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Characteristics of soluble microbial products in membrane bioreactor and its effect on membrane fouling☆

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ABSTRACT

In this study, the accumulation and characteristics of soluble microbial products (SMP) in the mixed liquor and the effluent of the membrane bioreactor (MBR) were measured and compared. It was found that the concentration of SMP decreased when the SRT was increased from 10 days to 30 days, and then stabilized as SRT was increased to 60 days. The molecular weight (MW) distributions of SMP indicated that the SMP of larger MW (>30 kDa) was the most abundant fraction in the MBR. The similar MW distributions of SMP in the mixed liquor and effluent implied that membrane fouling due to SMP in the initial slow fouling stage was not due to size sieving. After the MBR was operated for a period of time, only the SMP of relatively large MW (>30 kDa) was detected in the mixed liquor. The result indicated that size sieving of SMP occurred only after a cake layer was formed on the membrane surface although the effect was not significant and only worked on larger molecules. The accumulation of hydrophilic components of SMP in the mixed liquor of the bioreactor suggested that the hydrophilic fraction (in carbohydrates) could be the major cause for membrane fouling.

1. Introduction

Membrane bioreactors are being increasingly implemented to treat and reuse wastewater due to the many advantages over conventional activated sludge processes, including excellent effluent quality, small footprint, less sludge production, flexibility of operation, and the like [1]. However, membrane fouling which results in decreasing throughput and increasing frequency of membrane cleaning hampers the widespread application of MBRs. Many studies have been devoted to exam the mechanisms of fouling and mitigation of fouling in MBRs [1–3]. Despite such intensive efforts, there has not been a consistent conclusion on the cause of MBR fouling [4–10], which may be due to the complication of mixed liquor and influent, different membrane modules and different operation conditions implemented in studies. However, most studies have confirmed that extracellular polymeric substances (EPS) are important foulants in MBRs, in which polysaccharides in SMP were found the main factor affecting MBR fouling [8–10].

EPS are complex mixture of macromolecular polyelectrolytes including polysaccharides, protein, nucleic acids, and humic compounds. EPS are generally subdivided into two categories: (1) bound EPS (sheaths, capsular polymers, condensed gel, loosely bound polymers, and attached organic material) and (2) soluble EPS (soluble macromolecules, colloids, and slimes) [11]. According to Laspidou and Rittmann [11], soluble EPS are the same as soluble microbial products (SMP). SMP are defined as the pool of organic compounds that are released into solution from substrate metabolism and biomass decay [12]. SMP have been classified into utilization associated products (UAP) and biomass associated products (BAC) based on bacterial phase. SMP are mainly composed of polysaccharides, proteins, humic acids and the like although the exact composition is still not well-known. Process parameters such as hydraulic retention time (HRT), sludge retention time (SRT), organic loading rate, feed strength, substrate type, biomass concentration, temperature and reactor type affect the production of SMP [12]. Although EPS or SMP are mostly mentioned when regarding to MBR fouling, most studies correlate the quantity of EPS or SMP with fouling rate. Little information about the relationship of characteristics and components of SMP and MBR fouling is available.

Molecular weight distribution of SMP in MBR process was found to shift from larger MWCO to smaller MWCO due to the decomposition of larger molecular weight SMP by microorganisms [13,14]. Recently, it has been found that the accumulation of SMP was more pronounced in the bioreactor at shorter SRT and the molecular weight distribution of SMP was almost identical in the supernatant and effluent [15]. The study has suggested that the hydrophilic neutrals were most likely the main foulants in MBRs. Therefore, it can be concluded that not only the quantity of SMP but also the characteristics of SMP are the key factor in MBR fouling.

The objective of this research is to evaluate the effect of characteristics and components of SMP on membrane fouling in MBRs. SMPs were separated into fractions of different MW by the use of a series of ultrafiltration membranes. The SMPs were also categorized by difference

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in hydrophobicity by the use of XAD-8 and XAD-4 resins. SMP in mixed liquor and effluent were analyzed and compared to elucidate their effect on membrane fouling.

