Mechanism of calcium mitigating membrane fouling in submerged membrane bioreactors

ZHANG Hanmin∗, XIA Jie, YANG Yang, WANG Zixing, YANG Fenglin

Key Laboratory of Industrial Ecology and Environmental Engineering, MOE, School of Environmental and Biological Science and Technology, Dalian University of Technology, Dalian 116024, China. E-mail: zhhanmin@126.com

Received 18 September 2008; revised 12 December 2008; accepted 29 December 2008

Abstract

Two parallel membrane bioreactors (MBRs) were operated under different calcium dosages (168.5, 27 mg/L) to gain a better understanding of the mechanism of retarding membrane fouling by adding calcium. The results showed that the particle size of sludge flocs increased and the particle size distribution tended to be narrow at the optimum dosage (168.5 mg/L). Calcium was effective in decreasing loosely bound extracellular polymeric substances (LB-EPS) in microbial flocs and soluble microbial products (SMP) in the supernatant at the dosage of 168.5 mg/L by strengthening the neutralization and bridging of EPS with flocs. Furthermore, the amount of COD$_S$ and COD$_C$ decreased in both the mixed liquor and the fouling cake layer on the membrane surface. In order to compare the filtration characteristics of cake layers from the MBRs with the two calcium dosages, the specific cake resistance and the compressibility coefficient were measured. The specific cake resistance from the MBR with optimum dosage (168.5 mg/L) was distinctly lower than that with low dosage (27 mg/L). The compressibility coefficient of the cake layers under two dosages were respectively attained as 0.65, 0.91. Scanning electron microscopy (SEM) and three-dimensional confocal scanning laser microscope analysis (CLSM) images were utilized to observe the gel layer directly.

Key words: calcium; membrane fouling; loosely bound extracellular polymeric substances (LB-EPS); compressibility coefficient

DOI: 10.1016/S1001-0742(08)62383-9

Introduction

The membrane bioreactor (MBR) is commonly regarded as a promising technology for wastewater treatment because of simultaneous pollutants biodegradation and solid-liquid separation in a compact reactor. The advantages of MBR including a higher biomass concentration, stable efficiency, small footprint and low sludge production make it suitable for advanced wastewater treatment and wastewater resources regeneration (Ng et al., 2006). However, applications of new technology depend on not only a technical feasibility, but also an economic feasibility. A major obstacle for the application of MBRs is the rapid decline of the membrane use efficiency due to membrane fouling. Frequent chemical cleaning reduces membrane life and increases operation cost (Orantes et al., 2006).

Strategies to reduce fouling include pre-treatment (coagulation, adsorption), careful membrane material selection and operational parameters optimization. Kim et al. (1998) showed that the direct addition of powdered activated carbon into the submerged MBR could reduce the content of extracellular polymeric substances (EPS) in flocs, thus led to a higher flux. Lee et al. (2001) found that the particle size of sludge flocs increased by the flocculation effect of Al$^{3+}$ and thus decreased the cake resistance. Recently, calcium has been widely investigated to mitigate the fouling problem in membrane systems. Kim and Jang (2006) indicated that a higher concentration of calcium is beneficial to membrane fouling. The reduction in the cake layer resistance was assumed to be due to the decrease of filamentous bacteria, and a better flocculation caused by the calcium bridges and the increased hydrophobicity of EPS during the operation under optimum conditions. Arabi and Nakhla (2008) concluded that the lower membrane fouling rate in the calcium fed MBR at an optimum concentration can be attributed to cationic bridges with EPS in flocs. The reduction in membrane permeability at high calcium concentrations contributed to a significant inorganic fouling.

This study aimed to study the effect of calcium dosage on the characteristics of mixed liquor and the structure of the cake layer as well as the relationship between them. The study was also conducted to further probe the potential mechanism of calcium mitigating the fouling.

