Waste and Biomass Valorization
https://doi.org/10.1007/s12649-019-00926-0

ORIGINAL PAPER

The Study of Immobilized Media and Ni Ion Addition Effects on COD Removal of POME Using Anaerobic Filter Reactor

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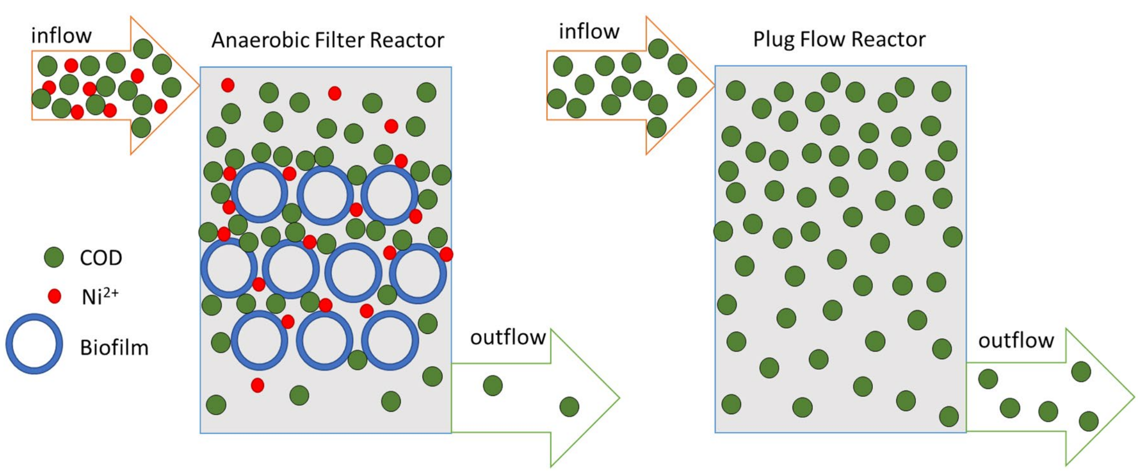
Received: 23 June 2019 / Accepted: 30 December 2019

Abstract

Palm oil mill effluent (POME) liquid waste contains high organic compounds. It has a high potential to be processed into biogas. One of the technologies that has been developed in processing POME is Fixed Film Bioreactor or anaerobic filter reactor (AFR). AFR is able to handle waste with high organic loading rate by using bacterial attached growth solid media on the surface of the media to form biofilm, which creates an optimum environment to microorganism growth and metabolism. Plastic balls (bio-balls) is one of the potential immobilization media due to chemically inert and lightweight. In addition, trace elements may enhance methanogens activities. This study aimed to evaluate the effect of bioball as an immobilization media and the addition of trace element Ni to anaerobic digestion process with POME substrate in terms of decreasing soluble chemical oxigen demand (sCOD) and methane production on fixed bed reactor in batch and continuous mode in sequence. The best performance of the reactor was able to reduce 92% of COD content inside the pome by 5 L/day of loading rate of 24,000 ppm POME.

Graphic Abstract



Keywords Anaerobic filter · POME · Immobilized media

Statement of Novelty

1. High strength wastewater (POME) can be treated effectively by AFR

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Published online: 07 January 2020

2. Addition of Ni^{2+} can enhance the anaerobic reactor performance
3. There is a synergetic effect of Ni^{2+} addition with bioballs as the packing media inside the reactor for sCOD removal

Introduction

Oil palm is one of the main commodities for Indonesia in non oil and gas sector trading. Within 5 years, oil palm plantations in Indonesia have increased by 29.8%, from 8.99 million hectares in 2011 to 11.67 million hectares in 2016, with a production capacity of Crude Palm Oil (CPO) of 30.95 million tons Ministry of Agriculture [1]. However, the palm oil industry is often claimed to be the potential cause of environmental degradation related to deforestation, forest fire, and environmental pollution caused by improper disposal of waste and emission. Liquid waste generated by the palm oil process is called palm oil mill effluent (POME), where from every ton of CPO produced, 3.05 tons of POME waste will be generated [2]. POME is quite difficult to be treated since it contains high organic compounds with mild acidity [3].

POME has a chemical oxigen demand (COD) content of 15,000–100,000 mg/L. By this organic content, POME has a biochemical methane potential (BMP) of 0.397 ± 0.009 L.CH_4/gVS under mesophilic conditions (37 °C) [4]. Therefore, the anaerobic technology of POME treatment that can significantly reduce COD content, normalizing pH, and produce renewable energy source is getting popular.

