Comparison of membrane fouling during short-term filtration of aerobic granular sludge and activated sludge

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Abstract

Aerobic granular sludge was cultivated adopting internal-circulate sequencing batch airlift reactor. The contradistinctive experiment about short-term membrane fouling between aerobic granular sludge system and activated sludge system were investigated. The membrane foulants was also characterized by Fourier transform infrared (FTIR) spectroscopy technique. The results showed that the aerobic granular sludge had excellent denitrification ability; the removal efficiency of TN could reach 90%. The aerobic granular sludge could alleviate membrane fouling effectively. The steady membrane flux of aerobic granular sludge was twice as much as that of activated sludge system. In addition, it was found that the aerobic granular sludge could result in severe membrane pore-blocking, however, the activated sludge could cause severe cake fouling. The major components of the foulants were identified as comprising of proteins and polysaccharide materials.

Key words: membrane bioreactor; membrane fouling; pore-blocking; cake layer resistance; aerobic granular sludge

Introduction

In recent years, membrane bioreactors (MBRs) have been used in wastewater treatment to achieve a higher effluent quality, which is often difficult to be effectively met by conventional activated sludge process. MBRs allow a high mixed liquor suspended solids (MLSS) concentrations, produce higher rate of removal of BOD and COD, a lower excess sludge production and the production of treated water can be reused (Yamamoto et al., 1989; van Dijk and Roncken, 1997). In addition, the space occupied by MBR systems is greatly reduced due to the absence of settling tanks and the reduction in bioreactor volume made possible by the higher biomass concentration. But a major obstacle for the application of MBRs is the rapid decline of the permeation flux as a result of membrane fouling (Drews et al., 2005, 2006; Meng et al., 2005a, 2006a; Le-Clech et al., 2006). The membrane fouling results in a reduction in productivity of MBRs and increase in maintenance and operational costs.

Aerobic granular sludge is the self-immobilized sludge under the aerobic condition. It not only contains more prolific microorganism, but also synchronizes the function of nitrification denitrification (Beun et al., 2002; Liu and Tay, 2004; Liu et al., 2005), while degrading the organic carbon. Moreover, it possesses the features of nice settleability, smooth microparticle, uniform morphology and large particle diameter. Therefore, aerobic granular sludge provides a new strategy for effectively controlling the membrane fouling (Li et al., 2005, 2007).

To date, most of related studies on membrane fouling focused on the membrane filtration of activated sludge suspension. Limited information is available regarding the filtration ability of aerobic granular sludge. In this work, a comparative study of membrane fouling during membrane filtration of activated sludge suspension and aerobic granular sludge was carried out to provide a new approach on the control of membrane fouling in MBRs. The treatment performance of aerobic granular sludge was investigated. The flux decline rate and fouling resistance of activated sludge system and aerobic granular sludge were compared, and the cake layer formed on the membrane surface was characterized by scanning electron microscopy and Fourier transform infrared (FTIR) spectroscopy technique.

1 Materials and methods

1.1 Experimental setup and feed water

The experiment adopts internal-circulation sequencing batch airlift reactor (SBAR) to cultivate aerobic granular sludge. The reactor height: 100 cm; total volume: 4 L; effective volume: 3.5 L. The vertical pipe diameter: 4 cm, height: 70 cm; the diameter of the outside sedimentation tube: 7 cm, height: 90 cm. The aeration is provided from the bottom of the reactor’s vertical pipe, air bubbles and granular sludge move up in the up-flow tube, and then enter...
the sedimentation tube from the top of the up-flow tube to form the circle. The reactor is shown in Fig. 1.

The feed water simulated municipal wastewater. COD 1000 mg/L, NH$_4$Cl 50 mg/L, KH$_2$PO$_4$ 40 mg/L, CaCl$_2$·2H$_2$O 31 mg/L, MgSO$_4$·7H$_2$O 94 mg/L, FeSO$_4$·7H$_2$O 22 mg/L. Add 1 ml microelement to per 1 L water; microelement: EDTA 15,000 mg/L; H$_2$BO$_3$ 14 mg/L; ZnSO$_4$·7H$_2$O 430 mg/L; CuSO$_4$·5H$_2$O 250 mg/L; NiCl$_2$ 199 mg/L; NH$_4$MoO$_4$·2H$_2$O 220 mg/L; Na$_2$SeO$_3$·5H$_2$O 210 mg/L and MnCl$_2$·4H$_2$O 990 mg/L.

The operation cycle was 282 min, including feed water entering: 5 min, aeration: 270 min, sediment: 5 min, draining: 2 min. The aeration was controlled at 0.15 m$^3$/h, and NaHCO$_3$ was added to the feed water to adjust reactor’s pH to about 7.0.

