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Insight into influence of iron addition in membrane bioreactor on gel layer fouling

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Abstract. Membrane fouling in membrane bioreactor (MBR) remains a primary challenge for its wider application. The focus of this study to investigate the influence of iron distribution in activated sludge on gel layer fouling in MBR. Significant reduction in the transmembrane pressure (TMP) rise rates was observed in the presence of iron as result of retarding the gel layer formation time. The spatial distribution of iron had a significant impact on the stratification structure of extracellular polymeric substances (EPS) fractions, such as proteins (PN) and polysaccharides (PS). A mitigation of PN or PS from the supernatant to the EPS inner layers was observed in the presence of iron. Compared with the control reactor, the reduction in PN and PS of the supernatant and lower PN/PS rates of the LB-EPS were beneficial to decrease the membrane fouling potential during the gel layer formation. Consequently, the iron addition managed to control gel layer fouling could be a useful strategy in MBR.

Keywords: membrane bioreactor (MBR); gel layer fouling; extracellular polymeric substances (EPS); stratification structure; transmembrane pressure (TMP)

1. Introduction

Membrane bioreactor (MBR) combined with conventional activated sludge (CAS) process and membrane separation, as a competitive alternative, has been applied for industrial and municipal wastewater treatment process due to its merits (Zhang *et al*. 2014a), such as small footprints, complete solids removal and high effluent quality, etc. However, membrane fouling remains the primary hindrance for its universal and large scale applications, which is directly influenced by the characteristics of the activated sludge, such as morphological properties, physical parameters and the biochemical components (Ji *et al*. 2010). Extracellular polymeric substances (EPS) have been found to be key substances, which have complex interactions or relationships with all these membrane foulants and fouling mechanisms in MBR (Le-Clech *et al*. 2006). EPS are often divided

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into two major fractions: soluble EPS (S-EPS) and bound EPS. The inner layer of the bound EPS consists of tightly.

It is generally agreed that the fouling layer of membrane surface can be further distinguished as gel layer and cake layer. The cake layer is loosely associated with the membrane surface as result of the adhesion and deposition of activated sludge, while the gel layer is more tightly bound to the membrane surface due to the gelation of the colloidal and dissolved matters (Zhang *et al*. 2015). Under sub-critical flux operation, membrane fouling is generally characterized by a two step fouling phenomenon, i.e., a gradual increase of transmembrane pressure (TMP) is followed by a sudden increase. The formation of gel layer on membrane surfaces leads to the gradual increase of TMP, which is reported that the resistance of gel layer was almost 100 times higher than that of cake layer (Hong *et al*. 2014). Therefore, the gel layer formation has been considered as an important form of membrane fouling in MBR due to significant reduction permeability of membrane (Wang *et al*. 2008, Hong *et al*. 2014).

Iron is commonly used in MBR as an aid to phosphorus removal as well as membrane fouling control (Zhang *et al*. 2008). It is observed that iron enhanced the filterability of activated sludge because iron is ideal for neutralizing sludge. For example, iron neutralizes negatively charged flocs and colloids, and thus allows them to flocculate with each other by electrostatic attraction. As a result of flocculation, an increase in floc size and a reduction in S-EPS are observed in the bulk solution. The theories pertaining to the role of iron in flocculation include adsorption and charge neutralization (Zhang *et al*. 2014a), multivalent bridging theory (Li *et al*. 2012) and Derjaguin-Landau-Verwey-Overbeek (DLVO) theory (Nguyen *et al*. 2014), which enhance bioflocculation of activated sludge. Moreover, the distribution pattern of PS and PN is associated with iron (Zhang *et al*. 2014a). For example, PN are more likely to be involved in electrostatic bounds with iron because of the high content of amino acids (Yu *et al*. 2008). Assuming that the different distributions of iron possess different characteristics of EPS, thus will effect on the formation of gel layer. To the best of our knowledge, the investigation of the spatial distribution of iron in multilayered structure of EPS has not been studied with respect to membrane fouling caused by gel layer in MBR.

The objective of the current study was to investigate the effect of iron on the distributions of EPS fractions as well as the gel layer fouling. And thus, the two parallel MBRs treating synthetic wastewater were applied in this study. One is under the addition of iron ($FeCl_3$) at concentrations of 10 mg/L in the influent (Fe-MBR), the other one without iron addition is control (C-MBR). TMP was selected as the key indicator to distinguish the membrane fouling stage. The distributions of iron, PN and PS in different layers of EPS, (such as in the S-EPS, LB-EPS and TB-EPS) were measured, respectively. In addition, the relations between the EPS fractions and the TMP rise rates were investigated.

