostingof EFB and POME

advanced oil separation technologies with zero dilution water and continuously sterilizing FFB is known to reduce POME production from about 0.65 m^3 per ton FFB to 0.45 m^3 per ton FFB (conventional sterilization and zero dilution water) and 0.25 m^3 per ton FFB (continuous sterilization and zero dilution water) respectively. These changes significantly influence the POME treatment processes and its cost (Schuchardt et al. 2008). POME is the main source of environmental pollution in a palm oil mill. Sources of POME are mainly sterilization (36%), clarification and purification of CPO (60%), and hydro-cyclone (4%) processes. The characteristics of POME are as follows: biochemical oxygen demand (BOD) ranging from 8,200 to 35,400 mg/L; chemical oxygen demand (COD) from 15.103 to 65,100 mg/L; oil and grease from 2,200 to 4,300 mg/L; total solids from 16,580 to 94,106 mg/L; and suspended solids from 1,330 to 50,700 mg/L

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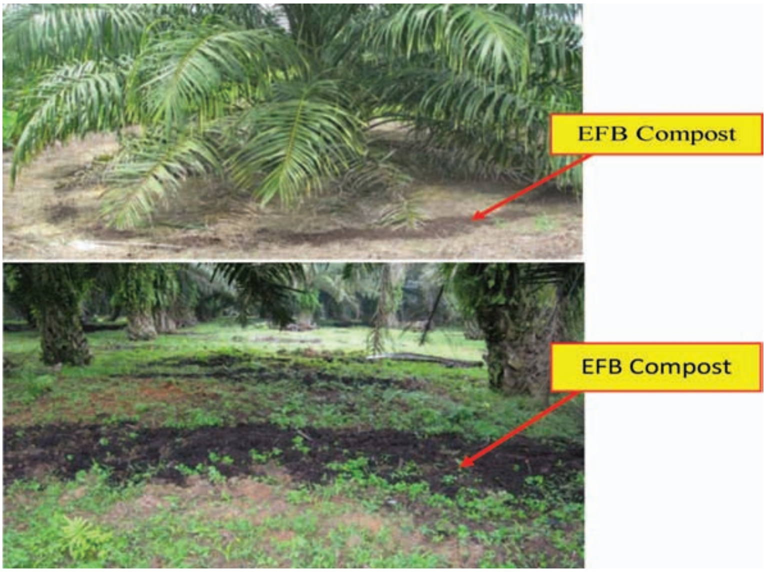

Figure 27.8. Application of EFB compost in an oil palm plantation

(Setiadi and Djajadiningrat 1996). Moreover, each ton of CPO production will generate about 2.5–3.0 m^3 of POME (Saidu et al. 2013).

27.3 PALM OIL MILL EFFLUENT MANAGEMENT–CURRENT PRACTICES

27.3.1 Anaerobic Wastewater Treatment

Wastewater treatment processes in palm oil industries usually apply conventional biological treatment. Generally, we can separate processes in the palm oil industryinto two types of treatment systems: a) biological treatment with land application; and b) biological treatment without land application. In biological treatment with land application, POME is treated in anaerobic ponds until BOD reaches a maximum of 5,000 mg/l. After that, treated POME is transferred to the plantation as liquid fertilizer. At present, biological treatment with land application is typical in palm oil industries. In Indonesia, land application of POME is regulated by the Ministry of Environment Decree number 28 and 29, 2003. According to this regulation, land application is prohibited if the oil palm plantation located in: (1) peat soil areas, (2) land with soil of permeability lower than 1,5 cm/h or higher than 15 cm/h, and (3) land where the depth of ground water less than 2 m.

Biological treatment without land application system should be implemented in palm oil industries which do not fulfil the requirements of Decree numbers 28

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Figure 27.9. Open anaerobic pond for POME treatment

and 29, 2003 by the Ministry of Environment. In this case, the effluent from POME treatment should fulfill the national effluent standard, which isset out in Decree number 51, 1995 by the Ministry of Environment. To satisfy national effluent standards, POME treatment usually consists of anaerobic ponds, facultative ponds, aerobic ponds, and sometimes sand bed filters as a polisher. This system needs a lot of energy for aeration and loses a lot of nutrients and organic materials. Figure 27.9 shows a typical open anaerobic pond for POME treatment.

An open anaerobic pond system is usually implemented to treat POME before further utilization or discharge to the environment. The anaerobic ponds emit a tremendous amount of strong greenhouse gases (i.e. methane) and the effluent from the ponds contains nutrients responsible for polluting surface and ground water. Also, open anaerobic ponds emit bad smells caused by hydrogen sulfide emission during anaerobic digestion.

27.3.2 Land Application for Palm Oil Mill Effluents

The Indonesian Government has regulations on the utilization of treated POME for land application in oil palm plantations. The regulationswere written in Ministry of Environment Decree number 28 and 29 in 2003. These regulationsaim to utilize some nutrients and organic materials which are known to contribute to maintaining soil quality in oil palm plantations. POME, either in fresh or treated form, contains a high level of plant nutrients. When the BOD is brought down to below 5,000 mg/l, treated POME is allowed to be utilized for land application in oil palm plantations. Studies by various groups have demonstrated that land application has been beneficial to oil palm, apart from extensive savings on fertilizer cost. The application of treated POME can also increase the productivity of plantation. Table 27.3 describes the effect of treated POME application on FFB

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Table 27.3. Productivity of FFB in oil palm plantation with and without treated POME application

Production Year 2005	*Planting Year*	*Productivity of FFB (kg/Ha)*	
		With treated POME	*Without treated POME*
January	1984	805.82	697.87
February	1984	222.51	151.22
March	1984	222.56	182.61
April	1984	201.56	180.00
Mei	1984	395.68	347.83
June	1984	526.80	425.15
July	1984	947.38	846.82
August	1984	1159.17	1018.26
September	1984	2161.10	2034.78
October	1984	2835.50	2675.74
November	1984	3679.87	3374.87
December	1984	2202.27	1687.30
Total		**15360.21**	**13622.45**

Source: Rejosari Palm Oil Mill internal report

production. Long-term studies have also established thatwater quality in the applied area is not affected. Tables 27.4 and 27.5 describe the effect of treated POME application on the ground water quality.

27.4 SUSTAINABLE PALM OIL MILL EFFLUENT MANAGEMENT

27.4.1 Conceptual Management of POME

Sustainabilityis a holistic conceptand encompasses three key pillars:social, environmental, and economic. These fundamental concepts are derived from the definition of sustainable development, namely “sustainable development seeks to meet the needs of the present without compromising the ability of future generations to meet their own needs” (UNWCED 1987). Based on this definition, sustainability is about the efficient management of present resources to meet future needs. In the context of the palm oil industry, sustainability is about the long-term security of the supply chain if the oil palm business is to continue with a holistic balance between social, environmental and economic needs of the country and people.

Proper management of natural resources would help protect their biological production potential and help maintain future options for their use. Indeed, a major objective of sustainable land management is the harmonization of agricultural priorities with economic and environmental concerns.

