Reduction of membrane fouling in MBR by ZSM-5 nano adsorbent in various sludge retention times for phenol removal

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1. Introduction

During recent decades, proper function of membrane bioreactors in wastewater treatment resulted in their ability to resolve the problem of water shortage in addition to removing toxic and usual pollutants from water (Rahimi et al. 2014). These systems can also reduce energy consumption in comparison with conventional systems (Atanasova et al. 2017). However, they have some disadvantages. Membrane cost is one of the major limitations of membrane bioreactors (Hazarati and Shayeeghan, 2011; Shaabani et al. 2018). Generally, membrane fouling would increase the operational costs through decreasing the system performance. Chemical factors such as membrane structure, antifouling properties, hydrophobicity and antibacterial activities contribute in membrane fouling (Rahimi et al. 2014). Commonly, adding adsorbents in MBR improve sludge and cake layer specification and thus reduces membrane fouling (Hazarati et al. 2018). Recent studies have demonstrated that nanoparticles adsorbents such as zinc oxide (Wang et al., 2014) can decrease cake layer resistance and reveals no significant adverse effects on its performance but silica adsorbent increase membrane fouling (Sibag et al. 2016). Also in other work, was evaluated the performance of membrane bioreactor (MBR) coupled with a modified walnut shell granular activated carbon (WSGAC) for tannery wastewater treatment (Alighardashi et al. 2017). In addition, some researchers have used natural zeolites for membrane fouling mitigation (Yuniarto et al. 2013), and demonstrated that it could be an excellent adsorb for adsorption of SMP and dissolved organic matter. Indeed, addition of adsorbents will increase the size of sludge flocs and the soluble organic materials will be diminished. Therefore, it can be concluded that by improving the properties of zeolite such as porosity, functional groups on them and crystallinity, it is possible to delay the membrane fouling. In addition, SRT has a significant impact on biomass properties (Ferrer-Polonio et al. 2018; Mirzavandi et al. 2019). Studies have found some relationships between EPS and SRT. For example, it was reported that increase of temperature and SRT resulted in decline of cake layer resistance; while particle and floc size was increased which decreased the membrane fouling (Mirzavandi et al. 2019). Also Ng et al., reported decrease of protein and carbohydrate of EPS by increase of SRT (from 3 to 10 d) (Ng et al., 2006). In contrary, Lee et al. expressed that increase of SRT from 20 to 60 d did not result in significant changes in EPS concentration (Lee et al., 2003). Generally, the effect of SRT on sludge features and membrane fouling vary from one study to the other.

Few studies have been reported regarding the presence of nano-adsorbent in different retention times. In this regard, this study is aimed at investigating SRT changes at the presence of nano-adsorbent. For this purpose, three SRT of low, medium and high (10, 50 and 100 d, respectively) were evaluated. The EEM results showed that in addition to reduction of SMP, the humic compounds were also reduced. The results showed the high efficiency of ZSM-5 nano-adsorbent for reducing of membrane fouling at the low SRT.

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2. Materials and methods

2.1. Experimental set up

Three lab scale MBR with a total working volume of 7 L and dimensions of 22×6.5×65 cm³ was used in this research (Fig. 1) and was named MBR1, MBR2 and MBR3. In MBR1, MBR2 and MBR3, the sludge retention time was 10, 50, and 100 d, respectively. The bioreactors were equipped with a PVDF flat sheet membrane with a

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pore size of 0.1 μm and a surface area of 0.11 m² (Sinap, China). Air diffuser placed blow the membrane in order to supply oxygen demanded by the microorganisms (biological processes) and reduced foulants on the membrane surface. To unify air movement on the membrane surface a plate as a baffle was settle behind the membrane. The channel width between the membrane and baffle was 7 mm. The sludge used in the MBR was supplied from Tabriz Petrochemical Company. The sludge was allowed to acclimate to the operating conditions was fed with synthetic wastewater. The synthetic wastewater had the following composition (mg/L): Phenol: 50; C₂H₅OH: 450; K₂HPO₄: 35; KH₂PO₄: 45; Urea: 560; MgSO₄·7H₂O: 13; CaCl₂·2H₂O: 7; FeCl₃: 5; NaHCO₃: 500. Furthermore, operational conditions are shown in Table 1.

