The influenced of PAC, zeolite, and Moringa oleifera as biofouling reducer (BFR) on hybrid membrane bioreactor of palm oil mill effluent (POME)

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Abstract

The main objective of this work was to determine the effectiveness of various biofouling reducers (BFRs) to operational condition in hybrid membrane bioreactor (MBR) of palm oil mill effluent (POME). A series of tests involving three bench scale (100 L) hybrid MBR were operated at sludge retention times (SRTs) of 30 days with biofouling reducer (BFR). Three different biofouling reducers (BFRs) were powdered activated carbon (PAC), zeolite (Ze), and Moringa oleifera (Mo) with doses of 4, 8 and 12 g L⁻¹ respectively were used. Short-term filtration trials and critical flux tests were conducted. Results showed that, all BFRs successfully removed soluble microbial products (SMP), for PAC, Ze, and Mo at 58%, 42%, and 48%, respectively. At their optimum dosages, PAC provided above 70% reductions and 85% in fouling rates during the short-term filtration and critical flux tests.

1. Introduction

Recently membrane bioreactors (MBRs) have been developed and replaced secondary clarification, as solids separation, in activated sludge systems (Ujang et al., 2007). However, high loading of MBRs system was affected to biofouling on the membrane surface. Sludge flocs is one of the important factor affecting membrane fouling at MBRs system (Ujang et al., 2005).

The need to remove nitrogen is to reduce its effects on eutrophication, oxygen depletion, and decrease chlorine disinfection (Xue et al., 2009). Biological nitrogen removal is a favorable choice compared with physical and chemical treatment process, because it is more efficient and inexpensive. Biological nitrogen removal process are widely developed, such as nitrification, denitrification, anaerobic ammonium oxidation (anammox), and its combined system including MBRs and hybrid MBRs (Teck et al., 2009).

The treatment process is necessary to remove the high content of organics in palm oil mill effluent (POME) (Damayanti et al., 2010) that would otherwise severely resulted in fouling of the membrane and to a shorter membrane life-span. Powdered activated carbon (PAC), zeolite (Ze), and Moringa oleifera (Mo) were types of biofouling reducers (BFRs) which have been used in many applications ranging from food, separation technology, and wastewater treatment. Activated carbon is widely used in the world as adsorbent, coagulant aid, to remove inorganic matters (Yang et al., 2009). The BFR in this study have been added to the last reactor, the aerobic MBR, and the wastewater was changed for each BFR dosage.

Zeolite consists of smectite minerals and functions as cation exchange and coagulant aid, because of its thixotropy, permeability, and viscosity properties. Furthermore, activated carbon requires complexing agents to improve its removal performance for inorganic matters (Damayanti et al., 2008). Despite of its prolific use, activated carbon is still assumed as an expensive material.

Moringa seed has been known since antiquity as a coagulant in African and South Asian countries (Bhatia et al., 2007). Moringa seeds as coagulants are used for water purification and removing turbidity to 99% (Muyibi and Okuofu, 1995). Adsorption and neutralization of M. oleifera are the main mechanisms of coagulation (Bhatia et al., 2007; Damayanti et al., 2008). Before using Moringa seed as coagulant, extraction of vegetable oil from its seed is necessary. The advantages of Moringa, is the affect it brings to the conductivity and pH, respectively. Another advantage from the use of Moringa in wastewater treatment i.e. POME treatment is that chemical cost could be reduced when used for pH adjustment (Bhatia et al., 2007).

The impact of three BFRs influenced on biofouling of hybrid MBR, and the removal of high nitrate nitrogen from POME is still limited and new based on the literature review. Furthermore, not many studies have been carried out with real effluent, whereby
this study uses raw POME with high MLSS of 15 g L$^{-1}$ in the aerobic reactor.

The objectives of this study were, first, to compare three types of BFRs by studying its adsorption capacity using jar test at several dosages from 4 to 12 g L$^{-1}$. Second, to investigate the impact of BFRs and their dosages, to short time operation, critical flux, and effluent quality of hybrid MBR.

