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Membrane fouling caused by soluble microbial products in an activated sludge system under starvation

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ABSTRACT

The behavior of soluble microbial products (SMP) and effects of SMP on membrane fouling under starvation of an activated sludge were studied. During a 16-day period, the experiment was investigated without nutrient addition to the closed system. Dissolved organic carbon (DOC) and molecular weight (MW) distributions of bulk solution were periodically monitored. The dead-end filtration tests were used to indicate the SMP effect on membrane fouling. Furthermore, the modified fouling index (MFI) was used to investigate the gel layer resistance of bulk solution closely related with the SMP. At last, an important increase in the concentrations of SMP with MW >10 kDa in the reactor was observed, which may be related to the cellular component degradation from endogenous metabolism. The gel layer resistance was observed to make the highest contribution to flux decline. Specially, the MFI is directly related to the concentration of high MW fraction. The SMP with MW >10 kDa was found to being strongly correlated with the MFI.

Keywords: Soluble microbial products; Membrane bioreactor; Molecular weight distributions; Modified fouling index; Gel layer resistance

1. Introduction

Membrane bioreactor (MBR) technology is a steadily growing wastewater treatment solution capable of generating high-quality effluent by retaining solids and soluble microbial products (SMP) [1]. Compared to the conventional activated sludge process, an MBR system has many advantages with respect to superior nutrient and organic removals, a high loading rate capability, low sludge production and small footprint [2]. However, membranes are prone to fouling from interactions between the membrane and the mixed liquor [3]. Membrane fouling significantly reduces membrane life, overall membrane performance and increases operating costs [4]. In the MBR process, SMP in the supernatant and extracellular polymeric substances (EPS) in the sludge suspension had been proposed as the main fouling factors [5,6].

EPS are of a biological origin and consist of non-soluble materials, which bind to active cells and perform a bridging among the cells [7]. Therefore, the EPS are also called bound EPS in previous study [8] whereas SMP are soluble cellular components, such as soluble macromolecules, colloids and slimes, which are produced by EPS release, cell lysis, hydrolysis products, and so on [6]. Although the influence of dissolved matter has been studied for a decade, the concept of SMP fouling in the MBR is relatively new as no report on SMP levels existed for MBR prior to 2001 [9]. During filtration, SMP adsorb on the membrane surface, block membrane pores and/or form a gel structure on the membrane surface [10]. In the previous studies [11-13], it was found that SMP demonstrated considerable influence on membrane permeate flux.

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Presently, the MBR has drawn special attention to the research field of zero discharge of activated sludge. A MBR in this operation mode is supposed to run at a very low F/M ratio (below 0.1 gCOD/gVSS·d), which subsequently leads to great reducing of sludge production [14, 15]. The operation at infinite SRT may lead bacteria to be in starvation and microorganisms respond to this by acceleration of endogenous respiration, accompanied with the release of organic cellular constituents (such as SMP) by secretion and cells autolysis. Simultaneously, SMP are released into the liquid phase and accumulated in MBR, which might induce the serious membrane fouling [16]. Since membranes are exposed directly to SMP in the bulk phase, portion of SMP have a greater influence on membrane fouling than the EPS fraction [17].

As stated above, many studies on membrane fouling in MBR have been carried out, but there have been few studies focused on the influence of SMP on membrane fouling under starvation. In order to examine the behavior of the SMP produced by microorganisms under nutrient deficiency, dissolved organic carbon (DOC) and MW distributions of SMP were periodically observed in closed equipment. The dead-end filtration test was used to indicate the effect of the SMP on membrane fouling. Furthermore, the modified fouling index (MFI) was utilized to investigate the relationship between membrane biofouling and SMP.

2. Material and methods

2.1. Experimental system and operation

Fig. 1 shows the schematic diagram of the experimental set-up used in this study. A 12 L glass jar was employed; 10 L of washed activated sludge was transferred into the glass jar to start up the experiment. Activated sludge was taken from a pilot MBR located in the Tianjin University municipal wastewater treatment plant, Tianjin, China. The WWTP was operated at an *F/M* ratio in the range of 0.3 to 1.5 kgCOD/kgVSS·d, and the SRT was maintained at 90 days. In order to remove the SMP from the activated sludge mixture, the activated sludge was washed as follow: (1) the activated sludge was settling for 2 h, (2) the supernatant was discharged, and then the biomass was re-suspended with de-ionized (DI) water. Such washing of activated sludge process was repeated three times.