1 Materials and methods

1.1 Operation of membrane bioreactor
The study consists of two parts, the long-term and short-term experiments. The long-term one was operated with constant flux under practical operation condition of MBR. The aim of the long-term experiment is to investigate the effect of calcium dosage on various constituents of the activated sludge in MBR. During the operation, additional membrane module was used to determine the influence of biomass characteristics on membrane fouling in different periods.

The MBR was operated with a gravitational filtration mode, which generated a constant transmembrane pressure ($P_{TM}$) in the short-term experiment. The membrane module was driven continuously with a fixed water head drop (WHD), $\Delta H = 92 \pm 0.5$ cm. The mode of constant TMP is necessary for the research on membrane fouling, because it can provide more information. A polyethylene hollow fiber membrane module with a total area of 0.2 m² and a normal pore size of 0.1 µm (Daiki, Japan) was used in the MBR.

As shown in Fig. 1, the experimental system basically consisted of two submerged activated sludge bioreactors (MBR-A, MBR-B), which were operated under two calcium dosages of 168.5, 27 mg/L, respectively. Higgins and Novak (1997) reported that when the sum ratio of the monovalent cation (Na⁺, NH₄⁺ and K⁺) concentrations to the divalent cation (Ca²⁺ and Mg²⁺) concentrations was greater than 2, flocc property deterioration would be caused. In this study, calcium concentrations of MBR-A and MBR-B were respectively determined at the ratio of 1.5 and 5.

The effective volume of the bioreactor was 12 L, hydraulic residence time (HRT) was maintained 10 h, and sludge residence time (SRT) was 30 d. The MBRs were operated continuously during the experiment, and were automatically controlled by a programmable logic controller (PLC). Filtration was intermittently performed by alternating 6 min of suction with a 2-min pause (idle time) in each 8 min cycle. Aeration intensity was 0.2 m³/h. Continuous aeration was provided through a perforated pipe from the bottom of the bioreactor to stir the mixed liquor and ensure the concentration of dissolved oxygen above 4 mg/L. Before one MBR start-up, the sludge was acclimatized by another. The MLSS concentration of activated sludge was adjusted to about 3000 mg/L with water prior to the membrane filtration. The feed water containing sucrose (400 mg/L), urea (76 mg/L) and dipotassium hydrogen phosphate (18 mg/L) was used for the activated sludge. Sodium bicarbonate (400 mg/L) was used as a buffer to adjust the mixed liquor pH to about 7.0.

1.2 Analytical methods

1.2.1 Evaluation of filtration resistance

Membrane resistance was evaluated by the resistance-inseries model as Eq. (1).

$$R_t = R_m + R_\phi + R_c = \frac{P_{TM}}{\mu J}$$  \hspace{1cm} (1)

where, $P_{TM}$ is trans-membrane pressure, $J$ is permeate flux, $\mu$ is viscosity of the mixed liquor. The experimental procedure to get each resistance value was as follows (Meng et al., 2008): (1) the resistance of membrane ($R_m$) was evaluated by measuring the flux of pure water; (2) the total resistance ($R_t$) was estimated by the final flux of sludge mixed liquor; (3) $R_m + R_\phi$ (pore blocking resistance) was measured after removing the cake layer by washing the membrane with tap water followed by filtration with pure water. $R_\phi$ was calculated from steps (1) and (3). Cake resistance ($R_c$) was obtained from steps (2) and (3) and related significantly to cake specific resistance and cake mass (Eq. (2)).

$$R_c = \alpha m_c$$  \hspace{1cm} (2)

where, $m_c$ is dry cake mass and $\alpha$ is specific resistance per unit cake mass, which varies with bulk matrix properties and $P_{TM}$. The study used an empirical formula to determine the relation between $P_{TM}$ and $\alpha$ (Chudacek and Fane, 1984) (Eq. (3)).

$$\alpha = \alpha_0 \times \Delta P_{TM}^n$$  \hspace{1cm} (3)

where, $\alpha_0$ is empirical constant that represents specific cake resistance in the absence of pressure difference, $n$ is coefficient of compressibility.

