



Immobilization of *Chetoceros* sp Microalgae with Silica Gel through Encapsulation Technique as Adsorbent of Pb Metal from Solution

BUHANI, SUHARSO and Z. SEMBIRING

Department of Chemistry, Faculty of Mathematic and Natural Sciences,
University of Lampung, Lampung, Indonesia.

(Received: January 05, 2012; Accepted: February 10, 2012)

ABSTRACT

Immobilization of *Chetoceros* sp microalgae with silica as supporting matrix has been carried out through encapsulation technique with using solution of Na_2SiO_3 sol. Identification of functional groups and surface morphology from adsorbent obtained was performed with utilizing infrared spectrophotometer (IR) and scanning electron microscopy (SEM). Adsorption process of Pb(II) ion on adsorbent was performed with batch method including determination of rate, capacity, and optimum pH of adsorption. Adsorption data found show that adsorption process of Pb(II) ion by *Chetoceros* sp biomass and *Chetoceros* sp-silica leans to follow pseudo first order kinetic model with each rate value (k_1) of 0.032 and 0.065 min^{-1} . Adsorption capacity (q_m) of Pb(II) ion on *Chetoceros* sp-silica adsorbent is higher than adsorption capacity of Pb(II) ion on *Chetoceros* sp adsorbent without immobilization with silica.

Keywords: Immobilization, Encapsulation, *Chetoceros* sp, Adsorption.

INTRODUCTION

Contamination of heavy metals in environment is one of serious problems to be controlled currently¹. This case occurs because of increasing of heavy metal use in industry followed by negative effects of spreading waste containing heavy metals in environment². As other environmental pollution sources, heavy metals can move as far as possible in the environment and they can be potential problem for our live in the next time. One of heavy metals which is more produced and broadly used is Pb metal. The biggest sources of Pb released to environment are derived from battery manufacturing, acid metal plating and finishing, ammunition, tetraethyl lead

manufacturing, ceramic and glass industries printing, painting, and dying³. As other heavy metal characteristics, adsorption of Pb metal in human body is very slow⁴, so that accumulation process can be progressive toxicity⁵.

In order to handle spreading of Pb metal in the environment, several programs have been applied to reduce spreading and concentration of heavy metals⁶ especially Pb metal in the environment as use of algae biomass as effective adsorbent to bind heavy metal ions *via* adsorption process⁷. Algae biomass from several species of algae is effective to bind metal ions from aquatic environment⁸⁻¹⁰ because algae biomass contains some functional groups which are play a role as

ligand toward metal ions^{11,12}. But, for the specific adsorbent material, algae biomass has some problems such as; low density and easy to be degraded biologically or chemically. These are to be ineffective to be purposed as a column filling material to be a continually adsorption process⁸. In order to control the weaknesses of algae biomass⁵ use as adsorbent, immobilization process has been applied with using several supporting matrixes as silica gel^{13,14}. The algae biomass used is *Chetoceros* sp microalgae which has big enough abundance in the ocean. In this research, it was performed immobilization of biomass with silica matrix through encapsulation process. Encapsulation technique is very potential because silica matrix can form cage for biomolecules to produce stronger sites for biomolecules¹⁵ and to be also used for immobilization of protein on biomass to keep its spectroscopy characteristics and biological activities¹⁶. Encapsulation process of *Chetoceros* sp biomass with silica will maintain active groups playing a role as ligands to bind metal ions and to produce chemically stable adsorbent. In order to know success of the encapsulation process, the adsorbent resulted from immobilization process was examined its adsorption characteristics toward Pb(II) ion in solution based on kinetic model and adsorption isotherm.

EXPERIMENTAL

Material and Instrumentation

Chetoceros algae biomass was taken from Lampung Sea Cultivation Bureau (Balai Budidaya Laut Lampung), Indonesia. Na₂SiO₃, strong acid cation exchange resin, phosphate buffer, Pb(NO₃)₂, HCl (37 %), and NaOH were ordered from Alba Chemical.