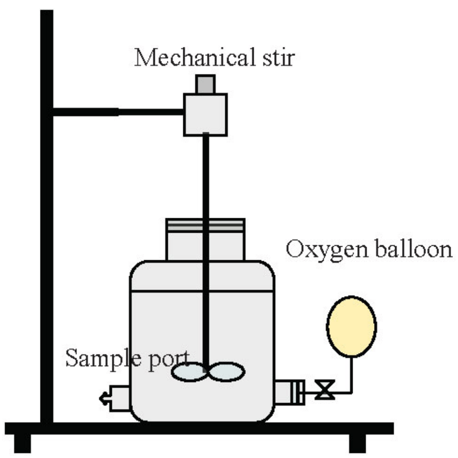

Fig. 1. Schematic of the experimental set-up.

To minimize the evaporation, the reactor was sealed with a large rubber stopper. Mechanical stirring was performed in order to mix well. An oxygen balloon was used to provide O_2 for microorganisms.

2.2. Filtration tests

Batch filtration tests were conducted to test the fouling characteristics of bulk solution using Amicon 8400 dead-end stirred cells (Millipore, USA). The cells have a volume of 350 ml and an effective membrane filtration area of 45.3 cm^2. All experiments were carried out at room temperature and constant pressure of 1.0 bar. The permeation flux was determined by weighing permeates on an electronic top loading balance connected to a personal computer equipped with an auto-reading program. A new flat sheet membrane (polyethersulfone, hydrophilic) with a pore size of 0.2 μm was used for each test.

When stirring speed was regulated at 180 rpm, the fouling resistance was estimated by following Darcy's equation:

$$R_t = R_m + R_p + R_c = \frac{\Delta P}{\mu J} \quad (1)$$

where R_t is the total membrane resistance (m^{-1}), R_m is the intrinsic membrane resistance (m^{-1}), R_p is the pore blocking resistance (m^{-1}), R_c is the gel layer resistance (m^{-1}), ΔP is the applied transmembrane pressure (kPa), μ is the dynamic viscosity of permeate (Pa s) and J is the membrane flux ($L/m^2 \cdot h$). The experimental procedure to get each resistance value was taken from Meng et al. [18].

Without stirring, MFI is analyzed from the plot of t/V vs. V using a general cake filtration equation at constant pressure [19]. MFI is defined as the gradient of the linear region found in the linear relationship between t/V and V:

$$\frac{t}{V} = \frac{\mu R_m}{\Delta P} + \frac{\mu \alpha C}{2\Delta P} V \quad (2)$$

$$MFI = \frac{\mu \alpha C}{2\Delta P} \quad (3)$$

Table 1
Characteristics of the activated sludge used in this study

Parameter	Raw	After washing
MLSS (mg/L)	6310	6203
MLVSS (mg/L)	4227	4095
DOC (mg/L)	95.3	0.8
pH	7.26	7.03

where t is the filtration time (s), V is the permeate volume per unit filtration area (m), α is the specific resistance (m/kg) and C is macromolecules concentration in bulk solution (mg/L).

2.3. Analytical items and methods

Analytical methods based on "Standard methods for the examination of water and wastewater" were adopted for MLSS and MLVSS [20] and pH was determined using a pH meter (Satoris PP15). The bulk solution was obtained by centrifuging the mixed liquor at 4000 rpm for 10 min, followed by filtration through a 0.45 µm membrane. The characteristics of the sludge before and after washing for this study are presented in Table 1. Soluble samples were used for fractionation using stirred cell ultrafiltration (UF) membranes (Millipore USA). Four UF membranes with pore size of 100, 10, 3 and 1 kDa were used and the DOC concentration were measured in series with the highest MW cutoff at first and the lowest at last. DOC was determined using a TOC analyzer (TOC-V, Shimadzu, Kyoto, Japan).

3. Results and discussion

3.1. Evolution of SMP concentration and MW distribution in bulk solution

In this research, the SMP was removed completely based on the procedures of experimental system and operation before the experiment. Thus, during the test, if any SMP was determined, it was believed to be produced by activated sludge.