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Table 27.4. Quality of ground water inareas with POME application

			2008		*2009*		*2010*		*2011*	
No.	*Parameters*	*Unit*	*Mar*	*Feb*	*Sep*	*Apr*	*Feb*	*Apr*	*Mar*	*Sep*
1	pH		8.64	7.7	8.2	7.9	8.29	8.45	8.6	8.285
2	BOD_5	mg/L	6.32	11	46	42	30	40	14	2.29
3	Pb	mg/L	0.001	0.022	0.006	0.049	0.081	0.001	0.007	<0.0001
4	Cu	mg/L	0.18	0.92	2.06	0.26	0.05	1.22	0.06	0.0554
5	Cd	mg/L	0.001	0.01	0.003	0.009	0.0048	0.0001	0.003	0.0182
6	Zn	mg/L	0.47	0.08	0.04	0.04	0.9	0.02	0.01	<0.0001
7	DO	mg/L	6.09	6.4	9.3	6.2	4.7	4.3	4.15	4.04
8	NH_3-N	mg/L	0.61	1.37	0.63	2.02	0.95	0.97	0.54	0.0446

Source: Rejosari Palm Oil Mill internal report

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Table 27.5. Quality of ground water in areas without POME application

			2008	*2009*		*2010*		*2011*	
No.	*Parameters*	*Unit*	*Oct*	*Sep*	*Apr*	*Oct*	*Apr*	*Mar*	*Sep*
1	pH		7.7	7.9	7.56	7.3	7.8	7.8	7.5
2	BOD_5	mg/L	6	14	16	5	41	5	0.81
3	Pb	mg/L	0.019	0.014	0.039	0.041	0.003	0.023	<0.0001
4	Cu	mg/L	0.25	0.03	0.16	0.08	0.05	0.05	0.0191
5	Cd	mg/L	0.005	0.006	0.005	0.0051	0.0	0.001	<0.0001
6	Zn	mg/L	0.26	0.01	0	0.03	0.005	0.03	0.0021
7	DO	mg/L	6.3	7.3	6.4	5.5	4.1	5.5	4.06
8	NH_3-N	mg/L	0.06	0.32	0.45	0.03	0.08	0.05	0.0609

Source: Rejosari Palm Oil Mill internal report

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In Principle 5 (environment responsibility and conservation of natural resources and biodiversity) of the Roundtable of Sustainable Palm Oil (RSPO), it is stated that:

a) waste is reduced, recycled, and disposed of in an environmentally and socially responsible manner;

b) efficiency of energy use and use of renewable energy is maximized; and

c) plans to reduce pollution and emissions, including greenhouse gases (GHGs), are developed, implemented, and monitored.

In line with the principle of protecting the environment, the palm oil industry should place astrong emphasis on environmental needs. The main source of environmental pollution from a palm oil mill is POME. The oxygen-depleting potential of POME is about 100 times more than that of domestic sewage. POME causes major environmental problems in the palm oil industries. Without proper POME treatment and handling, the palm oil mill becomes synonymous with POME pollution.

Implementing Principle 5 of RSPO is very much necessary to significantly reduce the environmental impact of POME. POME reduction and recycling through methane capture and land application of treated POME will not only significantly reduce the environmental impact of POME, but will also produce valuable products, increase energy efficiency, maximize renewable energy utilization, and reduce GHG emissions. The rapid growth of palm oil industries also has high potential to provide additional revenue and other intangible benefits from POME.

27.4.2 Example of Sustainable POME Management

27.4.2.1 Electricity Generation from POME

Generating electricity from POME through biogas or methane capture has attracted considerable attention across the palm oil industries. Not only will it generate additional revenue from the sale of surplus energy, it has vast potential for methane recovery as well. Benefits of methane capture from POME are additional revenues from the sale of surplus energy and carbon credits, and reduced carbon footprint of the palm oil mill, which is important to increase the market competitiveness of palm products, mainly palm biodiesel, to environmentally-sensitive markets such as the European Union and the United States. Figure 27.10 shows the benefit of methane capture from POME and their impact on reducing global and local environmental burdens. Methane capture from POME and their utilization to generate steam or electricity will also reduce dependence on fossil fuels, enhance fuel diversity and security of energy supply, and encourage technology innovation on the sustainable management of POME.

Methane capture from POME can be carried out using anaerobic digestion in several types of bioreactors, such as covered in ground anaerobic reactor (CIGAR), continuous stirred tank reactor (CSTR), and anaerobic baffled reactor (ABR).

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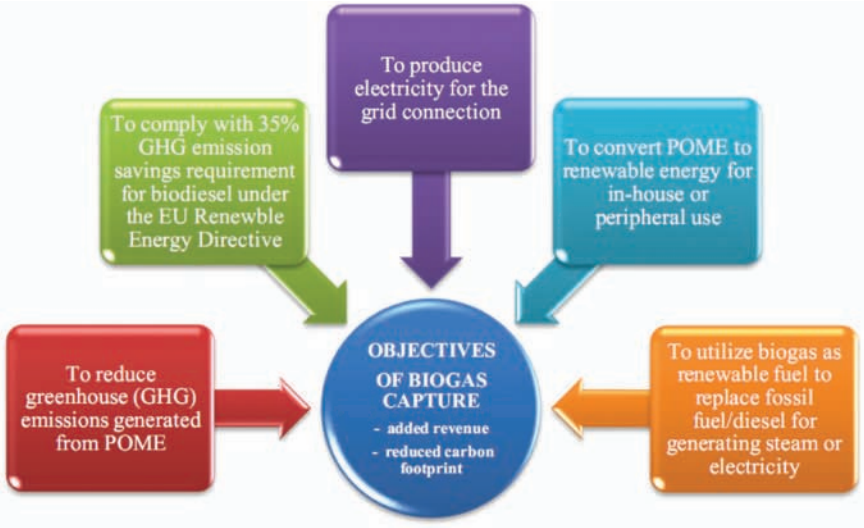


Figure 27.10. Benefits of methane capture from POME and their impact on reducing global and local environmental burden

Anaerobic digestion is a common technology used to treat POME. Conventional palm oil mills usually use open anaerobic ponds to treat POME. By covering the surface pond using the high-density polyethylene (HDPE), the open anaerobic pond will become a CIGAR. Figure 27.11 shows the process design forthe anaerobic treatment and utilization of POME.

The utilization of POME for generating heat and electricity in a palm oil mill has increased the potential of energy production from palm oil mill biomass waste. Through anaerobic digestion, a biogas plant reduces COD load by about 90%. A palm oil mill with a capacity of 45 ton FFB/hour will produce about 1.28 MW of electricity through POME treatment. In addition, biogas utilization for energy also will reduce GHG emissionsby about 6.38 ton of CH_4/day, which is equivalent to

