Membrane fouling reduction and improvement of sludge characteristics by bioflocculant addition in submerged membrane bioreactor

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ABSTRACT

The effectiveness of a green bioflocculant (Gemfloc®) on enhanced performance of a submerged membrane bioreactor (SMBR) was evaluated in terms of membrane fouling reduction and sludge characterization. Two MBRs were operated parallelly in this study, namely conventional MBR (CMBR) and MBR with Gemfloc® addition (MBR-G). Results showed mitigated membrane fouling through Gemfloc® addition in terms of cake layer formation and pore blocking. When compared to the CMBR, in spite of more extracellular polymeric substances (EPS) presented in activated sludge, the MBR-G demonstrated less soluble microbial products (SMP), larger sludge flocs, higher zeta potential and greater relative hydrophobicity of sludge flocs, which decreased cake layer resistance and pore blocking resistance. The reduced cake layer resistance in the MBR-G could be also ascribed to less growth of suspended biomass, lower sludge viscosity, as well as less EPS, SMP and biopolymer clusters in the cake layer. In addition, a modified resistance-in-series model was employed by considering SMP and mixed liquor suspended solids. The simulated results implied that the model could predict the influence of sludge characteristics on membrane fouling behavior of the SMBR.

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1. Introduction

Membrane bioreactor (MBR) has become an innovative and promising option for treatment and reuse of municipal, industrial wastewater and landfill leachate due to its distinct advantages (i.e., high effluent quality, small footprint, low sludge production) over the conventional activated sludge process [1–3]. However, membrane fouling is a long-lasting and inevitable issue along its development, which increases the hydraulic resistance to fluid flow, resulting in less permeability for constant pressure mode or transmembrane pressure increment for constant flux mode [4]. So far, numerous studies have been devoted to the mechanism and causes of membrane fouling and control strategies. Among six principal fouling mechanisms, biofouling has attracted a significant concern as it is a major cause of fouling in MBRs. Biofouling occurs through deposition and accumulation of undesirable microorganisms and bacterial cells or flocs at membrane surface [5,6]. It can lead to cake layer formation, which has been found to be the main contributor to total membrane resistance [4,5,7]. For a given MBR, biofouling and membrane filterability as well as cake layer formation are directly associated with sludge characteristics, such as mixed liquor suspended solid (MLSS) concentration, sludge viscosity, floc size, extracellular polymeric substances (EPS), soluble microbial products (SMP) and biopolymer clusters (BPC).

Currently, much more efforts have focused on addition of flocculants (e.g. inorganic flocculants, organic synthetic polymer flocculants and naturally occurring biopolymer flocculants) to MBRs for membrane fouling alleviation by modifying the characteristics of mixed liquor and cake layer. Table 1 summarizes the main factors affecting membrane fouling reduction in batch tests and short-term dead or cross-flow filtration tests. Studies on membrane fouling mitigation in terms of adding flocculants directly into submerged MBR have been investigated. Guo et al. [8] investigated the impacts of flocculants addition on the short-term performance of a submerged MBR. They reported that more stable sludge

Table 1
Flocculant addition induced membrane fouling reduction in batch tests and short-term dead end or cross-flow filtration tests.

Factors for membrane fouling reduction[a]	Flocculants[b]	References
Increasing EPS and decreasing SMP in mixed liquor	MPL30, MPE50, KD452, Poly-1 (Nalco®), Poly-2 (France Chitin®), CPE; PAM, Chitosan, Starch, CGMS, PAM–MGMS; Al₂(SO₄)₃, FeCl₃, PAC, PFS	[9,14,16,17,19,20]
Enlarging floc size	MPL30, MPE50, KD452, Poly-1 (Nalco®), Poly-2 (France Chitin®), CPE; PAM, Chitosan, Starch, CGMS, PAM–MGMS; FeCl₃, PAC	[9,14,16–20]
Enhancing charge neutralization	MPL30, MPE50, KD452, CPE; Al₂(SO₄)₃, FeCl₃, PAC, PFS	[14,16,17,19,20]
Increasing sludge hydrophobicity	CPE; Al₂(SO₄)₃, FeCl₃, PAC, PFS	[14,16,17]
Reducing gel layer and forming more porous and high permeable cake structures on membrane surface	CPE, Poly-1 (Nalco®); Chitosan	[16,18,20]