2. Methods

This study was divided into three stages. The first was a batch test to determine the adsorption capacity, extent of COD, and SMP removal for each BFRs adsorption capacity. The dosage with highest SMP removal percentage will be chosen as optimum dosage to proceed for the second phase.

In the second stage, a short-term filtration tests were conducted within two hours in constant flux modes (11 L m$^{-2}$ h$^{-1}$) to determine the influence of BFRs's concentration. Filtration test used the three dosages which were higher and lower compared with the optimum dosage from the first phase. After that, short-term operation test will use raw POME as control to compare with those used with BFRs.

In the third stage, critical flux was examined for MBR with optimum dosage of different BFRs using flux step method (Le-Clech et al., 2003). The same procedure was used for critical flux step test as a short time operation. The critical flux takes 10 min to test for every flux, from flux 0 to 3 L m$^{-2}$ h$^{-1}$. As an example for control raw POME, the procedures are as follows: start operation with duration time 10 min at flux 3 L m$^{-2}$ h$^{-1}$, and then followed by 0 L m$^{-2}$ h$^{-1}$ or rest time (only aeration, no permeate) for 5 min. The flux is then increased to 6 L m$^{-2}$ h$^{-1}$ for 10 min and then followed by 0 L m$^{-2}$ h$^{-1}$ for 5 min, and continued until flux step 30 L m$^{-2}$ h$^{-1}$ (Le-Clech et al., 2003).

Operation from lower flux step and rest time at flux 0 L m$^{-2}$ h$^{-1}$ after every flux step intends to examine the effect of biofouling between flux steps. With a rest time, trans membrane pressure (TMP) level in previous section could not be achieved again or irreversible fouling that occurs can be eliminated. The peristaltic pump speed was adjusted to find the flux values. TMP was measured for every fouling that occurs can be eliminated. The peristaltic pump speed

In summary, for acclimatization the MBR system was seeded with biological sludge taken from the wastewater treatment plant of the Felda Bukit Besar Palm Mill, Johor Bahru.

Seed biomass from sludge POME aerobic treatment plant was added at the start of the test. Acclimatization takes time about 40 days before steady state. The system was operated in steady state condition and run continuously during this study. Each BFR used new steady state ready-to-use in aerobic reactor of hybrid MBR. BFR is used at various concentrations from 4 to 12 g L$^{-1}$ at pH 5. The optimum conditions obtained from this preliminary analysis were then applied to test the equilibrium and rate adsorption experiment at various initial concentrations.

2.2. Lab-scale trials hybrid MBR with BFR

A lab-scale hybrid MBR has been used for this research. The schematic process flow diagram is shown in Fig. 1. The operating condition and specification of the MBR system is given in Table 1. In summary, for acclimatization the MBR system was seeded with biological sludge taken from the wastewater treatment plant of the Felda Bukit Besar Palm Mill, Johor Bahru.

Seed biomass from sludge POME aerobic treatment plant was added at the start of the test. Acclimatization takes time about 40 days before steady state. The system was operated in steady state condition and run continuously during this study. Each BFR used new steady state ready-to-use in aerobic reactor of hybrid MBR. The diluted POME was gradually increased to a final COD loading 35,000–45,000 mg L$^{-1}$. BFR is used at various concentrations from 4 to 12 g L$^{-1}$ at pH 5 using diluted POME with COD 10,000 mg L$^{-1}$. The reactor contains flat sheet type of membrane with chlorinated polyethylene material, membrane pore size 0.4 µm, membrane area per module 0.1 m$^{2}$, and used three sheets in module.

2.3. BFR preparation

This study used three types of BFR as seen in Table 2 at dosages 4, 8, and 12 g L$^{-1}$. The selected dosages for each BFR were based from the previous works (Ahmad et al., 2005; Bhatia et al., 2007).
The winged seed of *M. oleifera* and its coat were manually removed from which good quality *M. oleifera* seed was obtained. The kernel was then grounded into powder. The seed was stirred in a blender (Model Philip HR1721/06/BC) for 5 min. Oil content was extracted from dry *M. oleifera* seed using *n*-hexane. The extraction took about 1 h.