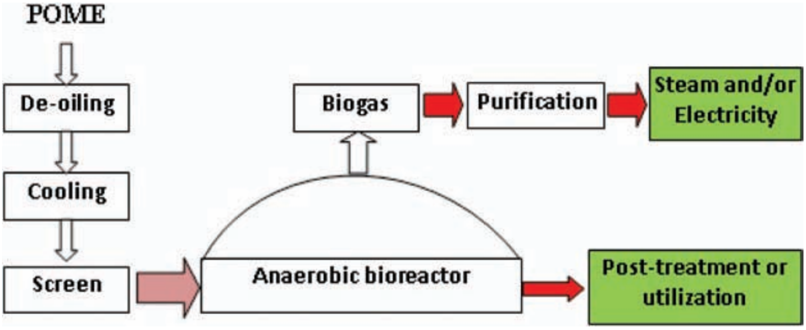
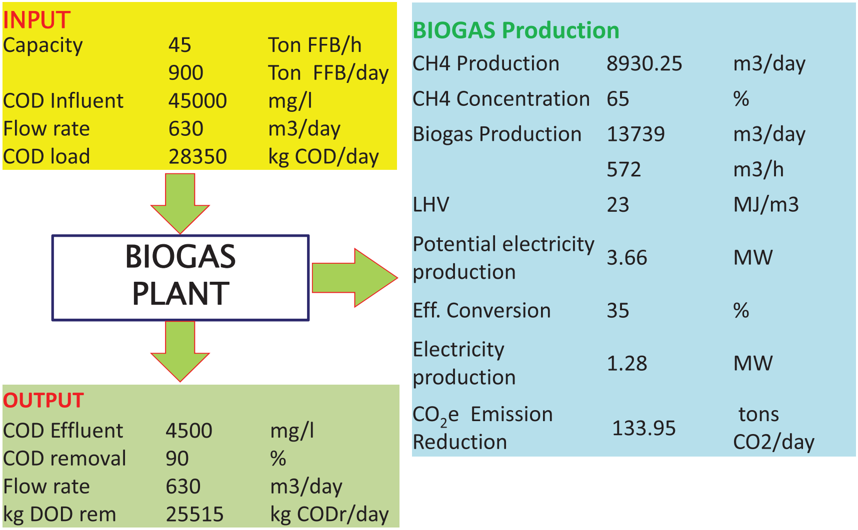


Figure 27.11. Process design for the anaerobic treatment and utilization of POME



INPUT

Capacity	45	Ton FFB/h
	900	Ton FFB/day
COD Influent	45000	mg/l
Flow rate	630	m3/day
COD load	28350	kg COD/day

BIOGAS Production

CH4 Production	8930.25	m3/day
CH4 Concentration	65	%
Biogas Production	13739	m3/day
	572	m3/h
LHV	23	MJ/m3
Potential electricity production	3.66	MW
Eff. Conversion	35	%
Electricity production	1.28	MW
CO_2e Emission Reduction	133.95	tons CO2/day

OUTPUT

COD Effluent	4500	mg/l
COD removal	90	%
Flow rate	630	m3/day
kg DOD rem	25515	kg CODr/day

Figure 27.12. Potential electricity production and CO_2e emission reduction from POME at a palm oil mill with a capacity of 45 tonFFB/hour

about 133.95 ton CO_2e/day. Figure 27.12 illustrates potential electricity production and CO_2e emission reduction from POME at a palm oil mill with a capacity of 45 ton FFB/hour.

27.4.2.2 Integrated Solutions for Zero-Waste Effluent and Palm Oil Solid Waste

The proposed concept for sustainable POME and EFB treatment can fulfill the following criteria:

- Alternative to conventional procedures such as open pond systems and dumping of EFB;
- Eliminating the pollution of surface water, groundwater and atmosphere (realization of zero waste concept);
- Minimizing nutrient losses and concentration of nutrients from POME and EFB in one product; and
- Possibility of biogas production by demand.

In this concept, utilization of POME for biogas production is onlycarried out if there is a demand or a market for biogas/energy (Schuchardt et al. 2008). The marketfor renewable energy in Indonesia is promoted through the Ministry of Energy and Mineral Resources Regulation Number 4, 2012. The National Electricity Company of Indonesia (PT. PLN) must buy renewable energy generated by some companies on a fixed tariff. Therefore, palm oil mills have a significant opportunity to sell the surplus energy through PT. PLN grids.

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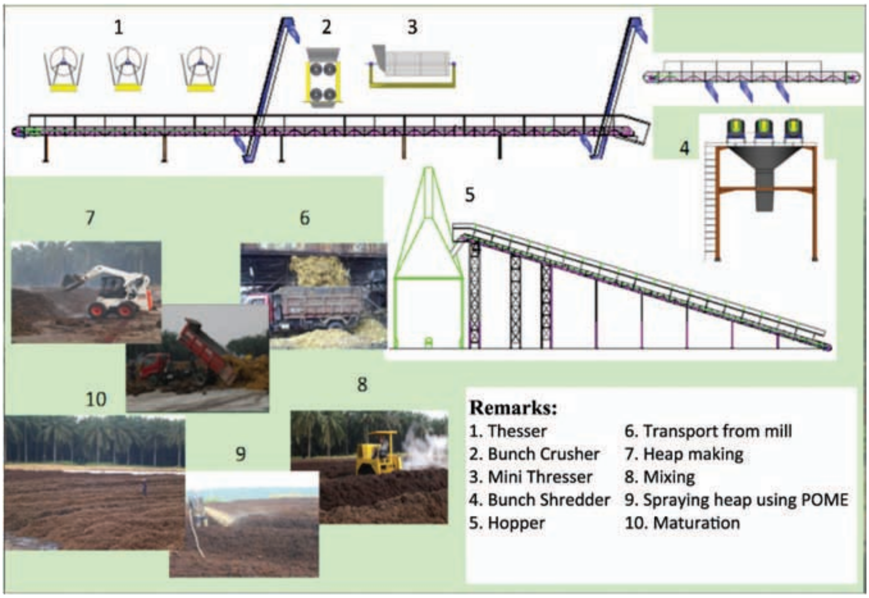

Figure 27.13. Diagram of EFB-POME compost production

Palm oil industries are currently using EFB waste for mulching and treated POME as a liquid fertilizer throughthe implementation of theland application system. Some other industriesuse EFB and POME together to produce compost. Composting EFB together with POME can minimize nutrient losses and concentratenutrients from POME and EFB into one product. Figure 27.13 shows the procedure for compost production. By co-composting EFB and POME, almost all the POME utilized is maintained at a moisture of around 60% during the composting process.A case study at an EFB-POME co-composting plant shows that about 0.091 m^3 of wastewater or about 13.06% of POME still remains and needs to be treated or utilized through land application. Table 27.6 shows the material balance in an POME-EFB co-composting process.

During replanting, the trunks and fronds are chipped and left in the inter-rows as mulch under zero-burning practices. Mesocarp fiber and palm kernel shells are burned as fuel for the boilers to produce steam and electricity. Other palm oil industries also utilizetreated EFB as fuel for boilers. Surplus energy is used at in-house or peripheral areas. Also, palm oil mills can sell the excess electricity through grid connections. Therefore, most of the wastes are now considered as co-products, especially renewable energy resources (Basiron and Weng 2004).