2. Materials and methods

The laboratory-scale submerged membrane bioreactor system was comprised of a 30-L aerated tank with two flat sheet membranes (type 203, Kubota Corporation, Japan). The flat sheet membrane had a nominal pore size of 0.4 μm and surface area of 0.1 m^2. The reactor was seeded with activated sludge from the wastewater treatment plant in National Chiao Tung University, Taiwan. The synthetic feed was prepared to simulate the municipal wastewater and the composition was as follows: sodium acetate: 210.58 mg/L; starch: 12.5 mg/L; beef extract: 20.83 mg/L; NH_4Cl: 55.83 mg/L; KH_2PO_4: 12.83 mg/L; $MgSO_4 \cdot 7H_2O$: 29.58 mg/L; CaCl2: 6.08 mg/L; $FeSO_4 \cdot 7H_2O$: 7.25 mg/L; $CuCl_2 \cdot 2H_2O$: 0.03 mg/L; $MnCl_2 \cdot 4H_2O$: 0.05 mg/L; $ZnSO_4 \cdot 7H_2O$: 0.06 mg/L; $CoCl_2 \cdot 6H_2O$: 0.01 mg/L; $Na_2MoO_4 \cdot 2H_2O$: 0.01 mg/L; H_3BO_3: 0.01 mg/L and KI: 0.01 mg/L. The imposed flux was maintained at 16 L/m^2 h and the HRT was 8.6 h. The SRT of the MBR was experimented at 10, 30 and 60 days and the mixed liquid suspended solids (MLSS) was around 3000 mg/L. Hydrochloric acid was used to maintain a pH of 7.2.

To obtain the soluble samples in the bioreactor, the MLSS was centrifuged at 4000 rpm for 10 min at 4 °C followed by the filtration through 0.45 μm filter paper. The filtrate was defined as the soluble fraction in the bioreactor. The soluble fraction of the MBR effluent was directly obtained from the effluent of the MBR. The soluble samples were fractionated by molecular weight using ultrafiltration membranes (Pellicon XL, Millipore, USA). The soluble samples were categorized into four groups: >30, 10–30, 5–10 and <5 kDa. The XAD-8 and XAD-4 resins were used in series to separate the organic matters of the soluble samples into hydrophobic, hydrophilic and transphilic fractions [16].

Total organic carbon (TOC) measured by a TOC analyzer (TOC-5000A, Shimadzu, Japan) represents the total amount of SMP in the soluble sample. A phenol–sulfuric acid method [17] with glucose as the standard was used to quantify polysaccharides. Protein was measured by the use of the Bradford protein assay (Bradford, Sigma) according to the manufacturer's protocol with Bovine Serum Albumin (BSA, Sigma) as the standard.

3. Results and discussion

3.1. SMP at different SRTs

It has been reported that the concentration of SMP decreased as the SRT increased [15,18], and higher fouling potential was found in shorter SRT. In this study the MBR was operated at 10, 30 and 60 days separately. The result showed that the SMP in mixed liquor decreased from around 17 mg/L to 4 mg/L when the SRT was switched from 10 days to 30 days, which was in agreement with previous studies. However, when the SRT was further increased to 60 days, the SMP in the mixed liquor still remained at around 4 mg/L, similar to those at SRT 30 (as shown in Fig. 1.) The transmembrane pressure (TMP) profile showed the order of fouling rate: SRT 10 > SRT 30 > SRT 60 (data not shown here.) Similar study by Liang et al., in which the SRT was up to 40 days, has shown a result conflicting to ours [15]. However, Pollice et al. has shown that the SMP in the mixed liquor decreased as the SRT was lengthened from 4, 10, 16, 22, and 30 days to infinite [18]. Therefore, further investigations are needed to evaluate the production of SMP at various SRTs especially when the SRT is longer than 40 days without wastage. In our study, the SMP of effluents remained between 2 and 3 mg TOC/L regardless of the SRT.

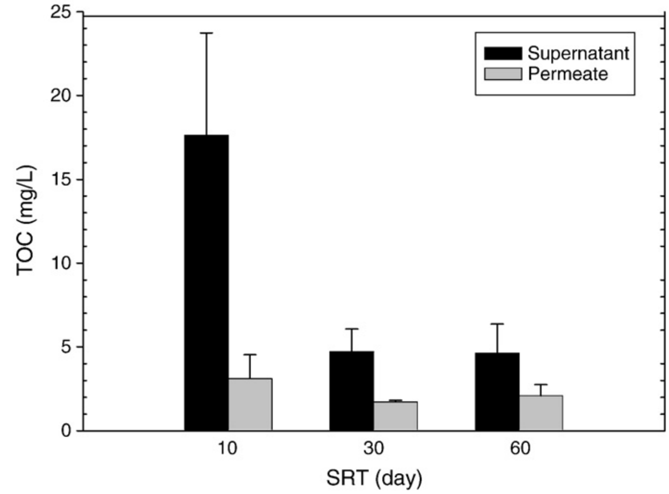

Fig. 1. Concentrations of SMP in mixed liquor and effluent at different SRTs.