*M. oleifera* stock solution was prepared from 5,000 mg *M. oleifera* after mixing with 100 mL distilled water. Muslin cloth is used to filter a resulting suspension. Flocculator (Stuart Science Flocculator model, USA) was used to adsorb organic contents of POME with *M. oleifera*. The stock solutions of each BFR were prepared in deionized water right before the batch tests.

### 2.4. POME samples preparation

The raw POME was collected from Felda Bukit Besar Palm Oil Mill, Johor, Malaysia. Upon sampling, the temperature of POME was measured approximately 80 °C and was cooled to 5 °C temperature and it will shake before used.

### 2.5. Samples analysis

*NO₃−N* method recommended by APHA (1998). *NO₃−N* in the suspension was determined for each sample of POME before and after study. Ambient temperature for this study was 25 °C ± 3 °C. SMP was prepared using methods referring to Le-Clech et al. (2003).

### 3. Results and Discussion

#### 3.1. Batch Test

##### 3.1.1. Effect of BFR dosages to COD removal used Batch Test

Effect of all BFRs were analysed for mixing time of 8 h, a mixing rate of 150 rpm, sedimentation time of 60 min and with its original pH 5.0. The COD removal in percent for each BFR (PAC, Ze, and Mo) was examined. From Fig. 2, all tested BFR at their optimum dosages provided COD removals in the range of 90–99.7% of the COD concentrations. COD removals achieved by BFR (PAC, Ze, and Mo) were 99.7%, 92%, and 95%, respectively. The optimum dosage for COD removal was reached at 8 g L⁻¹.

Activated carbon, zeolite, and *M. oleifera* adsorb the emulsified organic carbon of POME. The mechanisms of adsorption through adsorbing the COD and coagulating the suspended solid of POME. It was found that, the highest organic removal was PAC, follows by Ze, and Mo.

From this study, it was found that PAC is a good choice for COD removal compared to Ze and Mo, as other BFRs. Generally activated carbon showed good performance since it used for separation technology, as several example, color, organic compounds, inorganic compound removal in wastewater treatments (Zobir et al., 2001). For all BFRs (PAC, Ze, Mo), 8 g L⁻¹ was the optimum dosage.

##### 3.1.2. SMP removal of adsorbents

Fig. 3 showed SMP removal in percent for optimum dosage for each BFR was 8 g L⁻¹. SMP removals achieved by PAC, Ze, and Mo, as BFRs, were 58, 42, and 48, respectively. PAC has the best performance, reduced SMP concentrations above 50%. The lowest SMP removal observed for Ze and Mo was 42% and 48%. In addition, the removal of the protein fraction of SMP was consistently higher than that of the polysaccharide fraction for each BFR.

#### 3.2. The influence of BFR in hybrid MBR

##### 3.2.1. Impact BFR for short time operation in hybrid MBR used POME

Short-term filtration tests were applied to all BFRs. Three tests run has been carried out for each BFR with various dosages (4, 8, and 12 g L⁻¹), and one control without adding BFR. A new membrane sheet was used for each test. Run constant flux mode was
used in short-term filtration test with total duration of 2 h, and the changes of TMP was monitored continuously. All tests were completed in two weeks. Table 3 showed the filterability of control without adding BFR compared with other BFRs in various dosages. Table 3 also showed short-term filtration tests results as TMP average, fouling rate \((\Delta \text{TMP}/\Delta t)\), total resistance, and permeability values.

Fig. 4 showed the effect of PAC at different dosages on TMP during short-term filtration tests, respectively. Also from Table 3, PAC has the best performance when compared with other BFRs in term of TMP average, fouling rate \((\Delta \text{TMP}/\Delta t)\), total resistance, and permeability values.

Fig. 4 showed the effect of PAC at different dosages on TMP during short-term filtration tests, respectively. Also from Table 3, PAC has the best performance when compared with other BFRs in term of TMP average, fouling rate \((\Delta \text{TMP}/\Delta t)\), total resistance, and permeability values.