POME reduction technologies are also necessary to reduce environmental burden. POME reduction technologieswere developed through the implementation of PLC in the boiler and sterilization unit. Implementation of PLC reduces water consumption from 1.73 m^3 to 1.54 m^3 per ton of FFB. Reducing water consumption in the mill reduces POME production per ton of FFB from about

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Table 27.6. Material balance in a POME-EFB co-composting process

Parameters	*Unit*	*Amount*
FFB	Ton	1
Volume of POME	m^3	0.7
EFB	Ton	0.23
Volume water in FFB (moisture 60%)	m^3	0.138
Total POME spraying to EFB heap (3 m^3 of POME/ton EFB)	m^3	0.690
Total water evaporated, assumptionEvaporation rate 51 l/tonEFB/day[1,2]	m^3	0.657
Total non-evaporated water	m^3	0.171
Total weight of compost (65% of EFB)	Ton	0.150
Total water in compost (moisture 60%)	m^3	0.90
Total Leached production	m^3	0.081
Total un-utilized POME	m^3	0.010
Total wastewater produced	m^3	**0.091**
	%	**13.06**

Note: [1]Schuchardt et.al. (2002); [2]Assumption: effective evaporation conducted for 8 weeks (56 days)

0.6 m^3 to 0.55 m^3 or about50 liter per ton of FFB (*Personal communication with Rambutan Palm Oil Mill-PTPN 3, 2013*). Implementing continuous sterilization and zero dilution technology also dramatically reduces POME production to about 0.25–0.45 m^3 per ton of FFB (Schuchardt et al. 2008).

27.5 SUMMARY

Implementing POME reduction and recycling through methane capture and land application of treated POME will not only reduce its environmental impact, but also produce valuable products, increase energy efficiency, maximize renewable energy utilization, and reduce GHG emissions.

Generating electricity from POME through biogas or methane capture has attractedconsiderable attention across the palm oil industry due to (1) additional revenue from the sale of surplus energy, (2) the vast potential for methane recovery to use as a clean renewable energy, as well as (3) the mitigation of GHG emissions which is recognized by RSPO Principle 5.

The benefits of POME utilization for biogas production and composting are (1) renewable energy production, (2) reduced POME treatment cost in pond systems, (3) total utilization of the POME nutrients, (4) reduced cost of EFB transport and utilization, and (5) higher FFB yields in the plantation. With the process of mulching or compost production from EFB incombinationwith POME

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(with or without biogas production), it is possible to obtain a sustainable process in palm oil mills with zero waste.

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CHAPTER 28

Nanomaterials for Sustainable Society

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28.1 INTRODUCTION

Nanomaterial-based technology is one of the fastest growing and interesting fields in the 21st Century, and has beenplaying animportant role in development of a sustainable society (Burgi and Pradeep 2006; Fryxell and Cao 2007). Nanomaterial is typically defined as a material or a structure at a scale of less than 100 nanometers in at least one dimension. Nanomaterials are classified as zero-dimensional (such as quantum dots), one-dimensional (such as nanowires, nanofilms), two-dimensional (such as nanorods, nanotubes) and three-dimensional (such as nanocubes). Nanomaterial showsspecial phenomena, such as volumetric effect, quantum-size effect, macroscopic quantum tunnel and dielectric confinement effects. A sustainable society is to ensure the health and vitality of human life and culture and of nature's capitals, for present and future generations. These effects offer enhanced structural, magnetic, electrical, and optical properties, contributing to great potential to replace existing materials for sustainable society (Masciangioli and Zhang 2003; Roco et al. 2011; Zhang et al. 2009).

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This chapter reviews the role of nanomaterials in sustainable society, with a focus on nanomaterials for i) green process and engineeringto reduce environmental burden, ii) agriculture and food systems, iii) treatment of industrial and agricultural wastes, iv) renewable energy production and storage, and v) health care.

28.2 NANOMATERIALS FOR GREEN PROCESS AND ENGINEERING

Green process and engineering refers to measures to eliminate environmental burden in such areas as resources input, chemical substance use and energy consumption to the greatest extent possible from all the processes involved in manufacturing the products (Brennecke and Allen 2002; Pokhodenko and Pavlishchuk 2002). Nanomaterials are playing an important role in green process and engineering by material substitution, energy consumption reduction, source saving and sustainable development, and by reducing wastes and consumption of non-renewable natural resources, and cleaning up existing pollution (Anastas and Zimmerman 2003; Masciangioli and Zhang 2003). A new concept, green nanotechnology, has been proposed, which has been described as the development of clean technologies, to minimize potential environmental and human health risks associated with the manufacture and use of nanomaterials, and to replace existing products with nanomaterials that are more sustainable.

28.2.1 General Applications

With the increased emphasis on the green process, nanomaterials have also been developed toward adoption and implementation of sustainable society by minimizing the use of toxic chemicals, solvents, and energy. Nanomaterials can help resource saving, energize batteries, and reduce energy consumption by using lightweight, high strength materials based on carbon nanotubes and metal oxide frameworks as hydrogen storage materials. For example, carbon nanotubes are used to produce conductive and high-strength composites, energystorage and conversion devices, hydrogen storage media, interconnects, and so on (Baughman et al. 2002). Nanotechnology for information technology has several major applications, including i) information processing (e.g., electro-optic processing using supra-molecular structures and nanocomposites; electrically and optically switchable photonic crystals); ii) communication (e.g., reconfigurable photonic crystals, and 3-D plasmonic guiding and routing network); iii) information storage (e.g., 3-D two-photon storage and holographic storage with nanomaterials); and iv) displays (e.g., carbon nanotube computer displays). For example, nanostructured electrode materials have improved the performance of lithium ion batteries by significantly reducing the transportation and diffusion length of ions and electrons, thereby remarkably enhancing the kinetics of lithium storage (Booker and Boysen 2005; Westerhoff 2013). Lithium ions can be stored in silicon nanowires, resulting in a nanowire lithium battery that can hold 10 times the charge of existing ones that power laptops, iPods, video cameras, cell phones, and countless other devices. Batteries using nanotubes to modify electrodes have a very long shelf life because the nanotubes separate the chemicals from the electrodes when the battery is not supplying current, whereas conventional batteries have some reactions happening at a low level at the interface of electrodes (Krupenkin et al. 2004). Nanoparticles have been used in photoelectrochemical (PEC) cells to enhance water to give up electrons, a key step to speed up the PEC process (Booker and Boysen 2005).

Polymer nanocomposite materials have been very popular in the area of polymer and material science, electronics, and biomedical science (Giannelis 1996; Vaia and Gianelis 1997; Ray and Okamoto 2003). Owing to nanomaterials dispersed in the polymer matrix, the nanocomposites exhibit markedly improved mechanical, thermal, optical, and physicochemical properties when compared with the pure polymer or conventional (micron) composites, such as increased modulus, strength and heat resistance, and decreased gas permeability and flammability with very low loadings (5 wt%) of nanomaterials (Alexandre and Dubois 2000).

Hazardous materials in manufacturing processes can be replaced by nanomaterials with less toxicity and better performance that results in reduced production of wastes. For example, nano-structured catalysts make chemical manufacturing more efficient and more environmentally benign by providing higher selectivity for desired reaction products, helping to eliminate wasteful secondary reactions, and reducing energy consumption (Samorjai and McCrea 2001). Bimetallic alloy nanomaterials were widely used to control its activity, selectivity, and stability in certain reactions, which could significantly reduce the consumption of chemical reagents and production of hazardous substances (Lu et al. 1999). Nanostructured photocatalyst films have been demonstrated to be very effective in the synthesis of partial oxygenates from different precursors (Sahle-Demessie et al. 1999). Field emission displays constructed with carbon nanotubes can provide better functionality than the conventional cathode ray tubes (CRT) that contain many toxic metals (Socolof et al. 2001). Using carbon nanotubes in computer displays reduces environmental burden by eliminating toxic heavy metals and drastically reducing material and energy use requirements, whilst providing enhanced performance for consumer needs. New liquid crystalline displays are smaller, do not contain lead, and consume less power than CRT computer monitors (Socolof et al. 2001). In contrast to conventional processes that use harsh operating conditions and toxic materials, the processes using nanomaterials are environmentally benign with less industrial wastes. Therefore, nanomaterials have been offering a tremendous opportunity to evolve as a “green” industry, benefiting from the experience of previous industrial enterprises.