[a] EPS = extracellular polymeric substances, SMP = soluble microbial products.
[b] CGMS = modified corn starch, CPE = organic cationic polyelectrolyte, MGMS = modified corn starch, PAM = polyacrylamide, PAC = polyaluminium chloride, PFS = polymeric ferric sulfate.

volume indexes and higher specific oxygen uptake rates were obtained by adding natural organic flocculants such as chitosan, while inorganic flocculants (e.g. FeCl₃, polyaluminium chloride (PACl)) reduced SMP as well as lowered membrane fouling rates. Long-term filtration experiments were conducted by Iversen et al. [9] to investigate the effect of cationic polymers (NALCO MPE50, ADIPAP KD 452) and starch (TATE & LYLE Mylbond 168) on the performance of a pilot-scale plant. The results suggested that two cationic polymers could mitigate membrane fouling, while starch addition led to more serious fouling phenomena. Wu and Huang [10] reported that addition of polymeric ferric sulfate (PFS) could decrease the formation rate of gel layer on membrane surface due to the removal of high molecular weight organics, thereby retarding membrane fouling in long-term operation of the MBR system. Moreover, PFS also increased sludge floc size by supplying positive charges for organic particles and enhancing charge neutralization. PFS addition did not induce direct deposition of exotic Fe and severe inorganic fouling on membrane surface. For organic flocculants, submerged MBR with MPE50 addition exhibited significant improvement of the sustainable flux and membrane fouling reduction [11]. A more recent study conducted by Zhang at al. [12] mentioned that the addition of organic flocculant (MPE50) was an effective approach to membrane fouling control at high salt shock due to increase in floc size, relative hydrophobicity and bound EPS (especially proteins). Additionally, combined flocculants have also been exploited recently. A new combined inorganic–organic flocculant (CIOF) of FeCl₃ and MPE50 prepared by Nguyen et al. [13] was added to an aerated submerged MBR. The results indicated that the CIOF was successful in alleviating membrane fouling while maintaining stable SVI and low transmembrane pressure (TMP) development rate. Ji et al. [14] investigated the performance of modified starch (MGMS) and its polyacrylamide–starch composite flocculant (PAM–MGMS) on fouling minimization for submerged MBRs. It was shown that the flocculant had long effect duration on reducing SMP concentration, as well as prolonged the decrease in floc size due to irreversible breakage of aggregates (de-flocculation) caused by continuous shear stress in MBR and the degradation of the modified starches.

Although above-mentioned flocculants have their own merits for membrane fouling reduction, the development of a safe biodegradable natural flocculant is essential in order to have less impact on the environment and produce less 'secondary pollutants' through wastewater reclamation and reuse processes. Ngo and Guo [15] developed a new green bioflocculant (GBF) which was modified from a natural starch-based cationic flocculant (HYDRA Ltd., Hungary). It was found that GBF could significantly reduce membrane fouling (TMP increment of 2.5 kPa after 70 days of operation) and energy consumption (less backwash frequency) of a conventional submerged MBR. Based on this research, Gemfloc® was patented by University of Technology, Sydney (UTS). However, membrane fouling behavior related to sludge properties by Gemfloc® addition has not been well understood and explored yet. Therefore, in this study, the effectiveness of Gemfloc® on fouling reduction in the lab-scale submerged MBR under long-term sustainable operation was evaluated. Furthermore, fouling reduction through modifying the characteristics of mixed liquor as well as cake layer were also investigated in terms of SMP, EPS, BPC, zeta potential, apparent viscosity, relative hydrophobicity (RH), and floc size.