1.2.2 Soluble and colloidal COD analysis

Soluble and colloidal COD (COD₆, COD₇) was measured to determine the component that was mainly responsible for the flux reduction in sludge suspension (Park et al., 2005). Supernatant COD was determined after centrifuging the mixed liquor for 2 min at 3000 ×g. COD₆ was obtained after filtering the supernatant through a 0.22-µm membrane filter. The COD₇ was obtained by subtracting the COD₆ from the supernatant COD (Meng et al., 2008).

1.2.3 Bound EPS extraction and analysis

A physical extraction method was modified according to the method by Morgan et al., (1990) to extract loosely bound (LB)-EPS from the MBRs. A 25-mL sludge mixture was first dewatered by centrifugation in a 30-mL tube at 6000 ×g for 5 min. The supernatant was removed and the
sludge was re-suspended in 15 mL of 0.9% NaCl solution, and then it was treated by ultrasound for 2 min, shaking at 150 t/min for 10 min and ultrasound for 2 min again. After the final centrifugation in the 30 mL tube at 8000 ×g for 10 min, the organic matter in the supernatant was readily extractable EPS, and was regarded as the LB-EPS of the biomass.

For the extraction of the tightly bound (TB)-EPS, the heat extraction method was used. The sludge pellet left in centrifuge tube was re-suspended in 25 mL of 0.9% NaCl solution, and the sludge mixture was retreated by ultrasound for 3 min. Then the suspension was heated at 80°C in a water bath for 30 min. The sludge mixture was then centrifuged at 12000 ×g for 20 min. The supernatant was regarded as the TB-EPS extraction of the sludge. Both the LB-EPS and TB-EPS extractions were normalized as the sum of carbohydrate and protein, which were analyzed using phenol/sulfuric-acid method and modified Lowry method (Lowery et al., 1951), respectively.

1.2.4 Particle size analysis

The sludge particle size distributions of sludge suspension were determined using focused beam reflectance measurement (FBRM) (Model M400L, Lasentec, Redmond, USA).

1.2.5 Scanning electron microscope

The membrane surface was observed using a scanning electron microscope (SEM) (JEOL JSM-5600LV, Tokyo, Japan). Once the membrane filtration was stopped, a piece of membrane fiber was cut from the middle of the membrane module. The sample was fixed with 3.0% glutaraldehyde in 0.1 mol/L phosphate buffer at pH 7.2. The sample was dehydrated with ethanol, silver-coated by a sputter and observed in SEM.

1.2.6 Confocal scanning laser microscope analysis

The associated biopolymers attached to the membrane surface were observed using confocal scanning laser microscope analysis (CLSM) (Leica-TCS-SP2, Leica, Germany). Fluorescein isothiocyanate (FITC) was used to stain for gel layer of fouled membrane. After staining, the samples were washed gently with a phosphate buffer to remove unbound FITC. After that, the treated samples were immediately observed using CLSM.

1.2.7 Others

Dissolved oxygen (DO) concentration was measured by a DO meter (55/12 FT, YSI Corporation, USA). The mixed liquid of suspended solids (MLSS) concentration and mixed volatile liquid of suspended solids (MLVSS) concentration were evaluated according to standard methods (APHA, 1995)

2 Results and discussion

2.1 Behavior of membrane permeation

The running time of the experiment was 91 d. In the constant flux mode, $P_{TM}$ would increase during the filtration as a result of membrane fouling. When $P_{TM}$ was higher than 0.045 MPa, the membrane modules were taken out and flushed with water at a flow rate of 5–6 m/s to remove the fouling cake on the membrane surface, and then cleaned chemically using 0.03% NaClO solution. When the flux came back to more than 95% of initial level, the membrane modules were reloaded in the reactors. Since that, membrane fouling rate can be characterized by the frequency of membrane flushing.