2. Material and methods

2.1 MBR systems and operational condition

Two MBRs of identical working volume, C-MBR and Fe-MBR were operated. The schematic of the experimental setup was shown in Fig. 1. The two MBRs were run in parallel under the same conditions, expecting that 10 mg/L of $FeCl_3$ was added to the feed in the Fe-MBR. Each reactor had a working volume of 18 L. The membrane module used in each system was a bundle of

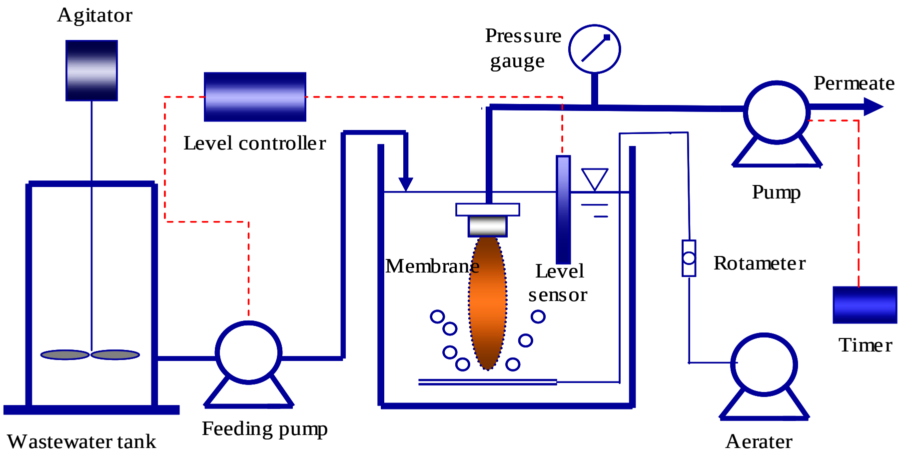

Fig. 1 Schematic diagram of the experimental set-up

hollow fiber membranes (polyvinylidene fluoride, PVDF) with a pore size of 0.22 μm and a filtration area of 0.3 m^2. Effluent was continuously withdrawn using a peristaltic pump (Model BT-300, Baoding Longer Precision Pump Co., Ltd., China) at a constant flux of 10 $L/m^2 \cdot h$, operated with an intermittent mode of 13 min on and 2 min off. Air was supplied to each reactor at 200 L/h. Hydraulic retention time (HRT) and sludge residence time (SRT) were maintained at 6 h and 30 days, respectively. The TMP was continuously monitored and the operation was stopped when the TMP reached 30 kPa. The seed sludge was taken from Jilin City Sewage Treatment Plant. Each MBR was seeded with 8 g/L of the acclimatized activated sludge. The synthetic wastewater was made by adding the following chemical: glucose of 280 mg/L, NH_4Cl of 100 mg/L, KH_2PO_4 of 20 mg/L, $NaHCO_3$ of 172 mg/L and other trace metals (10 mg/L as $CaCl_2$, 50 mg/L as $MgSO_4 \cdot 7H_2O$, 0.375 mg/L as $FeCl_3$, 0.1 mg/L as $CuSO_4 \cdot 4H_2O$, 0.15 mg/L as $NaMoO_4 \cdot 2H_2O$, 0.13 mg/L as $MnSO_4 \cdot H_2O$, 0.23 mg/L as $ZnCl_2$, 0.42 mg/L as $CoCl_2 \cdot 6H_2O$). The pH of the influent was maintained 7.0±0.6.

2.2 Analytical items and methods

The EPS extraction protocol in this study was modified based on previous studies (Yu *et al*. 2008). In briefly, a 25-mL sludge sample was centrifuged at 4000 g for 5 min at 4℃, and the supernatant was collected as the bulk solution. A NaCl solution with the same conductivity as the sludge sample was prepared and preheated to 70℃; then it was used to re-suspend the sludge pellet in the tube at its original volume. With no delay, the sludge suspension was sheared by a vortex mixed (G-560, Scientific Industries, Inc., USA) for 1 min; then, it was centrifuged at 4000 g for 10 min at 4℃, and the supernatant was collected as LB-EPS. The residual sludge pellet in the centrifuge tube was resuspended again to its original volume of 25-mL with the NaCl solution and then put in a water bath at 80℃ for 30 min, finally centrifuged at 12,000 g for 20 min to collect TB-EPS, and the left was the pellet.