The evolution of the SMP concentration in the system was monitored through determination of dissolved organic carbon (DOC) (as shown in Fig. 2). Three phases were observed distinctly. The first phase, day 1 through day 5 of the experiment, DOC increased slowly from 5.3 to 18.5 mg/L. From day 5 to day 11, DOC increased rapidly and reached highest value of 80.5 mg/L at the day 11, probably due to the lack of organic material in the reactor which resulted in the death of microorganisms. Subsequently, a large leakage of organic compounds from cell into bulk solution contributed to the increase in SMP production. In the last phase, a slow decrease of DOC occurred, which may indicate that some of organic compounds produced in the previous phases were biodegradable and available for their metabolism.

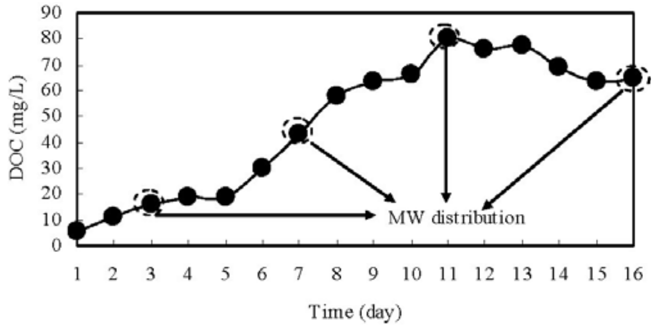

Fig. 2. Evolution of the SMP concentration against operation time (16 days).

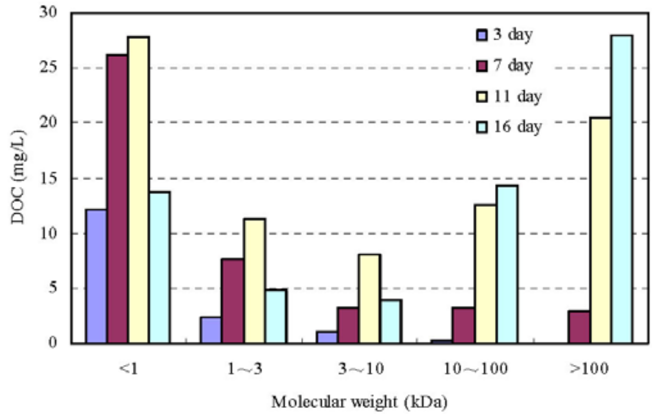

Fig. 3. MW distribution in bulk solution at day 3, 7, 11 and 16.

In order to examine the component of SMP, the MW distributions of the typical points in Fig. 2 were tested and the corresponding MW distributions are presented in Fig. 3. It was shown that at day 3 or day 7, DOC with lower MW (<1 kDa) was predominant. The MW distribution at day 11 or day 16 exhibited a bimodal shape with a minimum in the 3 kDa to 10 kDa, and a maximum in the <1 kDa or >100 kDa fraction. The high MW products at day 16 were much more than others. Compared with day 3, the concentrations of MW fraction in the bulk solution at day 16 were increased from 0 to 28 mg/L (>100 kDa), 0.3 to 14.4 mg/L (10–100 kDa), 1.0 to 4.0 mg/L (3–10 kDa), 2.3 to 4.9 mg/L (1–3 kDa), 12.1 to 13.7 mg/L (<1 kDa), respectively. Especially there was an obvious increase in the concentrations of SMP with MW >10 kDa from day 3 to day 16. The result is consistent with other research results [12].

3.2. Membrane fouling by SMP

Biofouling due to bacteria and their SMP is a significant problem in MBR. The SMP plays an important role