2. Materials and methods

2.1. Wastewater

Both MBRs were fed with synthetic wastewater simulating primarily treated domestic wastewater. The synthetic wastewater contains glucose, ammonium sulfate and potassium dihydrogen orthophosphate, which provides a continuous source of pollutants. Dissolved organic carbon (DOC), chemical oxygen demand (COD), ammonium nitrogen (NH₄-N), and orthophosphate of synthetic wastewater were 100–130 mg/L, 330–360 mg/L, 12–15 mg/L, and 3.3–3.5 mg/L, respectively. Sodium hydrogen carbonate or sulfuric acid was employed to adjust pH to 7.

2.2. Experimental setup and operating conditions

Two submerged MBRs with identical effective working volumes of 8 L, namely MBR-G (MBR with Gemfloc® addition) and CMBR (control MBR), were operated in parallel. A hollow fiber membrane module (polyvinylidene fluoride (PVDF), pore size 0.2 μm, surface area 0.1 m²) was submerged into each MBR. Activated sludge collected from a local Wastewater Treatment Plant was added into both MBRs, and synthetic wastewater was used for acclimatization afterward. During the operation period, no sludge withdrawal was performed (infinite SRT) except sampling activated sludge for analysis. Gemfloc® was supplied to the MBR-G at a dosage of 1 g/day (net weight). A feeding pump consistently delivered synthetic wastewater into both MBRs. Permeate through the submerged membrane module was withdrawn continuously and maintained at a constant flux of 12 L/m² h using a suction pump, corresponding to a HRT of 6.67 h. Membrane fouling was monitored by measuring TMP using a pressure gauge. 9–10 L/min air was supplied using a soaker hose air diffuser at the bottom of the reactor. During the experiment, the membrane was only backwashed two times/day with duration of 2 min/time by pumping a fraction of permeate back through the membrane module at a flow rate of 36 L/m² h. When TMP reached 35 kPa, the filtration experiments were stopped, and the membrane modules were taken out from the MBRs thereafter. Chemical cleaning was conducted by immersing each tested membrane in 0.5% citric acid for 6 h, followed by 0.4% sodium hydroxide for 6 h and 0.8% sodium hypochlorite for 6 h.

2.3. Analysis methods

The Analytikjena Multi N/C 2000 was used to measure DOC of the influent and effluent. COD, mixed liquor suspended solids (MLSS), and mixed liquor volatile suspended solids (MLVSS) were analyzed according to Standard Methods [21]. NH_4-N, NO_3-N, NO_2-N and PO_4-P analyses were conducted following photometric method called Spectroquant® Cell Test (NOVA 60, Merck).

The membrane module was taken from the bioreactor when the filtration was stopped. Cake layer on the membrane surface was removed and collected using a brush. Subsequently, the removed cake layer was dissolved in 100 mL of distilled water for foulant analysis. The cake layer and mixed liquor were extracted and analyzed with regard to EPS and SMP based on the methods as demonstrated in our previous study [23]. BPC were obtained by following the method proposed by Sun et al. [24]. In this study, the extracted samples were normalized as the sum of proteins (EPS_P, SMP_P, BPC_P) and polysaccharides (EPS_C, SMP_C, BPC_C). Proteins were determined according to modified Lowry method (Sigma, Australia), while polysaccharides analyses were made based on Anthrone–sulfuric acid method [25].

A rotational viscosity meter (Brookfield Viscometer M/OO-151-E0808, Brookfield, USA) was used to measure the apparent viscosity of mixed liquor. The zeta potential of mixed liquor was analyzed with a zeta potential meter (Zetasizer Nano ZS, Malvern Instruments, UK). The method reported by Deng et al. [23] and Ji et al. [17] was applied to determine the relative hydrophobicity (RH) of sludge flocs. Particle size distribution of sludge flocs was determined by analyzing the images obtained by the Olympus System Microscope Model BX41 (Olympus, Japan) with Image-Pro Plus software. The Microsoft Excel software was used for membrane fouling modeling.

2.4. Filtration characteristics

Membrane filtration characteristics were analyzed using the resistance-in-series model as follows [22]:

$$J = \Delta P / \mu R \tag{1}$$

where J is the permeate flux; ΔP is the TMP; μ is the viscosity of the permeate.