The $P_{TM}$ variation in the reactors is shown in Fig. 2. The membrane module from MBR-B was cleaned 4 times at day 24, 45, 67, and 84 during the operation. The module from MBR-A was cleaned just twice at day 45 and 88. The two reactors were running under the same operation condition except the calcium dosage, therefore, it could be inferred that calcium addition to the MBR lowered the rate of membrane fouling.

During long-term experiment, the short-time experiment (at day 40) was carried out (Fig. 3). Obviously, the membrane fouling process could be roughly separated into three phases. In phase I, the pore blocking resistant played a major role in the sharp drop of the flux in the initial 20 min. In phases II and III, the formation of the
cake layer dominate in the membrane fouling process, presented as the slowdown of the flux decline and the flux gradual stability. The decline of membrane flux in short-term constant-pressure study is consistent with the division of membrane fouling process proposed by Bae and Tak (2005). As shown in Fig. 3, the flux decline rate in MBR-A was obviously less than that in MBR-B in the three phases, indicating that a proper dosage of calcium reduced the pore blocking resistant and the cake resistance effectively.

2.2 Evolution of biomass characteristics

2.2.1 Effect of calcium on particle size distributions

The sludge particle size distribution in the reactors was measured. From the result of the 40th day operation (Fig. 4), the particle size distribution of MBR-A was relatively narrow, and the mean size of MBR-A was always bigger than MBR-B. The mean particle sizes of the sludge samples in MBR-A and MBR-B were 54 and 26 µm, respectively. It can be considered that the sludge particle sizes increased and particle size distributions tended to be narrow with the proper addition of calcium.

Calcium played a major role in neutralization and bridging the carbohydrate and protein of the cell surface between flocs, and calcium ions could bridge negatively charged functional groups within the EPS, thus enhance the bio-flocculation. All these led to an increase of particle size. Bruss et al. (1992) also found that the extracted calcium from sludge lead to the increase of small particles, which would cause a significant flux drop. It was explained that calcium combined with EPS formed gels which were the backbone of floc structure. Calcium played a major role in particle size increasing, structure forming and stabilizing. The relative small particles be considered as a reason to induce membrane fouling, because they could become bigger particles with less fouling tendency due to the calcium.

2.2.2 Effect of calcium on EPS

EPS can come from natural secretions of bacteria, cell lysis and hydrolysis products, consisting of carbohydrate, protein, lipids, nucleic acids and so on. Based on the distribution position feature of EPS on cell, EPS can be classified as bound EPS and soluble EPS (Murthy and Novak, 1998).

Bound EPS are likely to have a dynamic double-layered structure, composed with LB-EPS and TB-EPS that surrounds the cells (Laspidou and Rittmann, 2002). Recently, many MBRs studies have identified EPS as the most significant biological factor responsible for membrane fouling, which led to a more serious membrane fouling with increasing content (Chang et al., 2002). This study will emphasize on the relationships between calcium dosage and EPS components and their effects on membrane fouling.

As shown in Figs. 5a and 5b, carbohydrate and protein concentrations of LB-EPS in MBR-A were less than MBR-B, and TB-EPS was in the same way. The decrease of carbohydrate and protein of LB-EPS were in the range of 53%–41%, while that of TB-EPS was in the range 18%–15.4%. The optimum dosage 168.5 mg/L of calcium was effective in decreasing the content of LB-EPS of microbial flocs, especially in carbohydrate.

TB-EPS are located on the surface of cells (Li and Yang, 2007). Various macromolecule are aggregated densely and combined strongly with cell wall, and are hard to exfoliate, which has little effect on characteristics of sludge. LB-EPS diffused from TB-EPS has a loose structure, low density, large volume, immovable form and definite rheology. The LB-EPS content had a close relationship with membrane fouling and plays a decisive role in the sludge characteristics, such as flocculation, sedimentation, surface electrification and viscosity. Calcium was effective in retarding the membrane fouling by decreasing LB-EPS content.