Analytical balance (Mettler AE 160), sieve (with size of 200 mesh), oven (Fisher Scientific), magnetic stirrer, centrifuge (OSK 6474B), pH meter (Orion 4 Star), vacuum pump (Buchi VacR V⁵⁰⁰) were used as apparatus in this project. Atomic absorption spectrophotometer (AAS) (Perkin Elmer 3110) was applied to calculate metal concentration. IR spectrophotometer (Prestige Shimadzu) was performed to identify functional groups from adsorbent. SEM-EDX (JSM 6360 LA) was carried out to analyze surface morphology of adsorbent.

Preparation of *Chetoceros* sp biomass

Cultivation of *Chetoceros* sp was done for 8 days and it was centrifuged to get biomass. Biomass obtained was placed in solution of 0.12 M HCl, it was agitated for 20 minutes, and it was centrifuged to separate with HCl solution. These procedures were repeated for 2 times furthered with washing by water. Then, it was centrifuged and dried with freeze dryer for 24 hours to get dry biomass which is ready to be used.

Preparation of *Chetoceros* sp biomass immobilized silica gel

Encapsulation process of algae biomass with silica aquagel: 2.5 mL of Na₂SiO₃ sol solution were mixed with 5 mL water. The mixtures were added 1.95 mL strong acid of cation exchange resin until solution pH close to 4. Then, resin was separated with filtration. The filtrate obtained was added with HCl 2 M and was stirred by magnetic stirrer until sol was resulted at pH of 2. Then, the sol found was given phosphate buffer with ratio of 1 : 5 (v/v). After mixing, solution was removed into beaker glass to produce gel, added microalgae biomass, and continued with aging the gel for 24 h.

Biosorption process with batch method: to investigate kinetic and thermodynamic aspects, parameters of time effect, concentrations, temperatures, and optimum pH in the biosorption process were evaluated. Therefore, experiments performed consisted of:

a. Biosorption time: 20 mg of algae biomass which was immobilized were interacted with 25 mL of Pb(II) solution 10 mg L⁻¹ and they were mixed using magnetic stirrer. Interaction time was started from 5-80 minutes. Then, the mixture was centrifuged and filtrate was taken and analyzed metal concentration left in solution by AAS.

b. Various concentrations: 25 mL Pb(II) solution at various concentrations of 0 – 10 mg L⁻¹ was interacted with 20 mg of adsorbent at temperature of 27 °C and stirred at optimum time in experiment of a. Then, it was centrifuged to isolate filtrate and sediment. Concentration of Pb(II) left was measured by AAS.

c. Interaction of various pH: 25 mL Pb(II) solution with optimum concentration variety was placed into reaction tube containing 20 mg of adsorbent, then it was adjusted pH of 3-8. The mixture was stirred at optimum time (experiment of a). Then, the solution obtained was analyzed by AAS.

RESULTS AND DISCUSSION

Adsorbent characteristics

Adsorbent characteristics obtained from *Chetoceros* sp biomass immobilization with silica gel were performed with identifying functional groups and surface morphology as displayed in Fig. 1 and 2. In Fig. 1, adsorption band at 1087.85 and 964.41 cm^{-1} show stretching vibration of Si-O-Si and Si-OH, respectively. Existence of water adsorbed was reflected by vibration of νOH at 3444.72 cm^{-1} . Adsorption bands around 746.54

and 470.63 cm^{-1} were produced from vibration of Si-O. Adsorption characteristics on adsorbent resulted from immobilization of *Chetoceros* sp with silica gel (Fig. 2) were known at band around 2931.8 cm^{-1} , displaying vibration from CH group coming from *Chetoceros* sp biomass with silica gel⁶ and disappearing several adsorptions coming from functional group on silica. These facts prove that *Chetoceros* sp biomass exists on silica surface after immobilization process.

SEM analysis result of *Chetoceros*-silica adsorbent surface (Fig. 2b) shows that surface morphology of *Chetoceros*-silica adsorbent appears to be brighter than surface morphology of *Chetoceros* sp without immobilization with silica (Fig. 2a). This fact is caused on *Chetoceros*-silica adsorbent existing Si atom producing brighter color resulted from higher accelerating of Si atom than *Chetoceros* sp dominated by organic material.