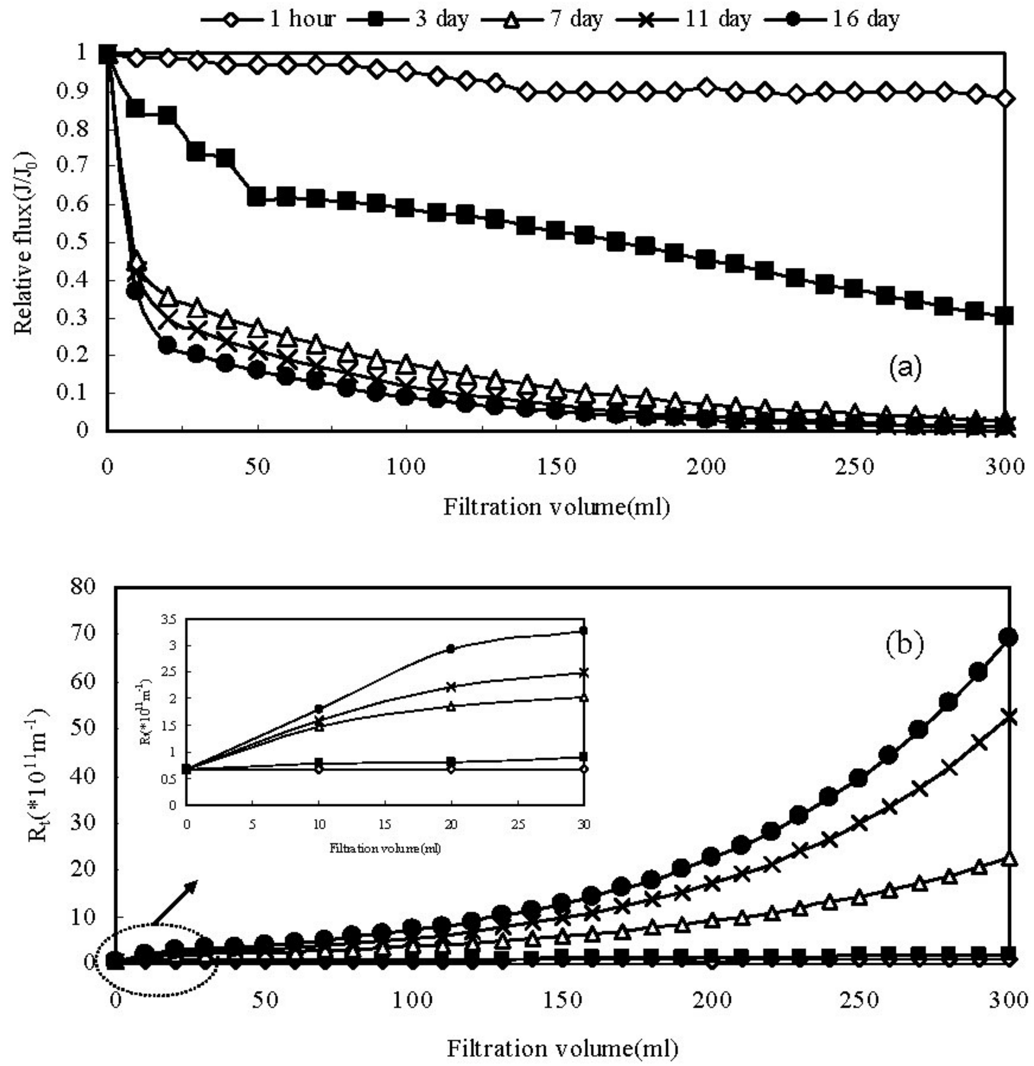

Fig. 4. Variations during the filtration of bulk solution. (a) Relative flux; (b) resistances (ΔP: 1.0 bar; stirring rate: 180 rpm; temperature: 20±2).

with respect to membrane fouling [2]. It has been reported that 52% of the total resistance was attributable to the soluble constituents [13].

A ratio of permeate flux to initial water flux, J/J_0, was plotted in Fig. 4a as a function to compensate for the difference in initial water flux (J_0) because the initial water flux of different membranes was different. Fig. 4a shows that the relative flux declined with filtration volume markedly at day 3, 7, 11 or 16. Especially, under the filtration volume of 300 ml, the J/J_0 was correspondingly 0.303, 0.030, 0.012 or 0.009 on the relevant day. The filtration resistances according to the relative filtrate volume are shown in Fig. 4b. It was obvious that the filtration resistances increased at day 7, 11 or 16. These results implied that excess accumulation of SMP in starvation had significant effect on membrane fouling. Due to the release of SMP by secretion and cells autolysis, flux reduction and resistance increase were very remarkable. For the slow back transport velocity of SMP, SMP could strongly deposit onto the membrane surface by permeation drag and be difficult to be detached by stirring [21]. Therefore, a secondary membrane or a gel layer formed on the surface of the primary membrane and controlled the filtration process.