28.2.2 Agriculture

The application of nanomaterials in agriculture mainly includes plant germination and growth, plant protection and production, pathogen detection, and pesticide/herbicide residue detection, as well as pesticide degradation. Nanomaterials can

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help faster plant germination/production, effective plant protection with reduced environmental impact as opposed to traditional approaches. Development of nano-phase soil additives (fertilizers, pesticides, and soil conditioners) is helpful to reduce the agricultural wastes, control global CO_2 levels and improve food quality through nanoscale processes that enhance nutritional compositions of foods. Nanostructural catalysts to convert vegetable oils and other plant wastes (e.g., cornstover) into bio-fuels and biodegradable industrial solvents have been studied. Nanosensorscan detect pesticide residues in the field. Production and processing of agriculture and food products can be made more secure by the development and implementation of nanosensors for pathogen and contaminant detection. Nanomaterials increase the efficiency of pesticides and herbicides, allowing lower doses to be used. Protection of the environment through the reduction and conversion of agricultural materials into valuable products can be made easier by nanomaterials. Harmful substances (pesticides) can be converted into harmless compounds by photo-catalysis process. Nano-sized metal oxides such as TiO_2 (Bhatkhande et al. 2001), ZnO (Li and Haneda 2003), and ZnS (Torres-Martinez et al. 1999) have been used for photocatalysis. Yu et al. (2007) reported that the attraction of peroxide or hydroxyl radical and electron transfer enables the photocatalytic degradation of organochlorine pesticides on the surface of TiO_2 nanomaterials. Organophosphorus and carbonate pesticides in tomato leaves and soil can be photo-catalytically degraded at a rate of 15–30% using Rhenium-doped TiO_2 nanomaterials, which are also capable for degrading furan at a rate of 55% (Zeng et al. 2010).

28.2.3 Food Industry

Recently, words such as “biodegradable,” “organic,” “environmentally-friendly,” “annually renewable,” “sustainable,” “green,” “biopolymers,” are oftenobserved keywords in food packages. This means concerns of people about environmental problems caused by non-biodegradable solid wastes and depleting of natural resources. With the increasing need of consumers for high quality foods and concerns on limited natural resources and the environment, the use of renewable resources to produce edible or biodegradable packaging materials, which can maintain product quality and reduce waste disposal problems, are being explored.

In food industry, food proteins are often 1–10 nm in size, and most polysaccharides (carbohydrates) and lipids (fats) are less than nanometers in size. Various additives or nano-sized ingredients are approved for use in food contact materials.Natural biopolymer-based nanocomposite film material with active packaging function has been emerging because of environmental concerns for high quality food products. Much research work on the application and preparation of bionanocomposite packaging with functional properties has been expected for biodegradable nanocomposite materials to replace or reduce the use of the existing petrochemical-based packaging materials available. Starch is one of the natural biopolymers, most widely used for developing environmentally-friendly packaging materials to substitute for petrochemical-based non-biodegradable plastic materials. In order to improve the properties, including

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the resistance to water and mechanical properties of starch plastics, reinforcement of starch with nano-scale minerals has been considered without interfering in biodegradability of the composites (Park et al. 2002; Ray et al. 2002, 2003; Huang and Yu 2006).

Food packaging with enhanced functions is constantly sought in response to the consumer concerns for market globalization, food safety and growing environmental awareness. Compounding of polymers with biofibre/nanoclay hybrid fillers is a technique which can complement the draw backs of conventional polymers and promise a new crop of stronger, disposal, short life, high barrier, and environmentally compatible food packaging materials (Henriette 2009; Silvestre et al. 2011; Timothy 2011). The use of biofibre/nanoclay based hybrid materials will contribute to sustainability and reduction in environmental hazards associated with disposal of synthetic polymer based packaging materials. Nanoclays have been reported to reinforce polymeric materials and to reduce the permeability of gases (Zhong et al. 2007; Paul and Robeson 2008; Balakrishnan et al. 2011), and have been used in multilayer film packaging, such as beer bottles, carbonated drinks, and thermoformed containers for industrial purposes (Silvestre et al. 2011). Nanoclay-composited plastic bottles can keep juice fresh and high shelf life up to 30 weeks.

Bacteria are the most primitive life forms, andare almost everywhere. Some are useful, but others are causing diseases. Green sensors equipped on a meat package may detect the presence of more than a threshold level of harmful bacteria (Busch 2008). Organic dyes are the most commonly used biolabels to detect the bacteria. Quantum dots (QDs) with bio-recognition molecules have been used as fluorescent labeling of detecting bacteria. The QDs have prominent advantages over organic dyes as the QDs are more efficient in luminescence and show excellent photostability (Vacassy et al. 1998), and their emission spectra are narrow and tunable. Su and Li (2004) reported a sensitive and rapid method for detection of *E. Coli* O157:H7 usingQDs as a fluorescence marker coupled with immunomagnetic separation. Besides, liposomal nanocapsules were used as delivery vehicles of nutrients, nutraceuticals, food additives, and food antimicrobials that could aid in the protection of food products against growth of spoilage and pathogenic microbes (Taylor et al. 2005).

28.3 NANOMATERIALS FOR TREATMENT OF INDUSTRIAL/ AGRICULTURAL WASTES

Nanomaterials can be fabricated with specific properties that can detect a particular pollutant within a mixture. The small size of nanomaterials, together with their high surface-to-volume ratio, can lead to very sensitive detection. These properties will allow developing highly accurate and sensitive pollution-monitoring devices. Nanomaterials can also be engineered to actively interact with a pollutant and decompose it to less toxic intermidiates.

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28.3.1 Photo-Catalysis

Although the treatment of industrial and agricultural wastes through the incineration process has many advantages (e.g., a high degree of destruction, the reduced land usage, the potential for energy recovery), waste incineration may cause serious environmental problems such as toxic dioxin emission from inadequate equipment or inappropriate incineration. Photocatalytic degradation of industrial and agricultural wastes by using nanomaterials due to the characteristics of nanomaterials (surface effect, adsorption and surface reaction, etc.)as photocatalysts has been studied as an eco-friendly alternative disposal method (Hidaka et al. 1996; Mills and Le Hunte 1997). Nano-materials could provide the following advantages: (1) a large quantity of particles can reach the surface leading to high photo-catalytic efficiency due to their small sizes; (2) charge transfer at the interface and photo-catalysis activity of nanomaterials can be detected due to the transparency and specially optical property of nanomaterials when they are dispersed in the medium. For example, catalytic degradation of solid waste by TiO_2 nanomaterials is 10 times faster than conventional TiO_2.