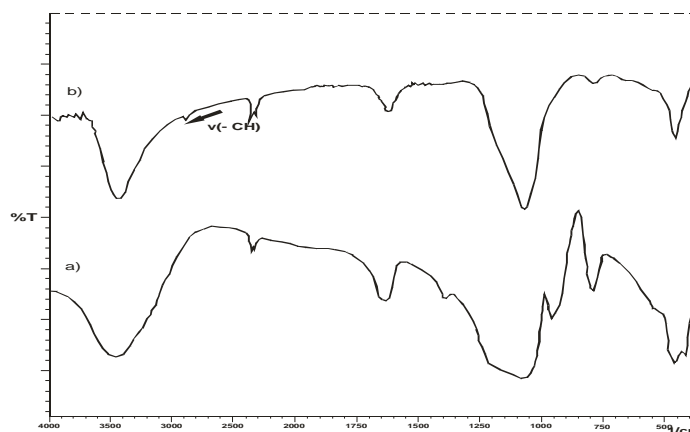


Fig. 1: IR Spectrum of a) Silica gel and b) *Chetoceros* sp biomass-silica

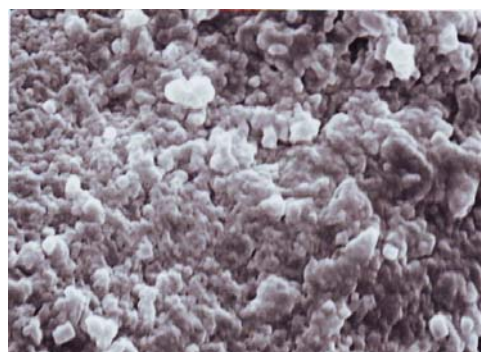
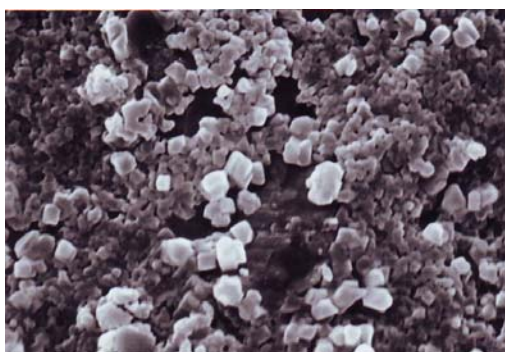


Fig. 2: SEM Images of a) *Chetoceros* sp biomass and b) *Chetoceros* sp biomass silica

Adsorption with batch method

Adsorption characteristics from *Chetoceros* sp biomass adsorbent of immobilization result via encapsulation process with silica aquagel were studied with evaluation of kinetic model, adsorption isotherm, and effect of Pb(II) ion solution pH adsorbent on the adsorbent. The amount of Pb(II) ion adsorbed q (mg g⁻¹) on adsorbent was calculated using Equation 1:

$$q = \frac{v(c_i - c_f)}{m} \quad \dots(1)$$

Where c_i and c_f are initial and final concentration of Pb(II) ion in solution, v is volume of solution (L), and m is adsorbent mass.

Correlation approach between the amount of Pb(II) ion adsorbed experimentally with batch method and the amount of Pb(II) ion adsorbed estimatically through kinetic model and adsorption isotherm was determined to know adsorption process optimization with evaluating of kinetic and adsorption isotherm parameters via determining value of the root mean squared error (RMSE) and Chi-square test (χ^2)^{17, 18} with these equations below:

$$RMSE = \sqrt{\left(\frac{1}{m-2}\right) \sum_{i=1}^m (q_{i,exp} - q_{i,cal})^2} \quad \dots(2)$$

$$\chi^2 = \sum_{i=1}^m \frac{(q_{i,exp} - q_{i,cal})^2}{q_{i,exp}} \quad \dots(3)$$

where $q_{i,exp}$ and $q_{i,cal}$ each was obtained from experimental and estimation result through adsorption isotherm equation, while m is the number of observation in the experimental isotherm. A smaller RMSE value shows a better curve fitting, moreover, if the data found from the model are near to the experimental results, χ^2 can be a small number^{17, 19}.