A series of resistances, calculated from bulk solution filtration when filtration volume was 300 ml, are presented in Table 2. The R_p increased obviously from day 7, indicating that irreversible fouling of membranes was caused by SMP during the experiment processing. The gel resistance (R_c) was observed to make the highest contribution for total resistance (R_t). In particular, at day 7, 11 or 16, R_c/R_t was more than 87%. Thus, it could be concluded that gel layer formation was the main fouling mechanism.

Table 2
A series of resistances during the microfiltration of samples in different time

Time	Item (%)			
	R_m ($\times10^{11}$ m^{-1})	R_p ($\times10^{11}$ m^{-1})	R_c ($\times10^{11}$ m^{-1})	R_t ($\times10^{11}$ m^{-1})
Day 3	0.73 (33.18)	0.56 (25.43)	0.91 (41.39)	2.20 (100)
Day 7	0.75 (3.35)	2.07 (9.23)	19.56 (87.42)	22.38 (100)
Day 11	0.75 (1.43)	5.17 (9.85)	46.59 (88.72)	52.51 (100)
Day 16	0.75 (1.08)	5.42 (7.82)	63.15 (91.10)	69.32 (100)

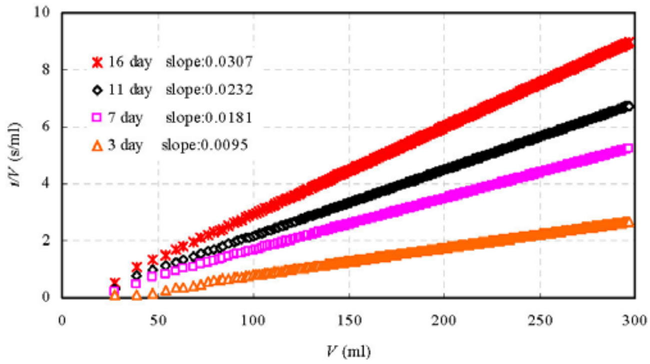

Fig. 5. Evolution of t/V vs. V.

As mentioned above, R_t became higher with the concentration of SMP increasing at day 3, 7 or 11. It seems that the higher SMP concentration results in the faster membrane fouling proceeds [22]. However, the concentration of SMP at day 16 was lower 15 mg/L than that at day 11, but the R_t at day 16 increased by 16.81×10^{11}m^{-1} than that at day 11.

To investigate the correlation between membrane fouling and SMP, MFI was applied in this study. MFI has been widely used to describe the fouling behavior by a single parameter [23]. Fig. 5 shows the corresponding lines of t/V vs. filtration volume. Slopes of the plot of t/V vs. V are the relevant MFI. In consequence of the declining performance of the filtration process with increasing of filtration volume, the corresponding increase of the linear slope was caused by an increase of membrane resistance. A higher MFI resulted in a higher fouling rate.

Fig. 6 shows the correlations between MFI and the concentrations of SMP or the concentrations of the MW fraction. MFI was positive correlation with the SMP concentration with a correlation coefficient of 0.681. However, the SMP with higher MW were found to have strong correlation with the MFI. And the MFI was found to be best related to 10–100 kDa (R^2 = 0.8813, Fig. 6e) or >100 kDa (R^2 = 0.8837, Fig. 6f) among all SMP fractions.