Prior to further characterizations, all the extracted S-EPS, LB-EPS, and TB-EPS solutions were filtered by 0.45 μm syringe filters (Sartorius Minisart) to remove the suspended components (Zhang *et al*. 2014b). The sum of total PS and PN was taken to be the total amount of EPS (Bura *et*

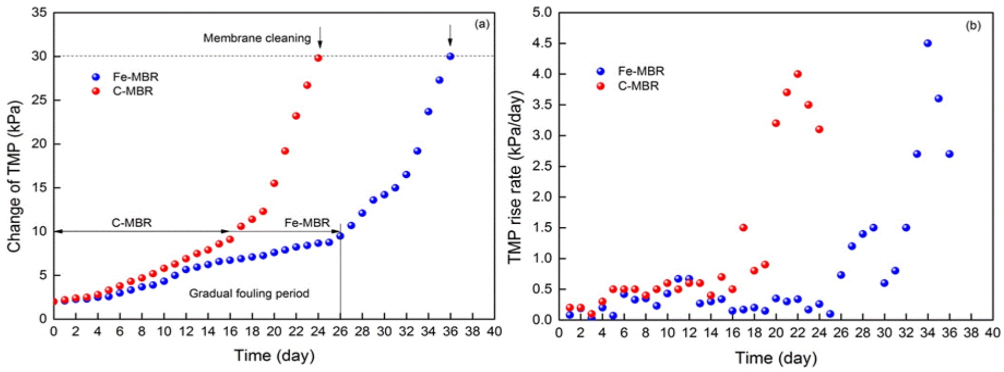

Fig. 2 Variations of TMP and its rise rates with operation time in the C-MBR and Fe-MBR: (a) Changes of TMP; (b) TMP rise rates

al. 1998). The PS in the EPS were determined using the phenol/sulfuric acid method with glucose as the standard (Dubois *et al*. 2002). The PN were quantified using a modified Lowry method with bovine serum albumin (BSA) as the standard (Bradford 1976).

3. Results and discussion

3.1 Changes of TMP and its rise rates

Fig. 2 demonstrated that the variations of TMP and its rise rates with the operation time in both MBRs. It was obvious that the TMP profiles exhibited two-stage process with a linear gradual TMP rise followed by a rapid TMP rise in both reactors (see in Fig. 2a), and the gradual formation of gel layer on membrane surfaces led to the gradual increase of TMP in the MBR (Wang *et al*. 2008). In comparison, a slower TMP rise in the Fe-MBR was observed, especially in the period of gel layer formation. For example, the time of the gradual TMP rise for the Fe-MBR was about 1.6 folds than that of the C-MBR, indicating that the positive effect of iron addition on the gel layer fouling mitigation. Similar result was also found in the study by Zhang *et al*. (2008). The TMP rise rates were computed based on TMP development each day (dTMP/day) through the experimental time (Fig. 2b), which are an important indicator for evaluating the development of membrane fouling in MBRs (Le-Clech *et al*. 2006). During the period of gel layer formation, the average TMP increase rate in the Fe-MBR (0.27 kPa/day) was 43% lower than that in the C-MBR (0.47 kPa/day), while there was not significant different during the rapid TMP rise stage (2.59 kPa/day in the Fe-MBR and 2.56 kPa/day in the C-MBR, respectively).

In fact, the formation of gel layer is different from the deposition of cake layer, which is closely related to the quality and quantity of S-EPS content in the supernatant (Li 2005, Wu and Huang 2008, Zhang *et al*. 2008) and the distributions of PN and PS in bound-EPS (Li *et al*. 2014, Zhang *et al*. 2014a), etc. The distributions of organic fractions in EPS are highly associated with cation (Zhang *et al*. 2014a), therefore, an insight into the effect of spatial distributions of iron on EPS compositions might be beneficial to understand the role of iron in gel layer formation.