Adsorption kinetic

Adsorption equilibrium time needs to be identified to obtain maximum adsorption of adsorbate on adsorbent surface, the shorter the reaction time, the higher the reaction rate. Interaction time additional does not increase the amount of metal adsorbed if equilibrium is reached. Adsorption kinetic is studied with determining adsorption rate constant based on data of time effect to the amount of Pb(II) ion adsorbed on *Chetoceros* sp encapsulated silica aquagel. In order to investigate the effect of time to adsorption rate of Pb(II) ion on biomass, pseudo first order (Eq. 4) and pseudo second order (Eq. 5) kinetic models may be used^{12,20}.

$$q_t = q_e(1 - e^{-k_1 t}) \quad \dots(4)$$

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \quad \dots(5)$$

Where, adsorption capacities of Pb(II) ions amount at time t and at equilibrium are displayed as q_t and q_e (mg g⁻¹), the first order and the second order rate constants are described as k_1 and k_2 , respectively. Linear relationship of kinetic model both can be seen in Fig. 3 and kinetic parameter data can be found in Table 1.

Table 1: Kinetic parameters of pseudo first order and pseudo second order

Kinetic parameters	R^2	Adsorption rate	q_e (mmol g ⁻¹)		RMSE	χ^2
Pseudo first order		k_1 (min ⁻¹)	Exp	Cal		
Chetoceros	0.991	0.032	0.0410	0.0401	0.0041	0.0009
Chetoceros-silica	0.995	0.065	0.0307	0.0309	0.1206	0.0004
Pseudo second order		k_2 (g mg ⁻¹ min ⁻¹)				
Chetoceros	0.923	3.139	0.0341	0.0231	0.0410	0.1049
Chetoceros-silica	0.984	6.195	0.0307	0.0269	0.0293	0.0594

From the data in Fig. 3 and Table 1, it can be seen that generally, kinetic model of Pb(II) ion on *Chetoceros* sp biomass and its immobilization result with silica is inclined to follow pseudo first order kinetic model with correlation coefficient value (R^2) 0.99 and this is also supported with value of

$RMSE$ and χ^2 which are relatively smaller than pseudo second order kinetic model. These cases indicate that only one species is influential to rate adsorption. In these cases, adsorbate or metal ion is as rate determining.