Large amounts of polystyrene (PS) and poly(vinyl chloride) (PVC) are used as conventional packaging materials in food service and retail industry, and protecting electronic instruments, household appliances, auto parts, and other fragile goods from damage. Due to its inertness, these plastic products are non-biodegradable in the natural environment and landfills, causing a serious environmental problem, the so-called "white pollution." Researchers have proposed to utilize an eco-friendly alternative strategy to treat PVC/PS wastes by the application of nanomaterials. It is wellknown that TiO_2 nanomaterial produces electron-hole pairs under illumination of UV-light and is a high-efficient photocatalyst. Photo-degradable PVC/TiO_2 nano-hybrids can be used as an eco-friendly alternative to the current waste landfill and dioxin-emitting incineration of post-treatment (Zhao et al. 2011).

28.3.2 Nanomembranes for Treatment of Water and Wastes

Nanomembraneis a monolayer or multilayer membrane composed of nanomaterials. The membrane can separate target material from mixture that containing various substance. Considerable studies have been conducted using membranes made with nanomaterials for treatment of water and industrial/agricultural wastes. Nanomembrane-consisted filtration (NF) is applied for wastewater treatment, drinking water production, and removal of viruses, bacteria (ven der Bruggen and Vandecasteele 2003), small organic compounds (Braeken et al. 2006) and color components (Frank et al. 2002). DeFriend et al. (2003) fabricated alumina nanomembranes using acetic acid surface stabilized alumina nanoparticles, which has a molecular weight cut-off in the range of <1000 g/mol and shows good selectivity to a range of synthetic dyes. Ericsson et al. (1996) reported that the removal of color and organic matter was almost complete (undetectable levels) with NF. Christen (2004) reported a chemically modified nanoporous ceramic that can remove contaminants from all types of waste streams faster and

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at a significantly lower cost than conventional technologies such as ion exchange resins and activated carbon filters. Binder et al. (1992) invented a nanofilter membrane and used it to filter the outflow of a food processing stream, which begins with starch slurry and ends with glucose syrup which, in its preferred form, is about 95% dextrose and 5% di- and trisaccharides. The nanofilter membrane is able to pass the dextrose while retaining the di- and trisaccharides. As a result, a purity of over 99% of dextrose is produced.

Carbon nanotube (CNT) membranes have been made for the transport of $Ru(NH_3)_6^{3+}$ (Hinds et al. 2004), multiple components of heavy hydrocarbons from petroleum, bacteria (Srivastava et al. 2004), water, ethanol, *iso*-propanol, hexane, and decane (Majumder et al. 2005a). Holt et al. (2006) found that the gas and water permeability of these CNT membranes are several orders of magnitude higher than those of commercial polycarbonate membranes (diameter = 15 nm), despite having pore sizes of an order of magnitude smaller. Thus, CNT membranes can be a new separation technique with great potential for applications in reduction/treatment of wastes and water purification.

Nanomaterials have been adsorbed onto the surface of microbial cells to form cell-nanomaterials complex in the biodesulfurization process for sulfur removal. Nanoparticles on the surfaces of microbial cells can increase the reaction activity of microbial cells by increasing mass transfer rate, and is helpful to lessen environmental pollutions. The biodegradation rate of polycyclic aromatic sulfur compounds increased over 2 folds by self-assembling nano-γ-alumina on cell surfaces (Shan et al. 2005a). Magnetite nanoparticles were adsorbed onto the surfaces of *P. delafieldii* cells and cell-nanomaterials had distinct super paramagnetic properties, which could be collected conveniently by application of an external magnet or operated in a magnetically stabilized-bed reactor (Shan et al. 2005b). A magnetically stabilized fluidized bed is a highly efficient bio-reactor that takes advantage of both fluidized beds and fixed beds.

28.3.3 Nano-Adsorbents for Pollutant Removal

The use of nanomaterials as adsorbents can improve the processes to reduce formation and emissions of industrial and agricultural wastes, including emission of ozone depleting gases (e.g., chlorofluorocarbons (CFCs), volatile organic (chlor-containing) compounds (VOCs) and “greenhouse” gases (CO_2, CH_4, N_2O, etc.). Nano-adsorbents also can enhance the processes for flue gas recovery (SO_x and NO_x), solvent vapor fractionation and solvent vapor recovery, wastewater treatment,as well as supply/production of drinking water and industrial solid aerosols (Dabrowski et al. 2001).

The nanostructured sorbent has an extremely small size and a high specific surface area, and provides better kinetics for adsorption of pollutants. The use of a nano-sorbent injection method to capture heavy metals in combustion environments has been widely studied. Several sorbent materials, including calcium, silica, complexes of aluminum-silicon, and other oxides, can have very high capture efficiencies. For example, capture efficiencies of lead exceeded 95% in a high-temperature environment by utilizing nanostructured silica sorbent.

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Semiconductor nanomaterials can be coated on the surface of walls or other substances as air photo-cleanser, which can absorb the harmful gas such as SO_2, H_2S, NO, NO_2, as well as methanol, sulfide, ammonia and other odor. Nanocrystals have been used to remove carbon dioxide released from the smokestack. When carbon dioxide lands on a nanocrystal composed of cadmium, selenium, and indium, the nanocrystal donates an electron to the carbon dioxide. This extra electron allows the carbon dioxide to react with other molecules and then becomes harmless (Booker and Boysen 2005).

Persistent organic pollutants(POPs), heavy metals, etc. pollutants in water and soil are the key factors that negatively impact the environmental quality. Even trace pollutants can enter human body and harm to human health. Nanomaterials provide a useful method for detection and treatment of trace pollutants in the environment. Nanomaterials were used as detection and treatment of POPs and heavy metals by using nanomaterial-based analytical technology. Mercury, primarily emitted from coal combustion systems (Rodriguez et al. 2004), is a toxic substance transported on a global scale. The carbon sorbents have been found to be most effective at the nanoscale with functional groups that have a high affinity for mercury, such as halogens and other chelating groups (Kwon and Vidic 2000). Mercury pollutants using titanium oxide nanocrystals under UV light can be converted into mercury oxide, a solid that can be easily removed. Nanomaterials can be anchored onto substrates for remediation of contaminated air and water streams by adsorption or absorption processes (Ponder et al. 2000). The adsorption of organic compounds to single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) correlates with varied physical-chemical properties (e.g., hydrophobicity, polarity, electron polarizability, size) (Chen et al. 2007). For example, carbon, zeolites, silica gel, alumina and membranes, are very common adsorbents for the treatment of contaminated streams and removals of organics and heavy metals. Carbon adsorbents in nano-sizes are novel manufactured materials, having widespread and more highly potential applications. For example, fullerenes, SWCNTs, and MWCNTs were investigated to remove/adsorb polycyclic aromatic hydrocarbons (PAHs), N_2, benzene, methanol, among other contaminants (Yang et al. 2006; Cho et al. 2008; Sun 2008). Hexane, benzene, trichloroethylene, toluene, methyl ethyl ketone (MEK), super greenhouse gas (Tetrafluoromethane), cyclohexane and acetone can be adsorbed on MWCNTs (Lu and Su 2007; Shim et al. 2007; Kowalczyk and Holyst 2008; Shih and Li 2008).