3.2 Spatial distributions of iron and its effect on PN and PS in EPS fractions

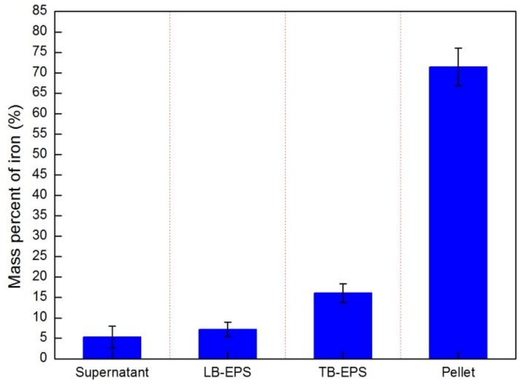

Fig. 3 Mass percentage of iron in the different layers of activated sludge for the Fe-MBR

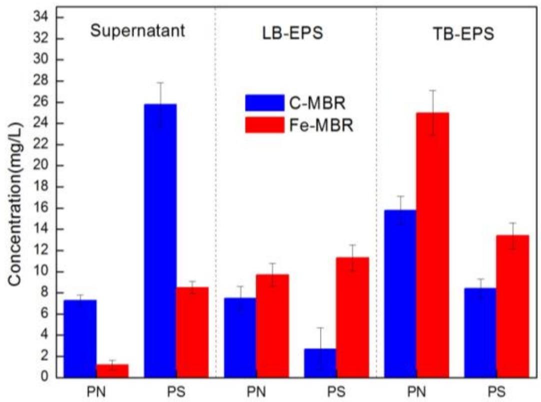

Fig. 4 Distributions of PN and PS in the EPS fractions for the C-MBR and Fe-MBR

The mass percentage of iron within the different layers of activated sludge for the Fe-MBR was shown in Fig. 3. More iron located in the inner layers of activated sludge than the outer layers, as nearly average 71.4% and 16.1% were concentrated in the pellet and TB-EPS, respectively. In comparison, only 7.2% and 5.3% on average were found in the LB-EPS and supernatant, respectively. Similar phenomena was also observed by our previously study (Zhang *et al*. 2014a). It could be explained that the trivalent cations possess higher valence states, polarizability and relatively smaller degree of hydration compared to bivalent or monovalent cations (Li *et al*. 2014), thus, most iron would tightly embedded in the pellet or TB-EPS. Moreover, according to the previous study (Wen *et al*. 2015), the amount of negative charges in different sludge components followed the sequence: pellet > TB-EPS > LB-EPS > S-EPS, suggesting the pellet or TB-EPS loaded more negatively charge groups, which also provided more bonding sites for iron.

The distributions of iron in activated sludge had a directly impact on the membrane fouling, for example, according the study by Waite *et al*. (2002), the supernatant iron was in the form of complex with S-EPS and amorphous ferric oxyhydroxide (AFO), which had a high membrane fouling potential in MBR, therefore, the lower iron in the supernatant had a benefit to membrane fouling suppression. On the other hand, the mitigation of iron from the supernatant to the EPS inner layers would change the distribution of PN and PS because the organic fractions in EPS were

Table 1 Correlation between the EPS fractions (x, mg/L) and the TMP rise rates (y, kPa/day) during the gel layer formation in both MBRs.

EPS fractions	Fe-MBR		C-MBR	
	Fitting equation	R^2	Fitting equation	R^2
S-EPS	y=6.26x+16.38	0.81	y=29.58x+11.69	0.79
LB-EPS	y=4.31x+9.62	0.57	y=17.12x+9.79	0.74
TB-EPS	y=6.95x+43.60	0.08	y=7.73x+53.79	0.02

highly associated with cation (Zhang *et al*. 2014a).

Fig. 4 presented the PN and PS distributions in the EPS fractions of the both MBRs. It could be obtained that the iron had significant impact on the stratification structure of EPS, especially to S-EPS. It could be seen that the PN and PS content in the supernatant significantly decreased for the MBR-Fe, reflected by about 83.4% and 67.1% reduction in PN and PS compared with the C-MBR, respectively. It could also be seen that the iron exerted a greater impact on reducing PN than PS in the supernatant, which was mainly due to the PN had an affinity for iron (Novak *et al*. 2007). It was also consistent with the report of Yu *et al*. (2008), who also stated that the iron exhibited higher affinity to protein-like substances.

The lower PN and PS content in the supernatant of the Fe-MBR indicated that a mass migration the S-EPS to the sludge flocs due to bioflocculation by the help of the iron, which was also confirmed that the LB-EPS or TB-EPS contents in the Fe-MBR was higher than that of the C-MBR (see in Fig. 4). Especially, an obviously increase of PN and PS in the TB-EPS was observed in the Fe-MBR compared with the C-MBR, suggesting a mitigation of PN or PS from the supernatant to the EPS inner layers occurred in the presence of iron.