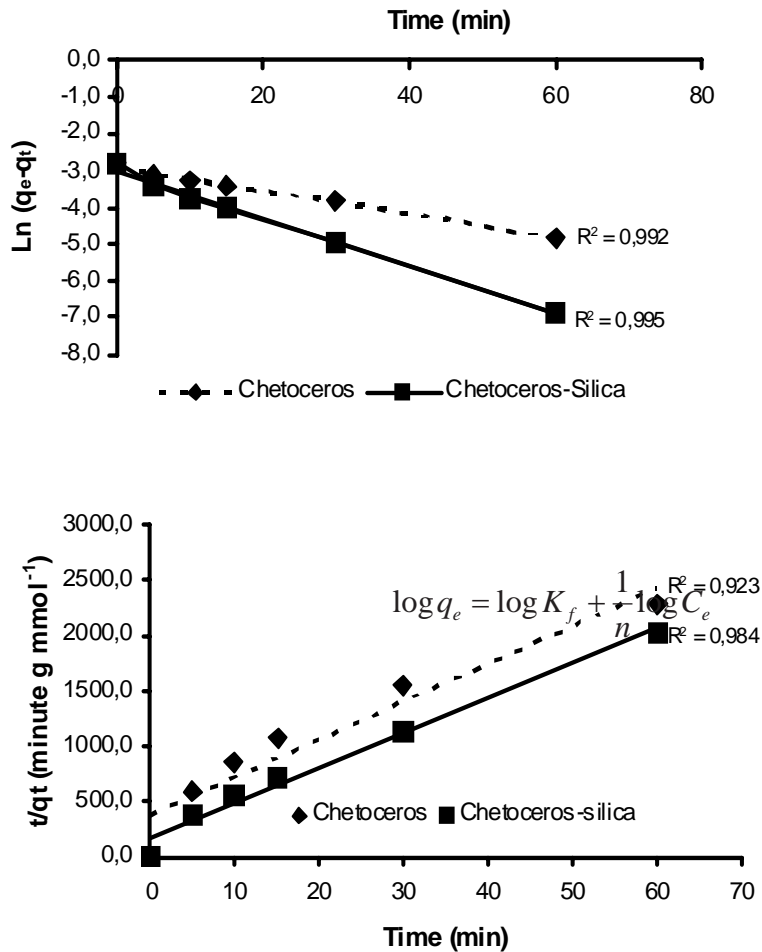


Fig. 3: Kinetic linear models of a) pseudo first order and b) pseudo second order on *Chetoceros* sp biomass and *Chetoceros* sp-silica

Adsorption isotherm

Data in Fig. 4 were analyzed with using equations of Freundlich and Langmuir adsorption isotherm (Eq. 5 and 6). Freundlich equation is equation commonly based on heterogeneous surface^{21,22}. Common model of Freundlich formula is $q_e = K_f C_e^{1/n}$, with K_f and n are factor of adsorption capacity and factor of intensity (1-10), respectively. Freundlich linear formula can be described as

follow;

$$\dots(5)$$

In addition, plot of $\log q_e$ versus $\log C_e$ may result K_f and exponent of n .

In the Langmuir isotherm, a number of active sites which are comparable with surface area is

obtained on adsorbent surface. Langmuir formula is displayed as follow;

$$C_e/q_e = 1/q_m K + C_e/q_m \quad \dots(6)$$

where, C_e (mg L^{-1}), q_e (mg g^{-1}), q_m , and K are metal ion solution equilibrium concentration, adsorption capacity of metal ion at equilibrium, adsorption capacity of adsorbent monolayer, and adsorption energy constant, respectively. Furthermore, a straight line for $1/q_m$ as slope and $1/q_m K$ as intercept are obtained from plot $\log C_e/q_e$ versus C_e . Then, Gibbs free energy formula can be used to calculate adsorption energy;

$$\text{Adsorption energy} = \Delta G^\circ_{\text{ads}} = -RT \ln K \quad \dots(7)$$

With, E , R , T , and K are the adsorption energy (kJ mol^{-1}), the universal gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), temperature (Kelvin), and the adsorption equilibrium constant, respectively.

Adsorption data of Pb(II) ion on adsorbents found from analysis result calculated from Freundlich and Langmuir formula can be seen in Table 2.

If the data in Table 2 is observed, it can be seen that ability of *Chetoceros* sp adsorbent encapsulated by silica to adsorb metal ions is higher than adsorbent derived from only *Chetoceros* sp. This indicates that functional groups on *Chetoceros* sp biomass encapsulated by silica are relatively more active in binding metal ions.

Adsorption energy of Pb(II) metal ion on *Chetoceros* sp biomass encapsulated by silica aquagel has around $12.303 \text{ kJ mol}^{-1}$. This value of adsorption energy is too small to be as chemical bonding energy but too high to be as physisorption. Therefore, this adsorption can be grouped as weak chemical interaction. This fact is supported by adsorption model following Langmuir model. Langmuir model shows that interaction among