Janga et al. (2007) concluded that soluble EPS was a main component of soluble TOC or COD in effluent from biological treatment. High aeration could not remove membrane foulants from membrane surface effectively (Meng et al., 2008). Some studies have identified SMP as a reason for membrane fouling (Drews et al., 2007). From Fig. 5c, it also can be seen that the amount of SMP in MBR-A was always lower than MBR-B. The carbohydrate and protein of LB-EPS decrease 57.2% and 37.9%, respectively. The carbohydrate and protein of LB-EPS have the similar decreasing range to those of SMP, indicating that LB-EPS had more impact on SMP content.

2.2.3 Effect of calcium on colloidal and soluble COD

Previous study showed that colloidal particles and soluble organics in the activated sludge and liquid mixture had a significant correlation with membrane fouling (Rosenberger et al., 2007). The size of colloidal particles varied from nanometer to micron, and the molecular weight distribution of soluble organics had a range of 1000–10000 Da. These small particles and macromolecular organic compounds affected the membrane fouling by their deposition/adsorption on membrane surface and change of cake layer structure.
Fig. 5  Variation of concentration over time. (a) loosely bound extracellular polymeric substances (LB-EPS); (b) tightly bound extracellular polymeric substances (TB-EPS); (c) soluble microbial products (SMP).

The mixed liquor components of two MBRs were measured. As shown in Table 1, the content of COD$_C$ and COD$_S$ decreased significantly by adding proper amount of calcium. In this study, the amount of COD$_C$ and COD$_S$ of two MBRs was consistent with the content of EPS and the degree of membrane fouling, which was higher in MBR-B. The result confirmed that COD$_C$ and COD$_S$ had a positive correlation to membrane fouling, and the content variation of EPS was the fundamental reason causing content changes of COD$_C$ and COD$_S$. MBR-A had a lower EPS (especially LB-EPS) concentration in the sludge suspensions than MBR-B (Figs. 5a and 5b). According to literature (Liao et al., 2002), as LB-EPS content increasing the interaction between sludge particles became weak and they were sensitive to the external force and the change of environment, which would cause them broken easily. Thereby, the content of colloidal particles increased, and the membrane fouling accelerated as well. Calcium ion interacted with alkalinity and formed CaCO$_3$ which was known to increase the content of suspended solids (SS).

2.3 Effect of calcium on characteristics of cake layer

2.3.1 Effect of calcium on foulants components of cake layer

The constant-pressure filtration experiment was operated with a fixed water head drop. When short-term operation was terminated, the two membrane modules were taken out from the bioreactors and flushed with water. The SS, COD$_C$ and COD$_S$ of the washed liquid were analyzed to quantify the foulants accumulated on the membrane surface (Table 2). Together with Table 1, it can be seen that there was a similar changing tendency of COD$_C$ and COD$_S$ in the reactors, namely MBR-A < MBR-B. SS on the membrane surface in MBR-A was much less than that in MBR-B, which was different from components of sludge suspension, which means that the increase of SS concentration by adding calcium would not cause the increase of sludge suspension content on the membrane surface. Sludge particle size and sludge density were possible increased by calcium addition. The flocs became bigger so that they were easier to be removed from membrane surface to sludge suspension by shear stress which was generated by air bubbles.

2.3.2 Effect of calcium on characteristics of cake layer

Fouled membrane samples were taken at day 60, and analyzed by SEM. Two pieces of membrane were cut from the middle of the membrane module which was used in long-term experiment (Fig. 6). The membrane fouling was mostly attributed to pore blocking as well as the formation of a cake layer. The membrane pore blocking was serious in MBR-B (Fig. 6c), while the membrane surface of MBR-A (Fig. 6b) had obvious pores.