2.2. Preparation of nano adsorbent

The solution of NaOH, sodium aluminate and deionized water was stirred for 30 min. TPABr was then added and stirred for 1 h (solution A). Simultaneously, silicic acid was dissolved in 100 mL of deionized water (solution B). The solution A was added to the solution B drop by drop under continues agitation and stirred for 2 h. Appropriate amount of sulfuric acid adjusted the pH of solution. The final solution included the molar composition of 20 SiO₂: 0.05 Al₂O₃: 1 TPABr: 1.5 Na₂O; 200 H₂O. The crystallization was in static state at 540 °C under autogeneous pressure for 48 h. The synthesized powder was passed through 0.45 μm filter.

2.3. Analytical methods

SMP and EPS were measured by the method described by Chang et al. (Chang and Lee, 1998). Protein fraction (SMPP and EPSp) was measured by Bradford's method (Zhang et al. 1999) while the corresponding polysaccharide fraction (SMPC and EPSc) was determined by phenol–sulfuric acid method. The cake layer that removed from the membrane surface was dissolved in 500 mL pure water. After that, about 50 mL of the solution were centrifuged for 10 min at 9000 rpm. The foulings pellet were placed in incubator for 48 h at 55 °C. The dry foulants used for FTIR analysis (Hazrati and Shayegan, 2016). The EEM was determined by LS 55; PerkinElmer. A three dimensional EEM spectra was obtained by collecting wavelength of both excitation over range of 200-400 nm and emission of 200-550 nm in stepwise 10 nm (Hazrati and Shayegan, 2016). For determining molecular weight of EPS of cake, the samples were centrifuged for 10 min at the rate of 9000 rpm. Then the remaining EPS was extracted by thermal methods. The obtained solution was then centrifuged by the same method and the supernatants were sent for GPC tests after passing through 0.45 μm filter.

2.4. Nano adsorbent characterization

The TEM image showed that synthesized ZSM-5 is in nano scale (Fig. 2). In addition, the XRD pattern, FTIR spectra for nano adsorbent were presented in the supplementary data.

3. Results and discussion

3.1. Microbial activity

Table 2 shows that COD removal efficiency had no significant changes in different SRTs. But biological phenol removal was better in SRT of 50 d (MBR 2) in comparison with the SRTs of 10 and 100 d (MBR 1 and MBR 3, respectively). For SRT of 10 d, although nano-adsorbent can be effective in increasing the efficiency due to lack of saturation, but MLSS was lower in this case; therefore, phenol removal was decreased relative to SRT of 50 d. On the other hand, despite higher MLSS for SRT of 100 d, but it had lower microbial activity. Moreover, nano-adsorbent was saturated with microbial products in this case; hence it could not adsorb high amounts of dissolved organic compounds. Ouyang and Junxin also expressed that biomass concentration increased by SRT enhancement and MLVSS to MLSS ratio reduced; (Ouyang and Junxin, 2009) hence F/M was declined and the microbial activity was decreased. Other studies have shown that increase of SRT up a specific value will increase removal efficiency; but further increase of SRT will reduce efficiency which could be due to over-reduction of microbial activity (Han et al. 2005). Hang et al. also expressed that the removal efficiency is independent of SRT for values of 5 to 40 d (Huang et al. 2001). However, biomass concentration and kinetics parameters of the growth will be reduced. In our system, SRT enhancement reduced SOUR bacterial activity but its decrease is not that much to induce further efficiency reduction.

3.2. TMP variation

In this study, all three bioreactors containing nano-adsorbent acted with similar and constant flux. Therefore increase of TMP reflects membrane fouling (Oulad et al. 2018). Fig. 3 shows increase of TMP for all three MBRs. At day 170, TMP was lower for the case with SRT of 10 d (MBR 1) compared to the cases with SRT of 50 and 100 (MBR 2 and MBR 3, respectively). When TMP was 15 kPa for MBR1, this value was 18 and 25 kPa for MBR2 and MBR3, respectively. One of the major reasons for low TMP of MBR1 is higher content of nano-adsorbent (since it had lower SRT). Therefore, it can adsorb more organic compounds; so, it reduced membrane fouling higher than MBR2 and MBR 3. It must be men that although TMP of MBR2 was more than MBR1, but it was not highly different; also, as the nano-adsorbent and excesses sludge of this case were less than MBR1, therefore, it can be said that MBR2 can be the best mode. Moreover, despite the fact that MBR3 had lower nano-adsorbent and sludge, but the fouling was significant and it can't be considered as a suitable mode.