3.3 Relation between the EPS fractions and the TMP rise rates during the gel layer formation

The relations between the contents of different EPS fractions (x) and the increase rates of TMP (y) during the gel layer formation in both reactors were displayed in Table 1. It showed a strong correlation between S-EPS contents and the TMP rise rates with an r-squared value of 0.81 (in the Fe-MBR) and 0.79 (in the C-MBR), respectively. Since S-EPS was found to be major foulants for the gel layer formation (Hong *et al*. 2014), and the higher S-EPS in the supernatant resulted in a higher TMP rise rate. It could be observed that the content of S-EPS in the Fe-MBR obviously reduced (see in Fig. 4), thus the reduction of PN and PS in the supernatant would result in a lower TMP rise rate in the Fe-MBR (see in Fig. 2b), which contained less S-EPS to attach the membrane surface and form the gel layer.

Compared with the Fe-MBR (R^2=0.57), the LB-EPS had a higher correlated to the rise rates of TMP in the C-MBR (R^2=0.74), indicating LB-EPS could play an important role in gel layer formation in the absence of iron. Regardless of the LB-EPS amount, the ratio of PN/PS in the LB-EPS was an important indicator of fouling propensity of sludge flocs (Lee *et al*. 2003, Gao *et al*. 2010). Evidences have shown that a higher PN/PS induced higher level of hydrophobicity (Sponza 2003), and then higher membrane fouling in MBR (Lee *et al.* 2003, Gao *et al*. 2010, Hong *et al*. 2013). The ratios of PN/PS in EPS fractions in the both reactors were shown in Fig. 5. It was noted that the lower PN/PS rate in the LB-EPS was observed in the Fe-MBR (0.85 on average)

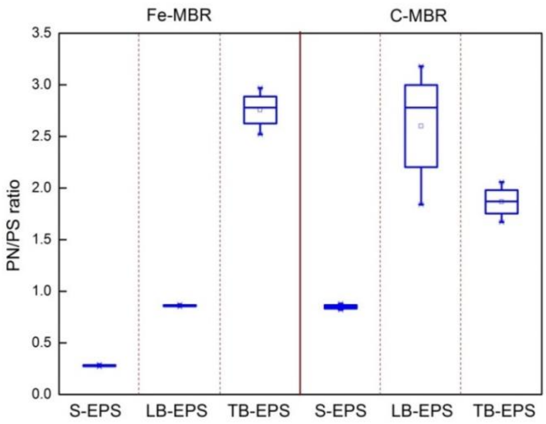

Fig. 5 The ratio of PN/PS in EPS fractions for the Fe-MBR and C-MBR

compared to the C-MBR (2.78 on average), suggesting that the LB-EPS had a lower membrane fouling potential in the presence of iron.

The TB-EPS exhibited a little effect on the gel layer formation for the both reactors (R^2=0.08 in the Fe-MBR and R^2=0.02 in the C-MBR, respectively), indicating that the gel layer fouling strongly correlated to the EPS outer instead of the inner, and thus, a mitigation of PN or PS from the supernatant to the TB-EPS in the Fe-MBR had a negligible effect on the gel layer fouling. In addition, a higher PN/PS ratio in the TB-EPS was observed in the Fe-MBR (2.97 on average) compared to the C-MBR (2.06 on average), which was confirmed that the iron had a more affinity for PN than PS again.

4. Conclusions

The iron addition significantly decreased the average TMP rise rate by about 43% compared with the C-MBR during the gel layer formation. It was found that more iron located in the inner layers of activated sludge than the outer layers, which had a significant impact on the stratification structure of EPS. The concentrations of both PN and PS in the Fe-MBR were respectively 83.4% and 67.1% lower than that of the C-MBR. Lower ratio of PN/PS in LB-EPS was found in the Fe-MBR (0.85 on average) compared to the C-MBR (2.78 on average). During the period of gel formation, the TMP rise rate had a significant correlation with the S-EPS (R^2=0.81) and LB-EPS (R^2=0.74) in the C-MBR, while it had only a strong direct correlation to the S-EPS amount in the Fe-MBR (R^2=0.79). The reduction of S-EPS content and the lower ratio of PN/PS in LB-EPS have a positive impact on gel layer fouling mitigation under the iron addition. Consequently, the iron addition was an effective method to mitigate the TMP rise rates during gel layer formation in MBR.

Acknowledgments

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