Table 1  Analysis results of the membrane foulants

<table>
<thead>
<tr>
<th></th>
<th>SS (mg/L)</th>
<th>COD$_C$ (mg/L)</th>
<th>COD$_S$ (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MBR-A</td>
<td>3842 ± 251 (n = 12)</td>
<td>17.67 ± 7 (n = 7)</td>
<td>32 ± 15 (n = 7)</td>
</tr>
<tr>
<td>MBR-B</td>
<td>3242 ± 379 (n = 12)</td>
<td>45.02 ± 15 (n = 7)</td>
<td>73 ± 24 (n = 7)</td>
</tr>
</tbody>
</table>

Data are expressed as mean ± S.D. n: numbers of measurements; SS: suspended solid; COD$_C$: colloidal COD; COD$_S$: soluble COD.

Table 2  Analysis results of the membrane foulants

<table>
<thead>
<tr>
<th></th>
<th>SS (mg/m$^2$)</th>
<th>COD$_C$ (mg/m$^2$)</th>
<th>COD$_S$ (mg/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MBR-A</td>
<td>24370 ± 2213</td>
<td>1215 ± 407</td>
<td>2742 ± 628</td>
</tr>
<tr>
<td>MBR-B</td>
<td>38719 ± 3200</td>
<td>3570 ± 395</td>
<td>5014 ± 1000</td>
</tr>
</tbody>
</table>

Data are expressed as mean ± S.D., the numbers of measurements are 6.
The membrane fouling resistance was measured by constant pressure filtration experiment at day 60 (Table 3). The ratios of the cake resistance to total resistance of MBR-A and B were 70.66% and 79.25%, respectively. It showed that the membrane filtration process of activated sludge was controlled by cake layer rather than membrane pore blocking resistance. The specific cake resistances of cake layer under the same pressure in the two MBRs were 2.48×10^{11} and 3.41×10^{11} m/g, respectively.

Zoogloea colonies are one of the main components of the solid matters in the active sludge. Because of their loose structure, sludge could be compressed during membrane filtration, and the resistance of the cake layer increased with the rise of the filtration pressure (Chong et al., 2008). Compressibility of the cake layer was measured by the coefficient of compressibility. In order to calculate the compressibility coefficient of cake, the relation graph of lnσ versus lnΔρ was performed and the compressibility coefficient of the two kinds cake layer was 0.65 and 0.91, respectively (Fig. 7). It indicated that the application of calcium was effective in decreasing the compressibility of the cake layer, thus its rigidity increased.

It was considered by integrated analysis that the addition of calcium resulted in the increase of both the sludge particle size and the porosity of cake layer. Furthermore, soluble organic matters and colloidal particles in the sludge suspension were reduced significantly by the optimum dosage of calcium, which not only reduced membrane pore blocking resistance, but also decreased the deposition/adsorption of soluble organic matters and colloidal particles on the cake layer. Thus, the rigidity of cake layer was enhanced and the specific cake resistance decreased. All of these have a contribution to the improvement of permeability.

2.4 Effect of calcium on characteristics of gel layer

Figure 8 shows the three-dimensional CLSM images of fouling cake formed on the membrane surface. In this way, it was possible to obtain the information about the morphology of the gel layer on the top of the membrane. Based on the images, it was apparently that the gel layer formed in MBR-A was more porous and thinner than that in MBR-B. The main composition of gel layer adhered to the surface of membrane was EPS produced from germ. From Section 2.2.2, we knew that optimum dosage of calcium was beneficial to decrease SMP and the thickness of gel layer.

2.5 Effect of calcium on inorganic fouling

The inorganic matter in the cake layer was analyzed by X-Ray fluorescence spectrometry. The major inorganic elements in the cake layer were P, Ca and S, followed by Cu, Fe, K, Zn, and Mg (Table 4). The biopolymers contain ionizable groups such as SO_{4}^{2−}, CO_{3}^{2−}, PO_{4}^{3−}, and OH− which with cations, such as Ca^{2+}, Mg^{2+}, Al^{3+}, and Fe^{3+}. In this experiment, the different dosage of metal ions in influent water led to the different content of inorganic matter in cake layer. Because calcium content in the cake layer of MBR-A was higher than that in MBR-B, inorganic fouling was not serious in MBR-A under this dosage. As shown by SEM image (Fig. 6), there was no obvious calcium fouling. The membrane modules were taken out and flushed with water to remove the fouling cake on the membrane surface, and then cleaned chemically using 0.03% sodium hypochlorite solution for 24 h. Under the suction pressure of 0.01 MPa, the pure water flux was measured. There was no obvious difference between the two MBRs, and membrane flux of tap water was 2.64×10^{−5} and 2.59×10^{−5} (m³/m²·s). The results showed that proper