Atoms on the surface of the nanometer metal, especially the atoms at the edge and corner, have high chemical activity; these atoms arethe active centers of catalyst and active sites of adsorbent. Nano-scale zerovalent iron (NZVI) has more surface areas and higher reactivity than the zero-valent iron (ZVI), and therefore, NZVI has an excellent performance in (physical) adsorption.NZVI is a suitable adsorbent for the removal of Ba^{2+} ions (Celebi et al. 2007), humic acid (HA), As (III) and As(V) (Giasuddin et al. 2007). Phosphorus is one importantnon-point source pollutant. Ligno-cellulose-based anion removal media (LAM) have been developed in association with iron nanocoating technology as means for

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phosphorus adsorption from contaminated water. Iron coated lignocellulose pellets have been proved as an efficient adsorbent for phosphorus removal from polluted water (Kim et al. 2006).

Silica-titania nanocomposites can be used to remove mercury from air or vapors, in which titanium can transform mercury to a less volatile form (mercury oxide) (Pitoniak et al. 2005).

28.3.4 Flame Retardant Nanocomposites

Flame retardant technology is to reduce flammability of polymeric material, prevent burning of materials and delay the spread of flames. Conventional flame retardant materials have shortcomings in mechanical performance, price, environmental pollution, and so on. Nanomaterials, when properly dispersed in polymer matrices, are known to contribute to the improvement of properties such as thermal, mechanical or enhanced flame retardancy. The new properties of these polymer nanocomposites fundamentally originate from the change in the polymer nature and the interaction between polymers and filler surfaces, and depend strongly on the effective surface area and dispersibility of the fillers in a polymer matrix. Good dispersions of fillers would result in a true nanocomposite at lower filler loadings than conventional materials (cf. below 3 vol% for typical layered silicates or 1 vol% for single-walled carbon nanotubes) (Laoutid et al. 2009; Son et al. 2007).

The first example of polymer nanocomposites formed by the addition of layered silicates at a nanoscale was reported in 1950 (Carter et al. 1950). Compared with nylon-6, nylon-6 clay-nanocomposite with 5% clay mass fraction shows excellent enhancement of mechanical properties, increase of heat distortion temperature (HDT) up to 152°C from 65°C, and 63% reduction of the peak heat release rate (HRR), the most important parameter for predicting fire hazard (Gilman et al. 1997; Kojima et al. 1993; Giannelis 1996). Different flame retardant mechanisms including barrier effect, char formation, 3Dnano-materials structure, and radical trapping, have been proposed to explain how/why nano-materials to reduce the polymer flammability. Chemical mechanisms are always accompanied by one or several physical mechanisms. There are synergistic effects to enhance the flame retardancy when two or more types of nanofillers are used or one type of nanofiller is combined with other flame retardant materials.The category, surface property, and content of nano-materials are critical factors affecting flame-retardancy of polymer nanocomposites.

Commercial and common nano-fillers include silicate materials (such as nanoclays), inorganic hydroxides (such as aluminum hydroxide), carbonous materials (such as carbon nanotubes), and particulate materials (such as polyhedral oligomeric silsesquioxanes), used in polymers to form polymer nanocomposites. Nano-clay is the most efficient nanomaterial used as flame retardants in flame-retardant polymer nanocomposites. Addition of about 5% of nanoclay can provide up to more than 60% reduction of PHRR. Surface modification of nanoclays for improving the dispersibility of nano-materials in polymer matrix can optimize flame-retardant property of polymer nanocomposites and further

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enhance the efficicency of flame retardancy, for example, 4% octadecylammonium-modified nano-clays in polypropylene-graft-maleic anhydride reduced 75% PHRR. LDH is another efficient nanomaterial and a usage of 10% LDH could reduce 60% PHRR.

Since 1990s, new categories of polymer nanocomposites have been well developed and widely applied in transportation, electrical and electronics, food package, and building industries.Flame retardant performance of polymer/carbon nanotubes composite system has been studied since 2002. To replace the modified layered silicate by organic carbon nanotubes has two obvious advantages: (1) easy to spread out, do not need to carry on the organic processing; and (2) do not need to use compatibilizer. Just 0.5% dosage of carbon nanotubes can make the heat release rate and mass loss rate of material reduced significantly. When carbon nanotubes and clay coexist, polymer nanocomposite provides excellent thermal stability and improves the densification degree of carbon layer that form combustion and make the flame retardant performance more superior.

28.4 NANOMATERIALS FOR RENEWABLE ENERGY PRODUCTION/STORAGE

Nowadays, renewable energy sources are essential to be a part of sustainable society. Nanomaterials, with tailored characteristics of small size, very high surface-to-volume ratio, tolerance of structure change and strain relaxation can play an important role in the development of renewable energy production and storage.

28.4.1 Dye-Sensitized Solar Cell

A dye-sensitized solar cell (DSSC) is a low-cost thin film solar cell (Zhang et al. 2013). It is based on semiconductor nanomaterials formed between a photosensitized anode and an electrolyte, a photoelectrochemical system. The cell consists of an anode made of a thin film of titanium dioxide nanomaterials deposited on a conductive transparent substrate. High surface area of TiO_2 nanomaterials can provide a large surface for the dye adsorption. After soaking the film in the dye solution, a thin layer of the dye is left covalently bonded to the surface of the TiO_2. DSSCs have many advantages over conventional silicon-based solar cells, such as, transparency, low cost, and high power conversion efficiencies under cloudy and artificial light conditions. The DSSCs with nanostructure titanium oxide/porphyrins dye thin films on TCO glass substrates achieve a solar efficiency as high as with 13% (Aswani et al. 2011). The development of TiO_2 nanomaterials has been widely focusing on to improve the efficiency of DSSCs (Kim et al. 2009). Carbon nanotubes and quantum dots are embedded in conductive polymers or mesoporous metal oxides for making non-silicon solar panels. By varying the size of the quantum dots, the cells can be tuned to absorb different wavelengths, which may be able to achieve up to 42% energy conversion efficiency due to the multiple exciton generation (MEG) (Shabaev et al. 2006).

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28.4.2 Lithium Battery

Nanomaterials are key in developing high-capacity energy storage technologies such as lithium-ion battery (Bruce et al. 2008). Significant breakthroughs have been achieved utilizing advanced nanomaterials to increase cycle life and enhance charging rate performance due partially to the excellent mechanical properties of nanomaterials, high surface area, and fast lithium and electron transportation (Su et al. 2013). First, the reduced dimension of nanostructured materials allows shorter transport distances for lithium-ion and the intercalation time decreases with the square of the particle size, that can increases the rate of lithium insertion/removal and electron transport. Second, the high surface area of nanostructures permits a high contact area of the electrode with the electrolyte and hence a high lithium-ion flux cross-section coefficient on the interface per mass of the electrode material. Third, the chemical potentials for lithium ions and electrons can be modified by tuning the size of the materials on the nanoscale. Fourth, nanostructures can provide facile strain relaxation, tolerate large volume change during lithiation and delithiation to prevent electrode pulverization and maintain effective electrical contact, allowing a large range of solid solutions. For instance, $LiFe_{1-2x}P_{1-x}O_{4-x}$ nanomaterials exhibited a good capacity of 130 $mA\,h\,g^{-1}$ even at a discharge rate of 50°C.

28.4.3 Fuel Cell and Hydrogen Storage

Nanomaterials have the potential to improve two major components of the hydrogen fuel-cell system, that is, producing and storing hydrogen. For example, homogeneous distribution of small Pt nanoparticles and the mesoporous surface of the TiO_2 hollow spheres apply in proton exchange membrane fuel cells (PEMFCs) can improve the performance of PEMFCs. Pt NPs/Nb-TiO_2 composites exhibit more enhanced activity and stability than those of the commercial E-TEK Pt/C catalyst (Sun et al. 2012).