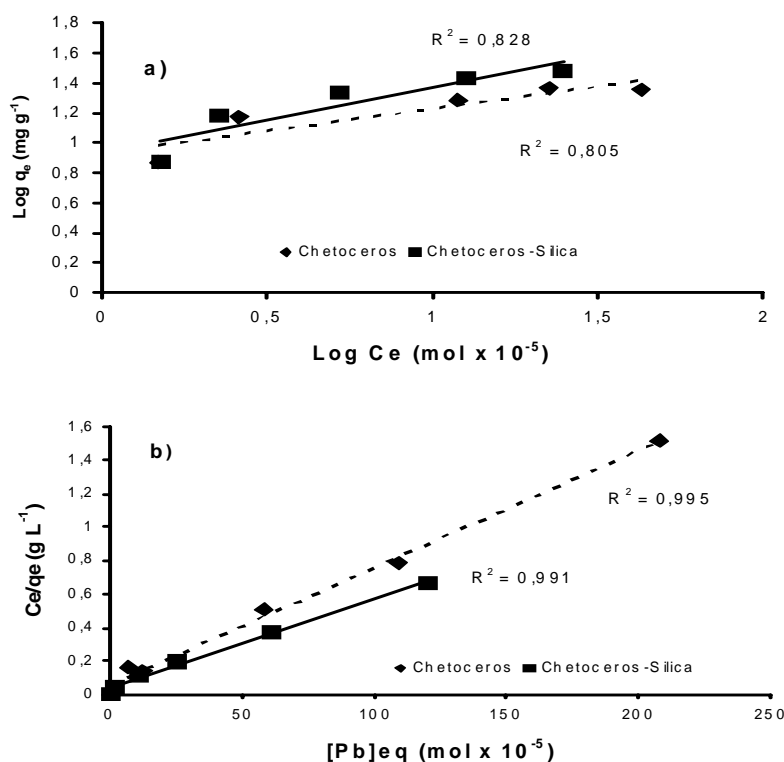


Fig. 4: Adsorption isotherm linear models of a) Langmuir and b) Freundlich on *Chetoceros* sp biomass and *Chetoceros* sp biomass-silica

Table 2: Adsorption data of Pb(II) ion on adsorbents

Adsorbents	Langmuir Parameters				
	$q_m \times 10^{-2}$ ((mol g ⁻¹))	$K \times 10^{-2}$ (mol ⁻¹)	R^2	RMSE	χ^2
Chetoceros	10.286	12.111	0.990	2.468	1.579
Chetoceros-silica	18.868	13.874	0.999	1.404	1.696
Adsorbents	Freundlich Parameters				
	$K_f \times 10^{-2}$ (mol g ⁻¹)	n	R^2	RMSE	χ^2
Chetoceros	4.145	3.379	0.830	3.301	2.203
Chetoceros-silica	4.065	2.247	0.827	2.284	2.615
Adsorption energy (ΔE) kJ mol ⁻¹					
Chetoceros	11.964				
Chetoceros-silica	12.303				

metal ions is dominated by chemical bonding and monolayer adsorption.

Interaction pH

pH is one of important factors in controlling adsorption process of metal ion. In this research,

influence of pH was studied with varying interaction pH at various pH of 3-8. Influence of pH on Pb(II) metal ion adsorption with *Chetoceros* sp biomass adsorbent immobilized by silica can be seen in Fig. 5.

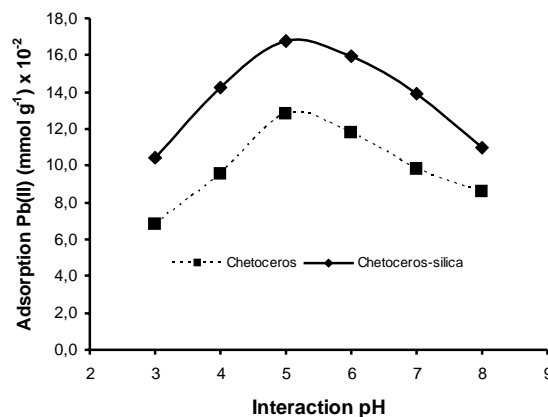


Fig. 5: Influence of interaction pH to Pb(II) ion adsorbed on *Chetoceros* sp biomass and *Chetoceros* sp biomass encapsulated with silica

Generally, adsorption of Pb(II) metal ion (Fig. 5) has relatively similar model as adsorption increases from pH 3 to optimum pH at around 5 and above pH 5 adsorption starts to decrease. This phenomenon can be explained based on qualitative study of metal ion species existence and adsorbent in solution as pH function. At acid condition, functional groups found on adsorbent may be protonated so that bonding of hydrogen

ion (H⁺) and hydronium ion (H₃O⁺) will occur. At the same time, metal ions in solution before adsorbed by adsorbent hydrolyzes firstly to produce proton.