![Fig. 6 SEM images of the surfaces of fouled membrane. (a) new membrane; (b) MBR-A; (c) MBR-B.](image-url)

### Table 3 Analysis results of membrane fouling resistances, cake mass, specific cake resistance

<table>
<thead>
<tr>
<th></th>
<th>R_m (10^{12} m⁻¹)</th>
<th>R_p (10^{12} m⁻¹)</th>
<th>R_c (10^{12} m⁻¹)</th>
<th>R_l (10^{12} m⁻¹)</th>
<th>m_c (g/m²)</th>
<th>α (10^{11} m/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MBR-A</td>
<td>1.1</td>
<td>1.4</td>
<td>6.02</td>
<td>8.52</td>
<td>24.32</td>
<td>2.48</td>
</tr>
<tr>
<td>MBR-B</td>
<td>1.05</td>
<td>2.7</td>
<td>14.32</td>
<td>18.07</td>
<td>42.05</td>
<td>3.41</td>
</tr>
</tbody>
</table>

### Table 4 Components of membrane foulants measured by X-Ray fluorescence spectrometry system (%)

<table>
<thead>
<tr>
<th></th>
<th>P_{2}O_{5}</th>
<th>CaO</th>
<th>SO_{3}</th>
<th>Cl</th>
<th>K_{2}O</th>
<th>CuO</th>
<th>ZnO</th>
<th>Fe_{2}O_{3}</th>
<th>MgO</th>
<th>Al_{2}O_{3}</th>
</tr>
</thead>
<tbody>
<tr>
<td>MBR-A</td>
<td>16</td>
<td>20.4</td>
<td>12.3</td>
<td>6.7</td>
<td>6.7</td>
<td>14.2</td>
<td>6.9</td>
<td>11.5</td>
<td>1.62</td>
<td>0.42</td>
</tr>
<tr>
<td>MBR-B</td>
<td>19.2</td>
<td>12.1</td>
<td>12.4</td>
<td>8.9</td>
<td>17</td>
<td>4.97</td>
<td>10</td>
<td>10.4</td>
<td>1.622</td>
<td>1.24</td>
</tr>
</tbody>
</table>
dosage of calcium would not cause inorganic fouling. The essence of inorganic fouling was that content of soluble inorganic salts exceeded the limit of solubility to form salt precipitation under concentration polarization. Therefore, controlling the dosage of calcium could effectively avoid membrane inorganic fouling.

3 Conclusions

This article presents a comparative and correlative study of the effect of calcium on membrane fouling. The membrane fouling mechanism investigated from two aspects: the characteristics of mixed liquor and the structure of cake layer. The following conclusions can be drawn based on the experimental results. (1) With the increase of calcium dosage, the sludge particle sizes increased and the particle size distributions tended to narrow within the experimental dosage range; (2) the optimum dosage of calcium had a significant impact on reducing the content of EPS, LB-EPS, SMP, and COD$_C$ and COD$_S$ of sludge suspension/membrane surface accordingly; (3) the cake layer formed by calcium-activated sludge particles had better rigidity than normal one. The compressibility coefficient of the cake layers from the MBRs with calcium dosage 168.5 and 27 mg/L was respectively attained as 0.65 and 0.91; (4) the appropriate amount of calcium was capable to slow down the membrane fouling rate and could not cause serious inorganic fouling.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (No. 50578024).

References