3.2. Molecular weight distribution of SMP in mixed liquor and effluent

The MW distribution of the SMP in mixed liquor and effluent after clean membranes was operated for 10 min is shown in Fig. 2(a). Fig. 2(b)

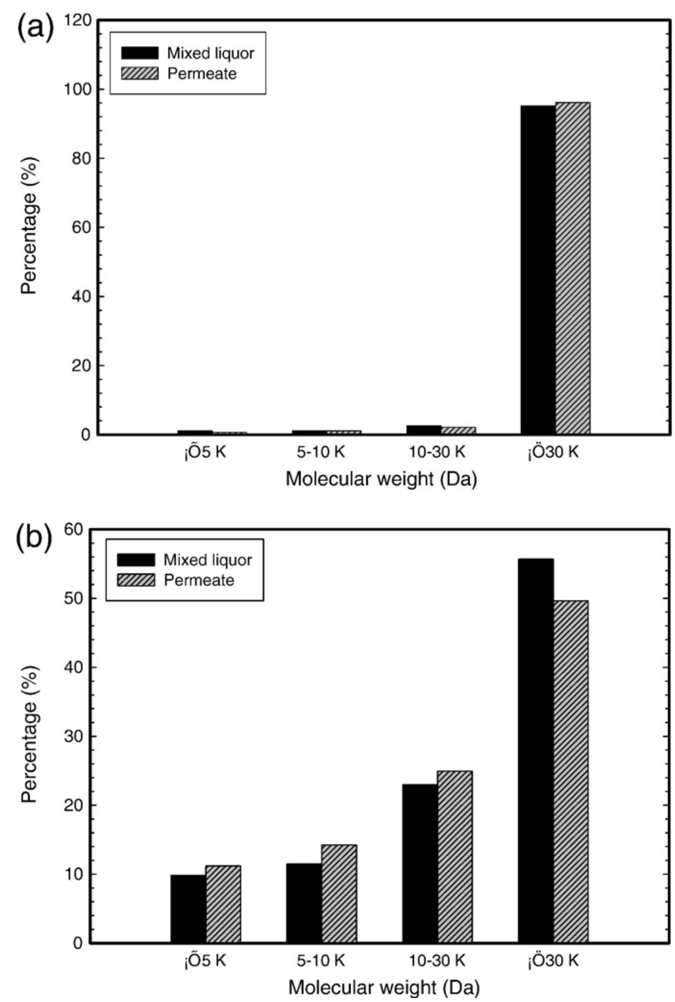

Fig. 2. Molecular weight distribution of the SMP in mixed liquor and effluents at SRT 10 (a) at the beginning of the membrane filtration (TMP at −4 kPa); and (b) after an extended period of fouling (TMP at −27 kPa).

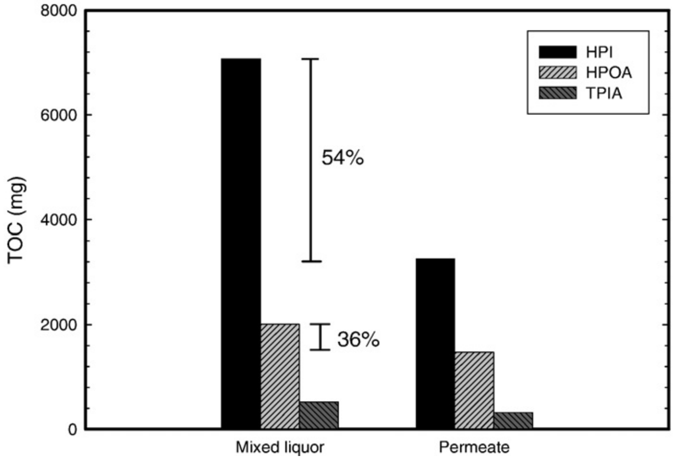

Fig. 3. Distribution of SMP fractions by hydrophilicity in the mixed liquor and effluent at SRT 10 (HPI: hydrophilic fraction; HPOA: hydrophobic acids; TPIA: transphilic acids).