Table 3 showed short-term filtration performance of raw POME and BFR additive.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(\text{TMP}_{\text{ave}}) (bar)</th>
<th>(\Delta \text{TMP}/\Delta t) (mbar/min)</th>
<th>(R_t) ((10^{11} \text{ m}^{-1}))</th>
<th>(K) ((\text{Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>POME control</td>
<td>0.25</td>
<td>0.0905</td>
<td>8.16</td>
<td>44</td>
</tr>
<tr>
<td>4 g L(^{-1}) PAC</td>
<td>0.17</td>
<td>0.0218</td>
<td>3.59</td>
<td>52</td>
</tr>
<tr>
<td>8 g L(^{-1}) PAC</td>
<td>0.15</td>
<td>0.0205</td>
<td>2.99</td>
<td>55</td>
</tr>
<tr>
<td>12 g L(^{-1}) PAC</td>
<td>0.13</td>
<td>0.0189</td>
<td>2.45</td>
<td>55</td>
</tr>
<tr>
<td>4 g L(^{-1}) Ze</td>
<td>0.21</td>
<td>0.0598</td>
<td>4.71</td>
<td>52</td>
</tr>
<tr>
<td>8 g L(^{-1}) Ze</td>
<td>0.19</td>
<td>0.0535</td>
<td>4.55</td>
<td>55</td>
</tr>
<tr>
<td>12 g L(^{-1}) Ze</td>
<td>0.20</td>
<td>0.0578</td>
<td>4.63</td>
<td>57</td>
</tr>
<tr>
<td>4 g L(^{-1}) Mo</td>
<td>0.20</td>
<td>0.0578</td>
<td>4.63</td>
<td>55</td>
</tr>
<tr>
<td>8 g L(^{-1}) Mo</td>
<td>0.17</td>
<td>0.0526</td>
<td>3.59</td>
<td>61</td>
</tr>
<tr>
<td>12 g L(^{-1}) Mo</td>
<td>0.16</td>
<td>0.0591</td>
<td>3.28</td>
<td>61</td>
</tr>
</tbody>
</table>

Fig. 4 also showed the effect of (b) Ze and (c) Mo as BFRs during short-term filtration tests at various dosages, respectively. Similar to PAC, Mo was also successful in fouling control. At its optimum dosage, Mo, which removed 48% of SMP removal, provided 56% reduction in fouling rate. At their optimum dosages, Ze provided 43% in fouling rates and SMP removals obtained was 42%.

However from this study, it could be observed that SMP removal and improvement during short-term filtration tests was not always correlated. In addition, other factors, such as SMP, viscosity, floc size, characteristics of the polymer, and mechanical stress affected the fouling and filtration processes in MBRs (Le-Clech et al., 2003; Koseoglu et al., 2008). In general, short-term filtration tests used various dosages, under and above the optimum dosage from batch tests, leading to improvement of filtration condition.

3.2.2. Critical flux tests

Critical flux tests were conducted for control without adding BFRs and with added BFRs. Critical flux is one of important parameter to examine MBRs operation. In general, fouling rate is proportionally related with critical flux.

Every critical test took about 5 h and all tests were completed in 2 weeks.

All critical flux tests were completed within 12 days. The critical flux values found for raw POME mixed liquors was 13 L m\(^{-2}\) h\(^{-1}\). These critical flux results indicated the effect of BFRs added in hybrid MBR operated continuously with POME.

Fig. 5 showed the critical flux values for PAC, Mo, and Ze were 22, 16, and 18 L m\(^{-2}\) h\(^{-1}\), respectively. Based on the critical flux
value of 12 L m⁻² h⁻¹ for the control mixed liquor, BFRs contributed to critical flux enhancement of 80%, 30%, and 40% for PAC, Ze, and Mo, respectively. Except Ze, other BFRs increased the critical flux value significantly. The result for Ze was unexpected since this BFR removed about 42% of SMP removal and COD removal 98%, at its optimum dosage, and improved 43% short-term filtration performance in 2 h tests. Thus, this results indicated that SMP removal with filtration performance, such as short-term operation and critical flux, was not correlated. Contradiction with Ze which was not in line with SMP removal, PAC showed consistently performance on critical flux value up to 21 L m⁻² h⁻¹ levels. PAC enhancement in filterability process has mechanisms, such as, in 2nd size, neutralization phenomenon, and pollutant entrapment/sorption into floc.