One of the anaerobic technologies that being developed in processing POME is Fixed Film Bioreactor or anaerobic fixed film reactor (AFR). AFR is proven to be able to handle wastes containing high organic loading rate [5, 6]. In AFR, microorganisms are immobilized in solid media (bio-carriers) to form a biofilm layer on the surface of the media. Biofilms can create a localized environment resistant to pH, inhibitors, and product-nutrient gradients [7]. Attached biofilm will be more stable from various changes in wastewater characteristics. In addition, with the formation of biofilms, there will be changes in crossfeeding, interspecies hydrogen co-metabolism and proton transfer which will stimulate the growth of microorganism microcolony [8]. Both of these biofilm functions lead to maximum growth and performance of microorganisms. In addition, bio-carriers also eliminate washout problem at high waste flow rates, which means increasing solid retention time (SRT) [9]. Bioball, a special plastic ball, is one of the potential immobilization media because it is light in weight and resistant to chemical attack.

In addition to the use of immobilization media, in anaerobic processing it is also beneficial to add trace nutrient. Trace elements commonly used in the anaerobic decomposition process are Co, Ni, Fe, and Mg [10–12]. Zhang et al. [13] examined that the anaerobic digestion process using food waste showed a correlation between process performance and trace element profiles during the process period, where performance of degradation was enhanced by trace element concentration in the system. Qiang et al. [12] conducted anaerobic digestion studies with solid food waste substrates, the results showed that Co, Ni, Fe had a significant influence on methane production. At the beginning of the batch process, where the amount of trace elements in the inoculum was still sufficient for the process, biogas was produced with high methane concentration. But when repeated substrate additions are made, slowly the methane production was reduced possibly due to insufficient micronutrient content. The methane production remaining optimum when the micro elements concentration of Co, Ni and Fe can be kept at 1 mg/L and 1 mg/L and 10 mg/L, respectively. Chusna et al. [14] also conducted anaerobic digestion research with POME substrate by adding trace elements of Ni and Zn, that was impregnated into zeolite as immobilization media. The results showed that the addition of Ni and Zn trace elements can increase methane production by up to 50% compared to controls. From the state of the art research above, it can be seen that Ni is an important element in the anaerobic digestion process, especially in terms of methane formation. Therefore, it is necessary to add Ni to the process, considering that POME generally only contains half the optimum concentration of Ni needed for biogas production, which is 0.49 mg/L [15], Irvan et.al. [16]. Other essential trace metal elements beside Ni are not necessary to be added, since POME generally already sufficient with various micronutrient. The further excessive addition of the metal content may lead to the toxic condition for microorganism.

This study aimed to evaluate the effect of bioball as an immobilization media and the addition of Ni ions to anaerobic digestion process with POME substrate in terms of decreasing sCOD and methane production using Anaerobic Fixed Film Reactor (AFR) in batch coupled with semi-continuous operation mode.

Material and Methods

Materials

POME was collected from waste water treatment unit of a crude plam oil (CPO) company in Bangka Island with the highest COD as much as 45,000 mg/L with pH 6.4. Then, POME was mixed with inoculum from an active digester effluent located in Agrotechnology Innovation Center UGM before loaded into the reactors. Inoculum was collected from the effluent of cow manure digester farm at PIAT-UGM with sCOD of 3400 mg/L and pH at 7. Nitrogen (N_2) No. CAS

7727–37-9 from PT. Samator Yogyakarta was used to flush filter reactor at the beginning of the process. The tube reactor was packed with plastic ball (bioball) with diameter of 2.5 cm for microbial support growth.

The chemicals used for analysis were H_2SO_4 (EMRE, 95–98%), NaOH pellet (Merck KgaA), $K_2Cr_2O_7$ (EMSURE), $AgSO_4$ (Merck), $HgSO_4$ (EMSURE), $Na_2B_4O_7.10H_2O$ (Merck KgaA, 99.5 purity), HCl (Merck KgaA, 37%).

Methods

This research was done in PIAT-UGM (Agrotechnology Innovation Center) Berbah, Sleman, Yogyakarta. Anaerobic digestion carried in vertical AFR with working volume of 40 L made from transparent acrylic tube with diameter of 63 cm and 200 cm in height, equipped with the sampling valves and the line for discharge and feeding wastewater. Plastic bioball as packing media was washed, dried and loaded into reactor in random order. AFR were filled with the mixture of substrate and inoculum with volumetric rasio of 2:1. The packed reactor configuration with side and end effluent sampling ports is represented in Fig. 1. A similar tube reactor without packing was also prepared as a control.