Nanomaterial-based catalysts, due to large specific surface area, good stability and high activity, show an excellent performance for hydrogen production (Table 28.1). Such as Pt-Ru-Mg/ZrO_2 catalyst applied on the SRE, can achieve 100% conversion rate at the temperature of 250°C (Josh et al. 2012). There are many nanomaterials used as hydrogen carriers (see Table 14.1, Dillon et al. 2003). For example, carbon nanotubes may hold 50 wt% hydrogen although <1% storage is practically accepted at cryogenic temperatures. Metal-organic framework-5 (MOF-5) with a cubic extended small porous structure can absorb hydrogen up to 4.5 wt% (17.2 hydrogen molecules per formula unit at room temperature, a pressure of 20 bar and 78 K (Rosi et al. 2003).

28.5 NANOMATERIALS FOR HEALTH CARES

Nanomaterials have been showing great potentials in biotechnology and health, with the important impact on the quality of health in a sustainable society. Nanomedicine is a discipline by applying nanomaterials to develop novel

Table 28.1. Hydrogen storage capacity of nanomaterials

Material	*Density (wt%)*	*Temperature (K)*	*Pressure (mPa)*
>**10 wt**%			
GNFs (Platelet)	53.68	RT	11.35
GNFs (Tubular)	~10	RT	10.1
CNFs	~10	RT	8–12
Li/K-GNTs (SWNT)	~10	RT	8–12
Li-MWNTs	20	~473–673	0.1
K-MWNTs	14	<313	0.1
GNFs	11.26	RT	11.35
1–10 wt%			
SWNTs (Low Purity)	5–10	273	0.04
SWNTs (High Purity)	8.25	80	7.18
CN nanoballs	8	573	0.1
Nano graphite	7.4	RT	1
SWNTs (High Purity + Ti Alloy)	6–7	~300–700	0.07
GNFs	6.5	RT	~12
CNFs	~5	RT	10.1
MWNTs	~5	RT	~10
MOF-5	4.5	78	2
SWNTs (High Purity + Ti Alloy)	3.5–4.5	~300–600	0.07
SWNTs (50% Purity)	4.2	RT	10.1
Li-MWNTs	~2.5	~473–673	0.1
IRMOF-8	2.3	RT	1
K-MWNTs	~1.8	<313	0.1
(9,9) Array	1.8	77	10
IRMOF-6	1.1	RT	1
MOF-5	1.0	RT	1
<**1 wt**%			
MWNTs	<1	RT	Echem
CNF	0.1–0.7	RT	0.1–10.5
(9,9) Array	0.5	RT	10
“Graphitic” Carbon (BASF, Germany)	0.3	RT	1
SWNTs	~0.1	300–520	0.1
“Active carbon” (CECA, France)	0.1	RT	1
Various	<0.1	RT	3.5
SWNT (+ Ti Alloy)	0	RT	0.08

Note: 1 mPa = 10 bar
Source: Dillon et al. (2003) and Rosi et al. (2003)

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diagnosis, therapies and improve existing treatments (Zhang et al. 2008). Atoms and molecules are manipulated to produce nanomaterials of the same size as biomolecules for interaction with human cells, in which can be treated by stimulating the body's own repair mechanisms. It will help the early diagnosis and treatment of diseases such as cancer, diabetes, Alzheimer's, Parkinson's and cardiovascular diseases. Preventive medicine may then become available.

Nanodrugs and nanodiagnostics have been developed to increase bioavailability profiles, enabling lower doses and thus minimizing the adverse impact found with conventional drugs in clinical practices and increasing the quality of patient health (Vizirianakis 2011). Nanovehicles, such as dendrimers, have been used as a therapeutic tool and designed to specifically accumulate in the sites of the body in which they are needed in order to improve pharmaco-therapeutic outcomes. Mesoporous silica nanomaterials can be used as an ideal drug delivery vehicle with its excellent drug loading capacity, easily synthesis, and biocompatibility. Doxil (a doxorubicin carrying nano-drug) was the first Food and Drug Administration (FDA)-approved nanomedicine used in the treatment of cancer patients (Gabizon et al. 2003). Long circulating PLGA–PEG NPs were used as biodegradable polymeric nanospheres for drug delivery (Gref et al. 1994). In 1996, the FDA approved polymer-coated iron oxide nanomaterials for clinical use as MRI contrast agent (Ros et al. 1995). In 2007, targeted nanomedicines like Genexol–PM (polymeric micelle NPs), CALAA-01 (a targeted cyclodextrin–polymer hybrid NP), BIND-014 (targeted polymeric NPs) and SEL-06812 (integrated polymeric nanoparticle vaccines) for cancer therapy entered into human clinical study (Kim et al. 2004).

Nanodiagnostics, the use of nanomaterials for clinical diagnostic purposes (Jain 2005), was developed to meet the demand for increased sensitivity in clinical diagnoses and earlier disease detection, including in vivo imaging and in vitro diagnostic. Nanomaterials have widely used as imaging contrast agents in many technologies, such as positron-emission tomography (PET), single-photon-emission CT (SPECT), fluorescence reflectance imaging, fluorescence-mediated tomography (FMT), fiber-optic microscopy, optical frequency-domain imaging, bioluminescence imaging, laser-scanning confocal microscopy and multiphoton microscopy (Weissleder and Pittet 2008). Nanobiosensors are revolutionizing the in vitro diagnosis of diseases. They allow healthcare professionals to simultaneously measure multiple clinical parameters using a simple, effective and accurate test. These devices can be used for high-throughput screening and for the detection of a single disease in various samples or of various diseases in a single sample. Nanomaterial-based microarray has allowed investigators to address previously intractable problems and identify novel potential therapeutic targets. Microarray technology has been used to identify cardinal aspects of growth and development and explore the underlying genetic causes of numerous human diseases (Debouck and Goodfellow 1999). Microarrays have been widely applied in the study of various pathological conditions, including inflammation (Heller et al. 1997), atherosclerosis, breast cancer, colon cancer and pulmonary fibrosis. Lab-on-a-chip has been used in real-time polymerase chain reaction (Kim et al.

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2009) and immunoassays to detect bacteria, viruses and diseases (Ghallab and Badawy 2010; Stybayeva et al. 2010).

Due to their unique photophysical properties, upconverting ceramics such as $NaYF_4:Er^{3+}$, Yb^{3+} nanoparticles have become promising optical materials for biological imaging. Further, $NaYF_4:Er^{3+}$, $Yb^{3+}@SiO_2$ core-shell nanocomposites, which contain highly absorbing NIR carbocyanine dyes in their outer silica shell, are designed and Proof-of-principle in vitro experiments are demonstrated the combined imaging and photo-thermal properties of this nano-composite (Shan et al. 2013).

28.6 SUMMARY

Due to their unique properties, nanomaterials have been playing an important role in a sustainable society. In this chapter, nanomaterials for "green" industry, agriculture, food industry, environmental protection, and renewable energy, as well as health care, are reviewed and summarized. Although the potential applications of such materials have been widely studied in many areas, more efforts are still needed for the continuing study of their practical applications in the future.

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