The reason for higher TMP in the MBR3 could be due to two reasons: more fouling of membrane pores and formation of more cake
layers. To estimate fouling mechanism, each of resistances were separately calculated (Table 3).

Table 2. Variations of some important parameters at the presence of nano-adsorbent in different SRTs.

<table>
<thead>
<tr>
<th>MBRS</th>
<th>MBR 1</th>
<th>MBR 2</th>
<th>MBR 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD removal, %</td>
<td>97 ± 1</td>
<td>98 ± 1</td>
<td>97 ± 1</td>
</tr>
<tr>
<td>Phenol removal, %</td>
<td>96 ± 1</td>
<td>99 ± 1</td>
<td>96 ± 1</td>
</tr>
<tr>
<td>MLSS, mg/L</td>
<td>3452 ± 194</td>
<td>5631 ± 169</td>
<td>6016 ± 137</td>
</tr>
<tr>
<td>SOUR, mg</td>
<td>0.88</td>
<td>0.91</td>
<td>0.86</td>
</tr>
<tr>
<td>Oics/gVSS h</td>
<td>8.43</td>
<td>11.26</td>
<td>6.53</td>
</tr>
</tbody>
</table>

Results showed that in MBR3, most of particles were deposited on membrane surface and therefore, it will result in increase of resistance in cake pores. As shown in Table 3, total resistance of MBR3 is more than MBR2 and MBR1 which could be mainly due to higher resistance of cake and pores.

Table 3. Results of fouling resistance distribution (×10^{12} m^{-1}).

<table>
<thead>
<tr>
<th>MBRS</th>
<th>R_m</th>
<th>R_p</th>
<th>R_c</th>
<th>R_t</th>
</tr>
</thead>
<tbody>
<tr>
<td>MBR1</td>
<td>4.1</td>
<td>4.2</td>
<td>4.7</td>
<td>13.0</td>
</tr>
<tr>
<td>MBR2</td>
<td>3.7</td>
<td>5.4</td>
<td>6.6</td>
<td>15.7</td>
</tr>
<tr>
<td>MBR3</td>
<td>2.8</td>
<td>9.4</td>
<td>10.5</td>
<td>22.7</td>
</tr>
</tbody>
</table>

3.3. SMP and EPS variation

Microorganisms’ metabolism such as SMP and EPS production has crucial impacts on membrane fouling; therefore, understanding of its effects is crucial (Hazrati and Shayegan. 2016). Some of the studies have shown that higher levels of SMP will result in more fouling due to blocking pores and reducing cake porosity (Hazrati et al. 2018). Moreover, Kimura et al. (Kimura et al. 2009) conducted a study on SMP in different SRTs and investigated its relationship with membrane fouling; then concluded that there is a close relationship between carbohydrates and membrane fouling. It was also expressed that higher EPS concentrations may result in blockage of biomass and formation of large flocs and finally reduction of fouling (Zuriaga et al. 2016).

Table 4 lists SMP and EPS concentrations for both carbohydrate and protein components of reactor sludge. As it is clear, SMP concentration of MBR1 and MBR2 is lower than MBR3. This could be due to several reasons; it may be adsorbed by nano-adsorbent or destroyed during biomass synthesis or discharged through membrane pores. In this study, as MBR3 had lower nano-adsorbent content (due to higher SRT), lower microbial products were adsorbed; so this reactor had higher SMP. On the other hand, it can be said that high SRT will increase SMP (Arabi and Nakhaei. 2009). Therefore, for the case of MBR3, both factors of high SRT and presence of nano-adsorbent play a crucial role in increase of SMP. Furthermore, EPS concentration variation is also depicted in Table 4 for all three bioreactors. Results showed that EPS concentration of MBR3 is far lower than MBR2 and MBR1. The reason could be higher SRT of MBR3. In high SRTs, biodegradation will be increased; so EPS will be declined. Decrease of EPS in MBR3 resulted in smaller sludge particle size in this reactor (See Fig. 4).