The reactors were operated in batch mode prior to semi-continuous feeding mode with two different flowrate of 5 and 8 L/days. In the batch mode, the reactor was filled with substrate of POME and inoculum mixture with sCOD initial (sCODin) of 24,000 mg/L for at least 25 days or until sCOD remain stable for at least three sampling times. Then, the batch mode is changed into semi-continuous mode by adding 5 or 8 L per day fresh substrate of POME with the same initial concentration of 24,000 mg/L sCOD without inoculum addition. The loading time of fresh substrate to the reactors is about 3 min at 09.00 am every morning during the semi continuous period. In the same time of loading, the same volume of effluent was also drawn from the reactor to maintain same level of wastewater inside. In a particular reactor, the substrate was added with trace elements Ni with the concentration of 0.264 mg/L in order to reach an optimal concentration of Ni in the substrate so that the anaerobic process runs optimally Trisakti et.al. [16].

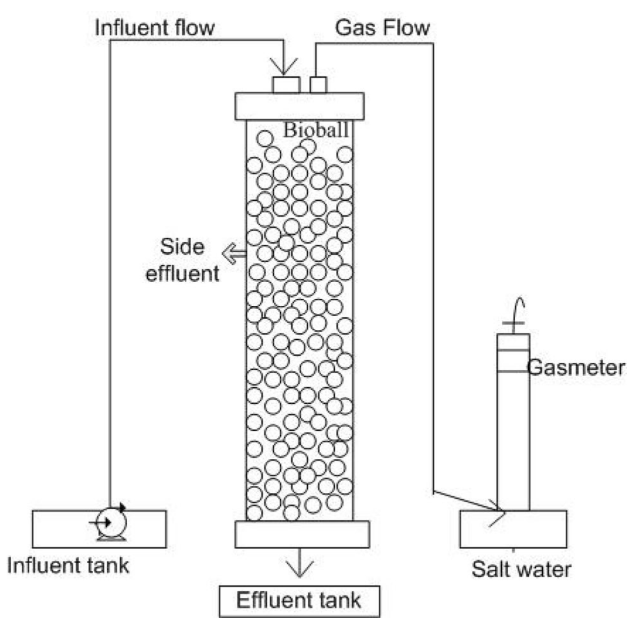

Fig. 1 Schematic diagram of countinous mode of anaerobic filter reactor

Sample form effluent were taken every 2 days (3 times a week) to measured sCOD, VFA, pH and methane concentration in biogas. During semi-continuous operating mode, the sample from side effluent port was also drawn and analysed. Soluble COD (sCOD) was measured using closed reflux colorimatric method and VFA was measured using the titrimetric method according to standard methods for examination of water (APHA, 5220-D). The gas volume was measured using gas-meter with water displacement method, and the methane content was analyzed using gas chromatography (GC) Shimazu GC 8A. For ease of identification, the sample from each different reaction condition dan sampling port has been listed in Table 1.

Result and Discussion

To evaluate the effect of microbial immobilized media and Ni ion addition to anaerobic digestion performance, batch processes followed by semi continuous mode has been done in sequence using the tube reactors. The sCOD profiles of reactor effluent have been provided in Figs. 2 and 3 for reactor without and with Ni addition respectively.

It is expected that a significant reduction of organic content in wastewater after passing an anaerobic filter. From Fig. 2 it can be seen that the reactor with immobilized

Table 1 Sample and reactor type identification

ID	Packed media inside reactor	Ni addition	Sampling port
NME	No	No	Effluent
ME	Yes	No	Effluent
NMSE	No	No	Side effluent
MSE	Yes	No	Side effluent
Ni-NME	No	Yes	Effluent
Ni-ME	Yes	Yes	Effluent
Ni-NMSE	No	Yes	Side effluent
Ni-MSE	Yes	Yes	Side effluent
M-Gas	Yes	No	Biogas line
NM-Gas	No	No	Biogas line