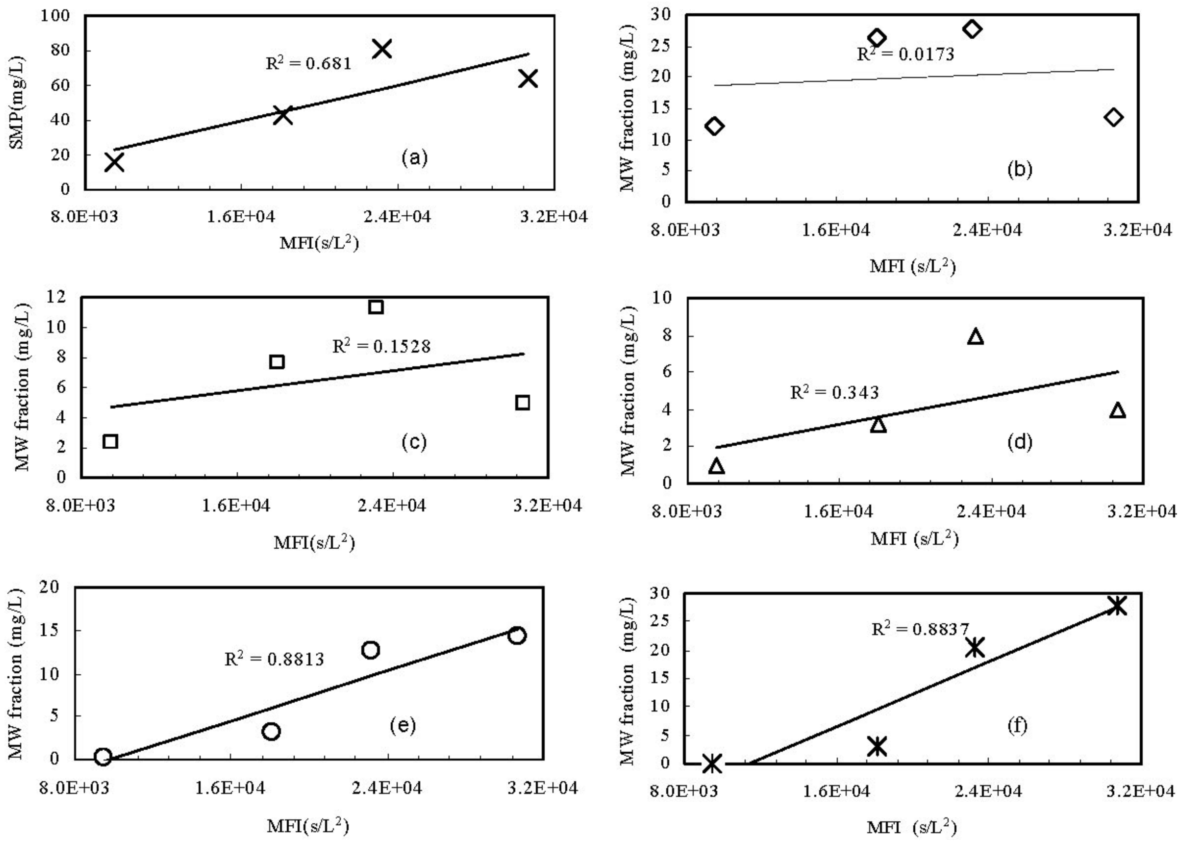

Fig. 6. Correlations between MFI and the concentrations of SMP or the concentrations of MW fraction: (a) SMP; (b) <1 kDa; (c) 1–3 kDa; (d) 3–10 kDa; (e) 10–100 kDa; (f) >100 kDa.

The concentration of MW fraction (<1, 1–3 or 3–10 kDa) have an insignificant impact on MFI (Fig. 6b–6d). This implied that membrane fouling was directly related to the concentration of SMP with high MW fraction. During filtration of SMP with high MW fraction, membrane pores were rapidly blocked by pore adsorption, causing more organics captured and accumulated on the membrane. However, the low molecular SMP, which are smaller than the MF membrane pores, can penetrate membrane pores easily.

4. Conclusions

The main objective of this study was to evaluate the SMP effect on membrane fouling under starvation. The experimental results can be summarized as follows:

1. During nutrient deficiency, microorganisms would utilize some SMP. However, large leakage of organic compounds from cell lysis led to prominent increase of the SMP concentration. An important increase of the concentrations of SMP with MW >10 kDa in the reactor was observed.

2. Accumulated SMP caused the significant membrane fouling under starvation. The gel layer resistance (R_c) was observed to make the highest contribution for total resistance (R_t).

3. MFI had a positive correlation with the SMP concentration. The SMP with higher MW was found to have strong correlation with the MFI. Consequently, it was concluded that in MBR system membrane fouling had a great affinity to the SMP with MW >10 kDa.

4. The procedure of this study for SMP under starvation might provide a means of assessing fouling mechanisms, which should be a feasible method to evaluate the effect of SMP on membrane fouling in MBR system.

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