Total fouling resistance comprised three main components, which was expressed as:

$$R_T = R_M + R_C + R_P \tag{2}$$

where R_T is the total resistance; R_M is the intrinsic membrane resistance, which came from membrane itself; R_C is the cake resistance induced by accumulation of sludge particles on membrane surface; and R_P is the pore blocking resistance caused by adsorption of dissolved matters and colloids with size close to pore size of the membrane inside/onto the membrane [5,6].

The measurement protocol of filtration resistances was shown as follows: (1) R_M was obtained by distilled water with a cleaned membrane before MBR operation; (2) at the end of MBR operation, R_T was determined by distilled water with a fouled membrane; (3) the filtration resistance obtained after removing cake layer on membrane surface yielded $R_M + R_P$. Thus, R_C was calculated from Eq. (2) by subtracting $R_M + R_P$ from R_T. R_P was given by deducting R_M from $R_M + R_P$.

3. Results and discussion

3.1. The performance of the MBR-G and the CMBR

Organic removal efficiencies for the MBR-G and the CMBR averaged 90% or more. More specifically, the MBR-G achieved

96.04 ± 6.33% and 95.36 ± 5.62% of DOC and COD removal, respectively, while lower removal efficiencies of DOC and COD were obtained for the CMBR (94.23 ± 7.69% and 92.76 ± 6.86%, respectively). It indicated that the addition of bioflocculants could improve organic matter removal.

In terms of nutrient removal, the MBR-G showed higher PO_4-P removal (90.12 ± 8.76%) than those of the CMBR (68.75 ± 6.98%) over the entire period of operation, suggesting that PO_4-P removal could be enhanced by enrichment of the activated sludge system with phosphorus accumulating organisms (PAOs) and biomass metabolism due to Gemfloc® addition [13,15]. Similar NH_4-N removal was found for the MBR-G (87.41 ± 7.52%) and the CMBR (86.41 ± 9.63%), indicating that both MBRs exhibited high degree of biological nitrification as nitrifying bacteria was retained during membrane filtration process at infinite sludge retention time [26]. Moreover, the MBR-G achieved higher T-N removal of 75.56 ± 6.72%, while only 32.45 ± 8.35% of T-N was reduced in the CMBR during the operation period. It was attributed to the fact that larger flocs obtained in the MBR-G (see Section 3.3) promoted the denitrification process inside the biomass due to oxygen gradient existing within the flocs [13].

TMP profile depicting fouling propensity for two MBRs is shown in Fig. 1. It was observed that the TMP of the CMBR developed gradually with a sudden jump on day 50 and then reached maximum operation pressure of 35.0 kPa on day 64, implying the requirement of chemical cleaning. Regarding membrane fouling rate, an initial rate of 0.160 kPa/d before 50 days followed by a higher rate of 1.679 kPa/d were obtained. On the other hand, the TMP of the MBR-G only increased from 3.5 to 9.5 kPa within the 75-day filtration period, indicating a fairly low fouling rate of 0.067 kPa/d. The results suggested that Gemfloc® could effectively alleviate membrane fouling in the MBR-G for long-term operation as well as improve filterability. As both MBRs were operated under similar feed characteristics, membrane materials, module configurations and operational conditions, the differences in fouling propensity between the CMBR and the MBR-G were mainly ascribed to the characteristics of mixed liquor and cake layer, which are further discussed in Section 3.5.

3.2. Mixed liquor suspended solids (MLSS) concentration, mixed liquor volatile suspended solids (MLVSS) and apparent viscosity

In this study, the concentrations of initial biomass were 5.00 and 5.04 g/L in the CMBR and the MBR-G, respectively. A consistently increasing trend of MLSS and MLVSS concentrations was observed in the CMBR and the MBR-G without sludge waste during
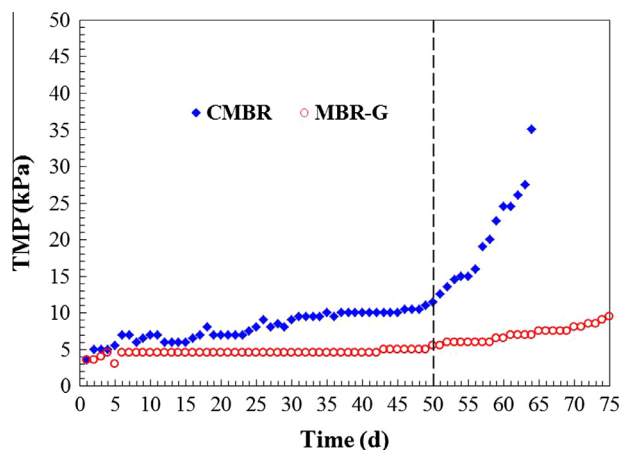

Fig. 1. TMP profile for the MBR-G and the CMBR.