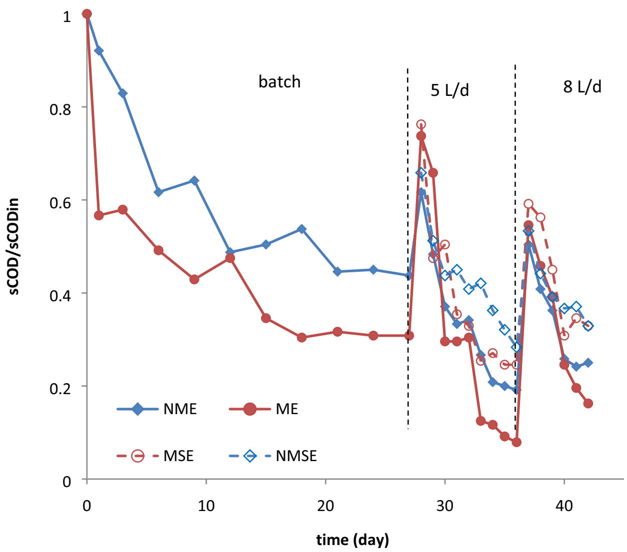

Fig. 2 sCOD concentration profile of AFBR reactor in batch and semi-continuous mode without Ni addition

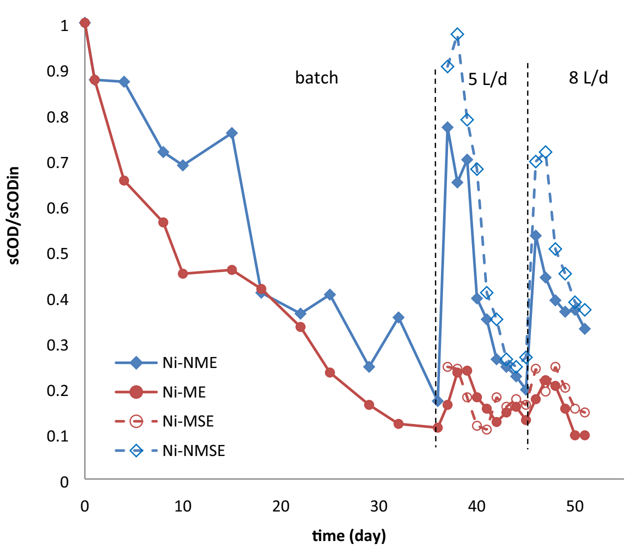

Fig. 3 sCOD concentration profile of AFBR reactor in batch and continuous mode with Ni addition

media has higher sCOD reduction in all operation mode. In batch mode, the reactor with packed bed gives a fast and steady decrease of sCOD while in the hollow tube reactor has a slight fluctuating sCOD profile. The sCOD removal of packed bed reactor is larger than tube reactor in batch mode indicating the better performance of immobilized media added reactor. This fact is in line with Setyowati et.al. [17], who treated POME anaerobically by adding zeolite as an immobilization media, where the addition of immobilization media increased the sCOD removal.

The immobilize media role in anaerobic digestion is also significant during transition time from bath to semi-continuous process. The fresh substrate loading during the mode switch gives a sudden rise of sCOD concentration. This could be due to an instantaneous mixing of high organic content substrate with remaining treated substrate in the tube reactor led to sudden increase of organic concentration inside the reactor as well as in the effluent line. Moreover, the microorganism inside the batch reactor has not yet prepared for the rapid change of organic concentration during mode shifting. Najafpour et al. [18] also observed that the sudden increase in sCOD load created an organic loading shock to the microorganisms. The microflora needs time for acclimation to the new loading scheme. After the adjustment, the sCOD removal level can be restored after 3 days of continuous operation with 5 L/day of fresh substrate.

After 5 days of semi-continuous mode operation, the sCOD level keep decreasing which can be a hint that the reactor can reach a reasonably high sCOD removal rate of more than 80% with residence time of 8 days. The reactor with immobilized media can reach removal rate faster to more than 90% or sCOD removal within 8 days of operation. Thus, the packing media is able to speed up the sCOD digestion inside the reactor.

After 9 days of semi-batch operation, the substrate loading flowrate is increased from 5 L/day to 8 L/day. A surge of sCOD level with the higher flowrate can be clearly seen even lower than the first shock during the switching mode. By this loading flowrate increase, the residence time inside the reactor decreased from 8 to 5 days. It can be observed that all the reactor is able to manage the loading change at about 4 days and again the reactor with immobilized media has better performance in reducing sCOD in this higher loading rate.

When the semi continuous reactor has reached a stable condition there is a significant sCOD concentration gap between the side effluent and bottom effluent. This can be a hint that there is a concentration gradient inside the tube, thus, the sufficient length of the tube is also important to be provided.