1.2 Short-term membrane filtration

To compare the membrane fouling under standardized conditions, the sludge suspension was filtered with a batch filtration unit. A hollow fiber membrane module made of polyethylene (Daiki, Japan) that had a total area of 0.1 m$^2$ and a normal pore size of 0.1 µm was used in the tests. In the batch filtration unit, the membrane module was submerged in 6 L of sludge suspension (activated sludge or aerobic granular sludge) with aeration, and membrane filtration was carried out by applying 9.81 kPa of transmembrane pressure with a water head drop (∆H = 100 cm). In this work, the MLSS concentration of each a sludge suspension was adjusted to 4500 mg/L with its permeate prior to the membrane filtration to exclude the effect of MLSS concentration on the permeate flux. The bioreactor was aerated at a flow rate of 0.20 m$^3$/h. The membrane permeate was recycled to the bioreactor. The temperature of the mixed liquor was controlled at 25.0°C with an electric heater. Filtration was continued for 240 min, which allowed the permeation flow rate to become stable.

To ensure that the condition and performance of the membrane module be the same in all experiments, post-cleaning was performed after every experiment to remove the fouling cake and the membrane module was immersed in 0.03% NaClO solution for 24 h to obtain a permeability recovery more than 96%.

1.3 Analysis of membrane resistance

According to Darcy law:

$$R_t = R_m + R_f = R_m + R_p + R_c = \frac{P_{TM}}{\mu \cdot J}$$  \hspace{1cm} (1)

$$R_f = R_p + R_c$$  \hspace{1cm} (2)

where, $R_t$ is the total hydraulic resistance, $R_m$ is the membrane resistance, $R_f$ is the membrane fouling resistance, $R_p$ is the pore blocking resistance, $R_c$ is the cake layer resistance, $P_{TM}$ is the transmembrane pressure, $\mu$ is the dynamic viscosity and $J$ is the membrane flux. The experimental procedure to determine each resistance value was as follows (Lee et al., 2001; Meng et al., 2005b, 2006b): (1) $R_m$ was estimated by measuring the water flux of de-ionized water; (2) $R_t$ was evaluated by the final flux of biomass microfiltration; (3) the membrane surface was then flushed with water and cleaned with a sponge to remove the cake layer. Then, the deionized water flux was measured again to obtain the resistance of $R_m + R_p$. The pore blocking resistance ($R_p$) was calculated from steps (1) and (3) and the cake resistance ($R_c$) calculated from steps (2) and (3). It must be pointed that flushing with tap water only removed reversible foulants, indicating that $R_p$ can also be used to characterize the irreversible fouling.

Cake resistance is significantly related to cake specific resistance and cake mass:

$$R_c = \alpha m_c$$  \hspace{1cm} (3)

where, $m_c$ is the dry cake mass, $\alpha$ is the specific resistance per unit cake mass, which varies with the bulk matrix properties and transmembrane pressure ($P_{TM}$). In this article, as the membrane filtration was terminated, the membrane module was taken out and flushed with tap water. The suspended solids content of the washed liquid was used to characterize the cake mass.

1.4 SEM and FT-IR analysis

The fouled membrane was observed with the help of a scanning electron microscope (SEM) (KYKY-2800B, Beijing, China). After 4 h, the filtration was terminated and 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 buffers at pH 7.2. The sample was dehydrated with ethanol, silver-coated by a sputter and observed in the SEM.

The fouled membrane module was taken out from the bioreactor and flushed with pure water as the operation of the MBR was terminated. About 200 ml washed liquid was taken and placed in a dryer at 105°C for 24 h to obtain dry foulants. The component of the membrane foulants was characterized by infrared spectrum analysis (EQUINOX55, Buluke, Germany).

1.5 Determination

The analysis methods of COD, ammonia nitrogen (NH$_4$N), total nitrogen (TN) and suspended solids concentration
of the washed liquid are based on the standard methods (APHA, 1995).

2 Results and discussion

2.1 Characteristics of aerobic granular sludge

After the reaction operating for two weeks, it appeared a great deal of the exiguous granule in the reactor, which means the successful inoculation of the granular sludge. After a steady operation for 45 d, it appeared the microscopically exiguous granules in the reactor, and the sludge sedimentation has been improved obviously. Fig.2a shows the granule size distribution, most of granule diameter was in the range $\leq 1.0$ mm, however, there were still a few of the sludge floc existing in the reactor. At the same time, aerobic granular sludge is spherical or elliptical with smooth surface (Figs.2b and 2c).