3.4. Investigation of inorganic compounds of cake layer

As formation of cake layer plays an important role in membrane fouling, study of the characteristics of cake layer is necessary. Generally, the substances which result in fouling can be divided into two major classes: 1) organic and 2) inorganic substances. Therefore, organic and inorganic compounds of membranes were also investigated. Table 5 provides the cake weights of both membranes as well as their total analysis. 11.4, 12.9 and 24.2 g of cakes were formed on MBR1, BR2 and MBR3, respectively. This table shows that the amount of both organic and inorganic materials was higher in cake of MBR3. Therefore, these compounds are probably the reason for higher fouling in this bioreactor. It must be noted that although organic and inorganic compounds of MBR1 were lower than MBR2, but this reduction is not significant. For further investigation of inorganic compounds of cake layer, the level of some ions (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, NO_{3}^{-}, SO_{4}^{2-}, PO_{4}^{3-}) was determined (Table 5). Presence of some ions even in small amounts reduces the cake porosity due to formation of bridge between biopolymers and will finally end up in fouling. Moreover, as it was mentioned, these substances will form MgNH_{2}PO_{4}, H_{2}O which plays an important role in membrane fouling (Hazrati et al. 2018) in this study, as suggested by Table 5, Mg^{2+}, Na^{+}, K^{+} and PO_{4}^{3-} ions exist in all three reactors which highest level in MBR3 in comparison with the other two MBRs. Therefore, one the reasons for higher fouling in MBR3 could be higher levels of inorganic compounds; which could be due to higher SRT resulting in more sludge accumulation.

3.5. EPS molecular weight distribution of cake

For further investigation of SRT impact at the presence of ZSM-5 nano-adsorbent on improvement of sludge features, EPS molecular weight distribution was examined. This parameter changed from 0.1 to 30 kDa in the three MBRs (See Fig. 5). Their comparison showed that MBR3 has more compounds with lower molecular weight (0.1 to 2 kDa). The reason for this is that nano-adsorbent cannot be effective in adsorbing lower molecular weight the efficiency due to saturation. On the other hand, compounds with high molecular weight (above 5 kDa) are also abundant which may be due to reduced microbial activity in

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Table 4. SMP variations in mixed liquor and analysis results of EPS components in mixed liquor and cake layer.

<table>
<thead>
<tr>
<th>MBRS</th>
<th>SMP, mg/L</th>
<th>EPS, mg/gVSS</th>
<th>EPS for cake layer, mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>MBR 1</td>
<td>15.4 ± 3.5</td>
<td>178.4 ± 6.7</td>
<td>213.5 ± 3.8</td>
</tr>
<tr>
<td>MBR 2</td>
<td>21.4 ± 5.1</td>
<td>152.9 ± 5.2</td>
<td>35.6 ± 4.1</td>
</tr>
<tr>
<td>MBR 3</td>
<td>42.6 ± 4.3</td>
<td>92.5 ± 4.5</td>
<td>65.1 ± 5.3</td>
</tr>
</tbody>
</table>

*Note: Results based on the EPS mass in cake layer per reactor volume.*
MBR3 as it has higher SRT. It was determined that compounds with molecular weight above 2 kDa are mainly removed by biological means. As substances with molecular masses below 1 kDa play crucial role in membrane fouling (Jin et al., 2013), it can be said that presence of these compounds could be one of the reasons of pore blockage in MBR3. Moreover, high-molecular weight compounds can completely cover the pores resulting in complete fouling and formation of cake. These findings verify results of fouling resistance distribution.