The results above is inline with study by Ng et al. (2006), which showed PAC polymer enhanced the flux three times lower than control. They found that polymeric coagulants were more effective for filterability improvement due to larger flocs formed by charge neutralization mechanism and decreased supernatant organic fractions (Ng et al., 2006 and Yang et al., 2009). As predicted PAC showed better performance compared with Ze in terms of quality. Mo as BFR showed good performance better than Ze, although this study was the first study to use Mo as BFR.

Overall, enhancements in critical flux values by the BFRs may be linked to activated sludge flocculation, the increased of floc enlargement, and porosity in the cake layer. Biofouling mechanisms reduction can be explained, PAC which has successfully formed flocs from organic and inorganic components in soluble material at MBR, better than Ze and Mo. Thus flocculant to floc enlargement, and successfully reduced biofouling phenomenon of the membrane.

From further studies, BFRs surface areas found that PAC and Ze have 3000–4000 m² g⁻¹ (Kaneko and Ishii, 1992) and 600–800 m² g⁻¹ (Yates, 1968). In addition activated carbon produced from Mo has surface area of 713–774 m² g⁻¹ (Warhurst et al., 1997). It was noted, PAC acted as highest BFRs removal because of its bigger surface area, compared with zeolite. However, since Mo in this study is used in its natural form, and not in powdered activated carbon form from surface area perspective (Warhurst et al., 1997), it still showed good performance, between PAC and Ze, in critical flux tests.

3.2.3. Effluent of hybrid MBR

The effect of three BFRs at three different dosages was observed to significantly improved the effluent quality for the hybrid MBR. The PAC as BFR has slightly better performance as potential nitrogen reooval, compared with zeolite and Mo. PAC achieved up to 99%, while Ze removed up to 96%, and Mo reached up to 97% removal. Normally, activated carbon is used for separation technology, i.e., color and organic compounds removal in water and wastewater treatments (Zobir et al., 2001). PAC 8 g L⁻¹ has a favorable nitrification compared to other types of BFRs, with influent ranges from 25 to 30 mg L⁻¹ and effluent ranges from 0.5 to 4.3 mg L⁻¹.

4. Conclusions

SMP removal obtained from PAC, Ze, and were 58, 41, and 44, respectively. The PAC exhibited the best performance compared with two BFRs in terms of SMP removal, followed by Ze and Mo. PAC has performed up to 70% reduction followed by Mo and Ze 56% and 42% in short-term filtration, respectively. Ze showed the least improvement in fouling rates. In addition, the critical values provided for PAC, Ze, and Mo were 21, 15, and 18 L m⁻² h⁻¹ respectively. Critical flux enhancement if compared with control for PAC, Ze, and Mo were 80%, 20%, and 40%, respectively. PAC performed well and consistently with short-term filtration tests, with critical flux reaching up to 21 L m⁻² h⁻¹ levels. BFRs enhancement in MBRs system reduced fouling rates, operated at higher flux, reduced membrane area, and finally reduced operational cost.

Generally, SMP removal and filtration test, such as short-term filtration test and critical flux operation was not correlated. In addition, fouling and filtration tests was affected by SMP, viscosity, floc size, polymer characteristics, and mechanical stress. However, batch tests were conducted to identify the optimum dosage of BFRs used in filtration tests, such as short-term filtration and critical flux tests. PAC as cationic polymers performed well compared with Mo and Ze. The performance of PAC was correlated with its surface area, which ranges from 3000 to 4000 m² g⁻¹, compared with Ze, which ranges from 600 to 800 m² g⁻¹. In addition, powdered Mo has surface area ranges from 713 to 774 m² g⁻¹. Biofouling mechanisms reduction can be explained by, PAC which has successfully formed flocs from organic and inorganic components in soluble material at MBR, better than Ze and Mo. Thus, flocculant to floc enlargement, and successfully reduced biofouling phenomenon at membrane.

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