At pH 5, adsorption is relatively high, this can occur because metal hydroxo complex (PbOH⁺) formed in solution is much more. In addition adsorbent surface will be negative charge with releasing proton. This case causes increasing of adsorption *via* electrostatic interaction. At pH > 6,

adsorption starts to decline because several species of Pb ion with different charge including $\text{Pb}(\text{OH})^+$ and $\text{Pb}(\text{OH})_2$ precipitation start to exist in solution³.

CONCLUSIONS

Immobilization of *Chetoceros* sp microalgae biomass with silica gel through encapsulation technique has been performed

successfully. Adsorption process of Pb(II) ion on *Chetoceros* sp biomass and *Chetoceros* sp–silica tends to follow pseudo first order kinetic and Langmuir adsorption isotherm. Adsorbent obtained from immobilization of *Chetoceros* sp–silica has adsorption rate and capacity to Pb(II) ion in solution higher than *Chetoceros* sp biomass. In addition, adsorbent immobilized is also more stable chemically as metal ion adsorbent in solution media.

REFERENCES

1. L. Hajiaghababaei, A. Badiei, M.R. Ganjali, S. Heydari, Y. Khaniani, and G.M. Ziarani, *Desalination* **266**: 182-187 (2011).
2. A. Bhatnagar and A.K. Minocha, *Colloids and Surface B: Biointerfaces* **76**, 544-548 (2010).
3. V.K. Gupta, S. Agarwal, and T.A. Saleh, *J. Hazard. Matter.* **185**: 17-23 (2011).
4. National Library of medicine, Hazardous Substance Data Bank (HSDB), (1996).
5. L. Yan-Hui, Z. Yanqiu, Z. Yimin, W. Dehai, and L. Zhaokun, *Diam. Relat. Mater.* **15**: 90-94 (2006).
6. Buhani, Suharso and Sumadi, *Desalination* **259**: 140-146 (2010).
7. K. Masakorala, A. Turner, M.T. Brown, *Environ. Pollut.* **156**: 897-904 (2008).
8. P.O. Harris and G.J. Ramelow, *Environ. Sci. Technol.* **24**: 220-228 (1990).
9. K. Vijayaraghavan, M. Sathishkumar, and R. Balasubramanian, *Desalination* **265**: 54-59 (2011).
10. S. Zakhama, H. Dhaouadi, and F. M'Henni, *Bioresource Technol.* **102**(2): 786-796 (2011).
11. V.K. Gupta and A. Rastogi, *J. Hazard. Mater.* **152**: 407-414 (2008).
12. Y.G. Bermúdez, I.L.R. Rico, O.G. Bermúdez, and E. Guibal, *Chem. Eng. J.* **166**: 122-131 (2011).
13. C. Tong, U.S. Ramellow, and G.J. Ramellow, *Intern. J. Environ. Anal. Chem.* **56**: 175-171 (1994).
14. E. Valdman, *Bioprocess Eng.* **22**: 171-173 (2000).
15. M.D. Trevan, *Immobilized Enzymes*, John Wiley and Sons, New York, 14-15 (1990).
16. E.H. Lan, B.C. Dave, J.M. Fikoto, B. Dunn, J.I. Zink, and J.S. Valentine, *J. Mater. Chem.* **9**: 45-53 (1998).
17. M.M. Montazer-Rahmati, P. Rabbani, A. Abdolali, A.R. Keshtkar, *J. Hazard. Mater.* **185**: 401-407 (2011).
18. N. Chen, Z. Zhang, C. Feng, M. Li, D. Zhu, and N. Sugiura, *Mater. Chem. Phys.* **125**: 293-298 (2011).
19. L. Vijayaraghavan, T.V.N. Padmesh, K. Palanivelu, and M. Velan, *J. Hazard. Mater.* **B133**: 304-308 (2006).
20. R. Patel, and S. Suresh, *Bioresource Technol.* **99**: 51-58 (2008).
21. Y.S. Ho, J.F. Porter, and G. McKay, *Water, Air, and Soil Poll.* **141**: 1-33 (2002).
22. J. Periaë, M. Trgo, and V. Medvidoviaë, *Water Res.* **38**: 1893-1899 (2004).