As the granular sludge was inoculated, the SBAR could reach a stability performance on nutrient removal. The reactor of SBAR could obtain a low effluent COD as the influent COD was 500–700 mg/L; the removal rate of COD reached more than 95% (Fig.3a). The removal rate of ammonia nitrogen reached more than 90%. The ammonia nitrogen concentration of the effluent was below 10 mg/L, which is shown in Fig.3b, while the phosphorous concentration of the effluent was below 1 mg/L. The TN removal rate could achieve more than 90%. These results indicate that the aerobic granular sludge in SBAR system could remove the COD and nitrogen simultaneously.

A sequencing batch airlift reactor, in which aerobic granular sludge (Beun et al., 2001), regular biofilm (Arnold et al., 2000) or flocculated activated sludge (Pochana and Keller, 1999) can be grown, is a suitable system for simultaneous COD and nitrogen removal (simultaneous nitrification denitrification, SND) (Wang et al., 2005; Ruan et al., 2006). Special circumstances, depending on floc, biofilm or granules size, oxygen concentration and COD/N ratio, can lead to a substrate-rich aggregate with an oxygen-free zone in the interior (diffusion limitation of oxygen), in which denitrification takes place. Because of the size and structure of granules and biofilms, SND can be maintained and controlled more easily in these aggregates than in activated sludge system. With the maturation of the aerobic granular sludge, the removal rate of the organic matter also is improved. As the granule diameter of the aerobic granular sludge increases, it forms a certain anaerobic area in the inner part of the granule, which will improve the denitrification process. Therefore the TN removal rate can be improved.

2.2 Comparison of membrane fouling

In order to investigate the prospective of aerobic granular sludge on membrane fouling control, the filterability of aerobic granular sludge and the conventional activated sludge were studied on the basis of short-term membrane filtration. In the case of activity sludge suspension, the membrane flux was declined rapidly as soon as the membrane filtration was started (Fig.4). Within 15 min, the flux declined 50%, and the final flux after the experiment was 21.00 L/(m$^2 \cdot $h). While in the case of the aerobic granular sludge, the decline of membrane flux was relatively slow and the final flux after the experiment was 40.44 L/(m$^2 \cdot $h), which is twice more than that of the activated sludge system. This result obtained from short-term membrane filtration indicates that the aerobic granular sludge could control the membrane fouling significantly.

The SEM images of the fouled fiber membrane show that the cake layer formed on the membrane surface is very dense with respect to activated sludge system (Fig.5b), and there were a great deal of sludge floc on the membrane surface. These indicate that in the activated sludge suspension the sludge floc had a stronger tendency...
to deposit on the membrane surface than did the granular sludge. While with respect to the aerobic granular sludge system, the cake layer formed on the membrane surface was relatively more porous and there were lots of the pore canals (Fig. 5a). This is the reason why the activated sludge system could result in a more severe decline of membrane flux than aerobic granular sludge. But after the hydraulic cleaning of the fouled membrane, the pore-blocking in the aerobic granular sludge system was much more severe than that in the activated sludge system (Figs. 5c and 5d).

The Carman-Kozeny equation provides an important implication that the smaller particles deposited on the membrane surface (or in the cake layer) would generate greater specific resistance (Bai and Leow, 2002), and the specific resistance of the cake layer has a close relationship with particle size. The specific resistance, $r_c$, may be estimated from the Carman-Kozeny equation as (Chellam and Wiesner, 1998):

$$r_c = \frac{180C_c^2}{d^2(1 - C_c)^3}$$

where, $d$ is the mean particle diameter. For poly-dispersed particles, $d$ may be replaced by an equivalent diameter. $C_c$ is the solid concentration or solidity of the cake in volume percentage. Eq.(4) indicates that the cake layer permeability will be increased as the sludge particle size increased.

In Table 1, the cake resistance, pore blocking resistance, cake mass and specific resistances were evaluated, respectively. With respect to the aerobic granular sludge, $R_p$ was 44.2% of the membrane total resistance, which was more than $R_c$ proportion (34.7%). This result shows that in this system the membrane pore resistance is the main factor of the membrane fouling. While with respect to the activated sludge system, $R_c$ was 72.68% of the membrane total resistance, which was far more than the $R_p$ proportion (16.56%), suggesting that in the activated sludge system cake layer resistance is the predominant factor influencing the membrane fouling.