Figure 3 shows the sCOD profiles of tube reactor with Ni addition. In general, the trend of sCOD removal is similar to the previous results, that reactor with immobilized media is superior than hollow tube reactor. On the other hand, the addition of Ni can further enhance the sCOD removal. For instance, after 25 days of operation the sCOD removal for Ni-added reactor with media is 77% and without media is 60% while for the same residence time without metal addition are 70% and 55% respectively. Chusna et al. [14] found the similar fact that the addition of Ni in anaerobic system was able to increase the sCOD removal to about 80%. Probably the most significant result of Ni addition effect is found in the semi-continuous stage for the reactor with immobilized media, during the initial fresh loading period there is no significant sCOD level shock can be observed. It seems that the effect of media has been enhanced by the Ni addition. Even using 8 L/day of loading, the sCOD peak is minimum for ME and MSE samples. For the reactor without media the addition of Ni is insignificant to deal with operation mode changes.

Mostly, sample from side reactor effluent (MSE and NMSE) has higher level of sCOD level than the end effluent (ME and NME) since it is drawn before the effluent, so that the residence time is lower. This difference can be an indication of concentration gradient along the reactor length or the reactor is can be considered as plug flow reactor.

In terms of VFA concentration in Fig. 4, since this compound is the middle product of methane generation, the concentration is preferably in a low level. High acids can become inhibitor to methanogenic bacteria metabolism Bouallagui et.al. [19]. Lee et al. [20] stated that VFA concentration values up to 5000 mg/L still did not inhibit the anaerobic process. It can be observed that the concentration of VFA in the effluent of reactor with immobilized media (ME) in most of the time can be kept lower than effluent from hollow tube reactor (NME). In the presence of bio-balls, most acidogens and methanogens microorganisms will stick and grow on the bio-balls surface to form a biofilm layer for promoting the fast of organic content to methane. In the twice shock loading from batch operation to semi-continuous and increasing of loading rate the media can suppress the VFA surge better than non-packed bed reactor. The best reactor performance in controlling VFA concentration especially in semi-continuous mode with loading rate fluctuation is the reactor with packed bed and Ni^{2+} addition as shown by Ni-ME sample VFA profile.

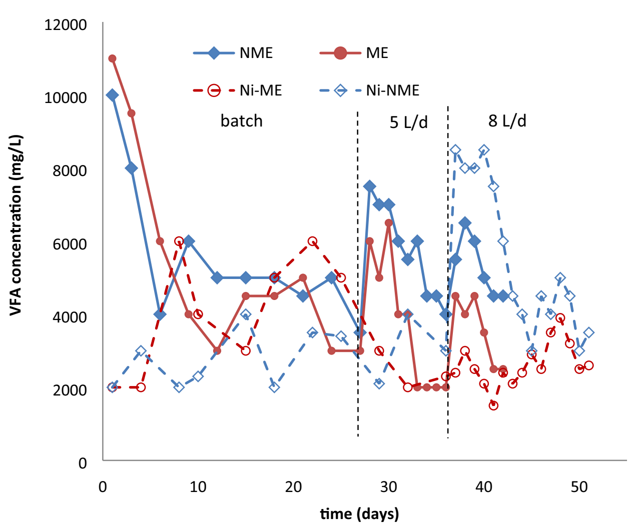

Fig. 4 VFA concentration in bottom effluent of fixed bed reactor with and without Ni addition

The biogas volume produced per gram COD removed by process with immobilized media is lower than that produced by process without immobilized media as shown in Fig. 5. The low volume of biogas in the reactor with immobilized media is compensated with high methane content inside the biogas as shown in Fig. 6. The low biogas volume per COD removed can be an indication that the two reactor behaves differently. The reactor with immobilized media tends to reduce sCOD faster without generating voluminous biogas. Thus, it can be said that the solid media addition will enhance the early part of biogas conversion which are hydrolysis and acidogenesis. Meanwhile, it can be observed as well that the addition of Ni will enhance the volume of biogas production in any reactor type.