<p>| Table 5. Results of the components of fouling cake on membrane surface. |
|------------------------|-------------------|-------------------|-------------------|</p>
<table>
<thead>
<tr>
<th>MBRs</th>
<th>Inorganic matter, g</th>
<th>Organic compounds (VSS), g</th>
<th>Total cake, g</th>
</tr>
</thead>
<tbody>
<tr>
<td>MBR 1</td>
<td>2.4 (21 %)</td>
<td>8.3 (72 %)</td>
<td>11.4</td>
</tr>
<tr>
<td>MBR 2</td>
<td>2.8 (22 %)</td>
<td>9.1 (70 %)</td>
<td>12.9</td>
</tr>
<tr>
<td>MBR 3</td>
<td>6.1 (25 %)</td>
<td>15.8 (65 %)</td>
<td>24.2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Details of measured inorganic matter</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₄²⁻</td>
</tr>
<tr>
<td>------------------------</td>
</tr>
<tr>
<td>MBR 1</td>
</tr>
<tr>
<td>MBR 2</td>
</tr>
<tr>
<td>MBR 3</td>
</tr>
</tbody>
</table>

3.6. FTIR analysis

FTIR analysis was conducted on the cakes of all three MBRs as shown in Fig. 6. The results show the presence of the important peaks at 1290, 1547 and 1649 cm⁻¹ in both reactors indicating protein in cake layer. Moreover, presence of O-H and C=O functional groups in cake layer of all three reactors reflects the presence of polysaccharides. Generally, the peaks observed in previous works were as follows: the peaks at 3000, 3600 and 2845 cm⁻¹ (Kumar et al. 2006) related to O-H functional group; the peak at 2926 (Jin et al. 2010) and 3400 (Zhou et al. 2007) cm⁻¹ related to C-H group. The peak at 1650 and 1653 cm⁻¹ attributed to C-N functional group of first type amide; 1540 and 1550 cm⁻¹ related to type 2 amide and 1235 and 1385 cm⁻¹ assigned to third type amide; (Zhou et al. 2007) the peaks at 1405 and 1481 cm⁻¹ which may be related to phenols and at 1055 and 1065 cm⁻¹ which are attributed to C-O (polysaccharides). The important conclusion from FTIR spectra is that proteins and polysaccharides content in MBR3 were more than MBR1 and MBR2. These results verify EPS analysis for cake layer (See Table 4).

3.7. EEM analysis

Table 6 shows EEM analysis for EPS derived from cake layer. In all three MBRs, two major peaks can be observed at Ex/Em = 220/310-320 and Ex/Em = 375/435-438. The former is related to protein-like substances (Wang et al. 2009) while the latter indicates presence of humic acid. Presence of humic acid in active sludge system was also mentioned them as one of the substances resulting in membrane fouling (Alresheedi and Basu, 2007). Presence of humic acid in active sludge system was also mentioned them as one of the substances resulting in membrane fouling (Alresheedi and Basu, 2007). Presence of humic acid in active sludge system was also mentioned them as one of the substances resulting in membrane fouling (Alresheedi and Basu, 2007). Presence of humic acid in active sludge system was also mentioned them as one of the substances resulting in membrane fouling (Alresheedi and Basu, 2007). Presence of humic acid in active sludge system was also mentioned them as one of the substances resulting in membrane fouling (Alresheedi and Basu, 2007).

![Fig. 5. Molecular weight distribution for EPS of cake layer on membranes.](image)

In fact, they used media to reduce these compounds. But the more important result of this test is that the intensity of humic acid and protein will get higher at high SRT. Therefore, it can be said that humic compounds were formed in all three SRTs but in lower SRTs, humic compounds were easily adsorbed by nano-adsortent.

4. Conclusions

In this study, the synthesized nano-adsortent was applied to reduce membrane fouling in MBR including different SRTs. The results can be summarized as follow:

- Removal efficiency of COD is almost the same at three SRTs because all three of them are in standard range. But phenol removal efficiency was higher in SRT of 50 d as the microbial activity was better in this condition. The lowest membrane fouling was obtained at SRT of 10 d. Although membrane fouling was about 15% more in SRT of 50 d compared to 10 d, it could be selected as the best condition due to the low discharge of the excess sludge. GPC results revealed that higher fouling in MBR3 was related to the high molecular weight compounds. EEM analysis showed that reduction of protein and humic acids through nano adsorbent at SRTs of 10 and 50 d were higher compared to 10 d. It is recommended that optimum dosage of adsorbent to be determined in future studies. Also it is important that high concentration of phenol to be investigated in other studies.

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