Table 1 also shows that the cake layer formed by activated sludge had a higher specific resistance ($4.91 \times 10^{13} \text{ m/kg}$) than the cake layer formed by granular sludge ($1.60 \times 10^{13} \text{ m/kg}$). This further indicates that cake layer resistance is the major factor of the membrane fouling during membrane filtration of activated sludge suspension. This phenomenon can be explained by the Carman-Kozeny equation that mentioned above.

After hydraulic cleaning the membrane flux of granular sludge system was 90 L/(m$^2$·h), which recovered 46.58%. While after hydraulic cleaning the membrane flux of activated sludge system was 126 L/(m$^2$·h), which recovered 65.22%. The low recovery of membrane flux after hydraulic cleaning in aerobic granular sludge suggests that the granular sludge could result in a more severe irreversible membrane fouling than the activated sludge.
However, we must point out that the result reported here just reflects the short-term membrane fouling behavior, it can not reflect the long-term operation of MBRs. The reversibility of membrane fouling by activated sludge or granular sludge is a significant parameter during the operation of an MBR (Defrance and Jaffrin, 1999). The reversibility of membrane fouling has strong relation with TMP, initial membrane flux, and biomass characteristics. In this paper, the difference of the reversibility of the two sludge system resulted from the biomass characteristics, so a further study will be carried out to explain this phenomenon.

SEM images in Figs.5c and 5d indicate that with respect to granular sludge system the membrane surface still had a severe pore blocking after hydraulic cleaning. With respect to activated sludge system, however, there were significant membrane pores after hydraulic cleaning. The result indicates that the irreversible membrane fouling was mainly resulted from the deposition of small particles or soluble matter into the membrane pores.

2.3 Analysis of membrane foulants

To testify the deposition behavior of EPS on the membrane surface, the membrane foulants was analyzed by FT-IR in this study. The result in Fig.6 shows that the substance structure of the two membrane foulants formed by activated sludge and granular sludge was similar to each other. The absorption of 3600 and 3000 cm\(^{-1}\) indicates the existing of O–H functional group; at 2926 cm\(^{-1}\), the absorption peak is C–H functional group (Kumar et al., 2006). As shown in Fig.6, there are two peaks at 1652 cm\(^{-1}\) and 1540 cm\(^{-1}\) in the spectrum unique to the protein secondary structure, called amides I and II (Maruyama et al., 2001). The peaks of 1385 cm\(^{-1}\) and 1235 cm\(^{-1}\) imply the presence of amide III. This result indicates that there were proteins in the membrane foulants. The broad peak of 1065 cm\(^{-1}\) is a peak due to polysaccharide or polysaccharide-like substances (Kimura et al., 2005). By the FT-IR spectra, the major components of the foulants were identified as proteins and polysaccharides materials. Proteins and carbohydrates which are the dominant components typically found in extracellular polymeric substances (EPS).

It also can be seen from Fig.6 that the intensity of membrane foulants formed with granular sludge system was stronger than that of activated sludge system, indicating that the relative content of EPS in total membrane foulants formed with granular sludge was higher than that formed with activated sludge. In the case of granular sludge system, there were large granular, colloids and solutes; however, the activated sludge suspension consisted of sludge flocs, colloids and solutes. So, the membrane foulants formed with granular sludge mainly consisted of colloids and solutes due to the high back transport of granular. With respect to activated sludge system, sludge flocs could deposit onto the membrane surface. As soon as sludge flocs deposited onto the membrane surface, the membrane foulants such as EPS, soluble organics, colloidal particles and so on, could be rejected or biodegrade by the cake layer composed of living microorganisms. Thus, the EPS had fewer chances to deposit on the membrane surface. Therefore, the relative content of EPS in the membrane foulants formed with granular sludge was higher. This is the reason why the granular sludge could result in severe pore-blocking and irreversible membrane fouling.

3 Conclusions

The aerobic granular sludge had a high ability of COD removal and nitrogen. SND occurred during react, and complete nitrification was achieved.

The aerobic granular sludge could mitigate membrane fouling significantly during short-term membrane filtration. After the short-term membrane filtration, the flux could reach twice of that in the activated sludge system. In the activated sludge system, \( R_c \) attributed 72.66% to the membrane total resistance, and the main membrane resistance is the cake layer resistance. While in the aerobic granular sludge system, \( R_p \) is 44.2% of the membrane total resistance, which is higher than \( R_c \) proportion. Therefore, the membrane fouling in the aerobic granular sludge was mainly due to the membrane pore-blocking during membrane filtration of granular sludge.

After hydraulic cleaning of the fouled fiber membrane, the recovery degree of the membrane flux in the aerobic granular sludge system was smaller than that in the activated sludge system. The aerobic granular sludge could result in severe irreversible membrane fouling.
References