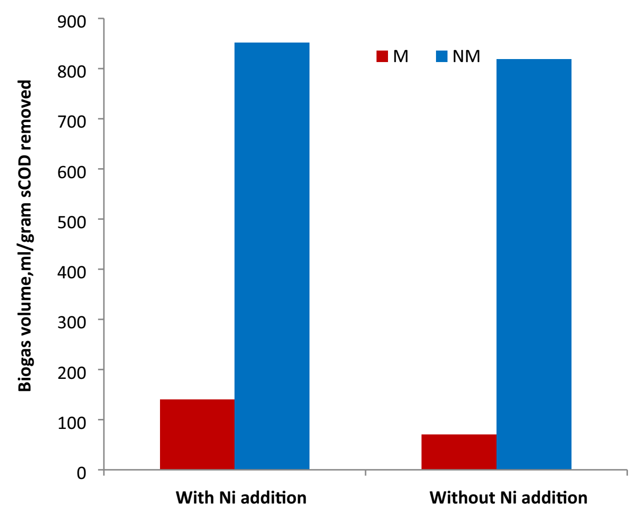

Fig. 5 The volume of biogas produced per gram sCOD removed

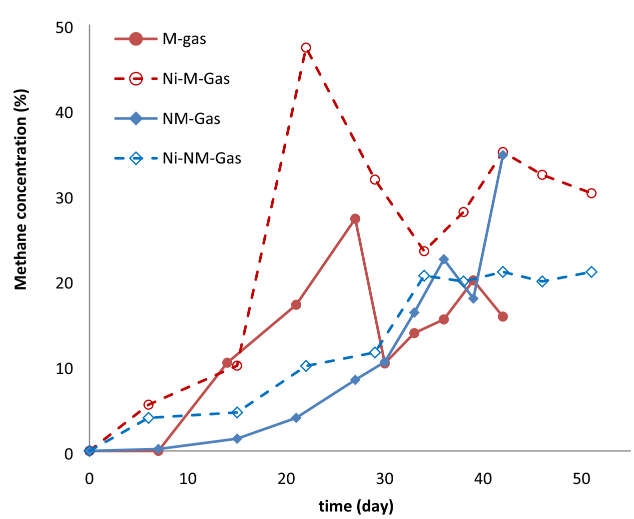

Fig. 6 Methane concentration profile

Figure 6 shows the methane concentration in the biogas for each reactor configuration. This concentration profiles have strong correlation with sCOD and VFA profile in previous results. The highest methane content by reactor with packing and trace metal (Ni) addition is as expected since this reactor can reduce sCOD higher than other while keep the VFA in low concentration. It can be observed that methane concentration is fluctuating quite severe due to variation of organic loading. Since methane is the end product of a complicated route of microbiological activities, the steady organic loading is necessary to ensure the stable production level.

The concentration of methane produced is quite low, and this is possibly due to the inhibition of long chain fatty acids (LCFA). POME is not an easily degraded substrate in anaerobic digestion because the dispersed oil will turn into LCFA during the process. It has been known that LCFA is inhibitory to methane production Labatut et.al. [21]. LCFA inhibition in the substrate can also be indicated from the lower levels of methane produced by the process without immobilization media compared to those produced by the process with immobilization media. Microorganisms, especially methanogens that are susceptible to LCFA inhibition, will adhere and grow on the surface of the media to form a biofilm layer. Biofilms can create an internal environment conducive to microorganisms due to the presence of biofilm resistance, which causes a substrate concentration gradient, pH, and concentration gradient of inhibitors, including LCFA [7]. With this gradient, the biofilm will be more stable from various conditions and changes in the waste substrate.

From Fig. 6, it is interesting to note that for Ni added reactor the methane concentration is already exist start from the beginning stage of batch operation. This phenomenon is also seen in the research conducted by Damayanti et.al. [22], where with the addition of trace elements, higher concentrations of methane have occurred at the beginning of processing time. It is an indication of very fast growth and metabolism of methanogen consortium most probably from inoculum. Thus it can be said that metal addition can accelerate the acclimation stage of inoculum bacterial consortium to the new environment inside the rector tube. This fact has a good correlation with the data in Fig. 4 that VFA for Ni added reactor are very low in the early stage compare with the other reactors. Low concentration of VFA could be due to the further conversion of VFA to methane gas.

Conclusion

The results showed that the use of bioballs in packed bed reactor increased sCOD removal compare with the hollow tube reactor. Meanwhile, the addition of Ni accelerates the VFA conversion to methane. The combination of packed media and Ni addition will provide a robust anaerobic filter reactor due to fast degradation performance and withstand by the organic loading fluctuation for POME treatment.

Acknowledgements This study was supported by RTA Grant form UGM. We also gratefully acknowledge the funding from USAID through the SHERA program-Centre for Development of Sustainable Region (CDSR).

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