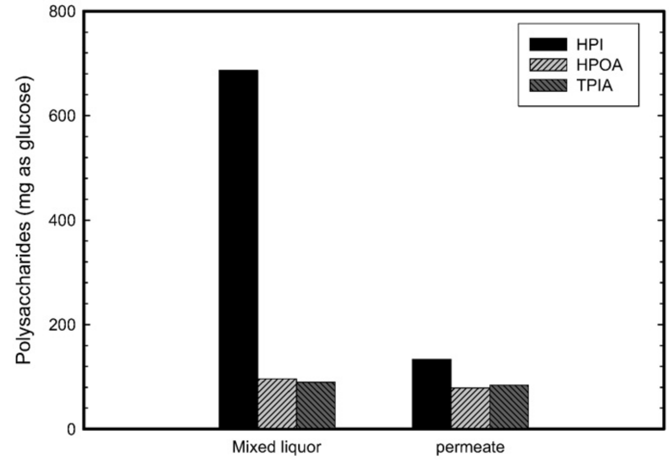

Fig. 4. Fractionation of polysaccharides by hydrophobicity in the mixed liquor and effluent at SRT 10.

illustrates the MW distribution of the SMP in mixed liquor and effluent when the membranes were operated for a period of time when serious fouling in the MBR occurred. The diagram shows that large MW (>30 kDa) comprises the largest fraction, which contradicts to other studies. MW distribution of SMP showed a bimodal pattern in other studies [15,19]. This could be due to the difference in method of separation, feed characteristics, and operation condition. In the beginning of the operation, similar MW distribution pattern was found in the SMP of the mixed liquor and effluent. It implied that SMP membrane sieving could not be retained on the membrane in the beginning of the operation, and that there must be other mechanisms responsible for membrane fouling in the initial stage of membrane operation. When TMP increased as the cake layer (hydrodynamic membrane) was formed on membrane surface, the SMP larger than 30 kDa in the mixed liquor was 5% higher than in the effluent. The small reduction might be owing to the formation of hydrodynamic membrane on membrane surface, resulting in the accumulation of SMP in MBRs. Microfiltration membranes (0.4 μm) used in this study were much larger than the MW of SMP, and, therefore, membrane sieving was not the answer.

3.3. Hydrophobic characteristics of SMP in mixed liquor and effluent

Distribution of SMP fractions by hydrophilicity is shown in Fig. 3. The hydrophilic fraction of SMP was the most abundant fraction in MBR at SRT 10, which disagreed with the observation by Liang et al. [15] possibly due to the difference in feed characteristic and operational condition. Fig. 3 also showed that 54% of hydrophilic fraction accumulated in mixed liquor and 36% of hydrophobic fraction accumulated in mixed liquor. The result implied that hydrophilic fraction had more significant effect on SMP accumulation in the MBR. Hydrophobic interaction is generally considered important mechanism regarding to fouling [20]. However, since less hydrophobic SMP accumulated in the mixed liquor, hydrophobic interaction does not appear to be the major fouling mechanisms of SMP in our study. SMP are mainly composed of carbohydrates and proteins. Proteins are more hydrophobic than carbohydrates [14]. Distributions of polysaccharide fractions by hydrophobicity in the mixed liquor and effluent at SRT 10 are shown in Fig. 4. It clearly demonstrates that carbohydrates are dominated by hydrophilic characteristics in the mixed liquor. Therefore, it is concluded that the hydrophilic fraction of carbohydrates in SMP is most likely the main foulants for the MBR, which was consistent with the result of Liang et al. [15].

4. Conclusions

The concentration of SMP decreases with the increased SRT (from 10 days to 30 days) in MBR operation. Prolonged SRT (60 days) shows identical SMP concentration with SRT 30. SMP of MW larger than 30 kDa is the most abundant fraction at SRT 10. When membranes are not seriously fouled, membrane sieving has little effect on SMP MW distribution. Membrane fouling is related to the reduction of SMP larger than 30 kDa in the effluent, which is due to the retention of large SMP by the formed cake layer. Hydrophilic fraction is the dominant species in SMP, which accumulates in the mixed liquor. Hydrophilic carbohydrates are most likely the major foulants in the MBR.

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