64 days and 75 days of operation, respectively. At the end of the experimental period, MLSS concentrations increased to 15.22 g/L and 15.12 g/L in the CMBR and the MBR-G, respectively. Moreover, lower MLVSS concentration was obtained for the CMBR than that for the MBR-G, with the values of 12.94 g/L and 13.08 g/L, respectively. The biomass growth rate in terms of ΔMLSS/Δt was 0.16 g/L d in the CMBR, which was higher than the rate in the MBR-G (0.13 g/L d). The CMBR showed higher sludge viscosity (5.5 ± 0.6 mPa s) than that in the MBR-G (5.4 ± 0.5 mPa s), pointing out that sludge viscosity was positively correlated with MLSS concentration in both MBRs.

3.3. Particle size distribution, zeta potential and relative hydrophobicity (RH)

Results of particle size distribution in this study showed different sizes of sludge flocs in two MBRs. The size distribution of biomass particles in the MBR-G was larger (from 80 to 200 μm), whereas the CMBR had smaller sizes of biomass particles, ranging from 20 to 120 μm. These results were confirmed by microscopic images of sludge flocs in mixed liquor in both MBRs at different days of operation (Fig. 2). It was observed that the CMBR contained less number of smaller and compacted sludge flocs, while in the MBR-G, the flocs were characterized by more number of larger and looser flocs. The results elucidated that Gemfloc® addition could promote the aggregation of sludge flocs in the MBR-G. Generally, hydrophobicity and surface charge affect flocculation ability of the sludge flocs through hydrophobic interaction and electrostatic repulsion, respectively [27,28]. In this study, higher zeta potential values (−0.86 ± 1.07 mV) of activated sludge were measured in the MBR-G than those in the CMBR (−11.41 ± 5.06 mV), which demonstrated the negative surface charge of the microbial flocs was reduced or neutralized by Gemfloc®. Subsequently, the flocs could attach to each other and promote the production of larger flocs through the charge neutralization mechanism [29]. Ji et al. [14] also reported similar results that the charge neutrality was responsible for enhancing flocculation ability of sludge flocs when adding PAM–MGMS into the MBR. In addition, it has been found that the formation of more number of larger permeable sludge flocs is associated with higher RH [30]. Thus, the increased sludge flocs in the MBR-G demonstrated higher RH (72.19 ± 6.53%) than that for the CMBR (35.64 ± 5.34%), proving that the formation of larger flocs could reduce the retention of water among sludge flocs, resulting in higher hydrophobicity. Moreover, higher RH decreased the interaction between the hydrophobic flocs and hydrophilic membrane, thereby improving membrane performance. Overall, increased zeta potential and enhanced hydrophobicity of sludge flocs contributed to better flocculation ability of biomass particles in the MBR-G.

3.4. EPS and SMP in mixed liquor

In this study, polysaccharides and proteins were analyzed as the major fractions of EPS and SMP. Figs. 3 and 4 present the profiles of SMP and EPS of the mixed liquor in both MBRs as well as the average values of SMP_P, SMP_C, EPS_P/EPS_C for different operating period. In the CMBR, SMP levels were stable before the fouling period (from day 0 to day 50), with the value of 22.83 ± 9.31 mg/L. The variations of SMP_C and SMP_P were marginal (17.80 ± 5.03 and 5.40 ± 2.11 mg/L, respectively). After 50 days (fouling period with rapid TMP increase), a significant rise in SMP was observed (up to 51.22 ± 14.26 mg/L), while SMP_C and SMP_P increased to 38.45 ± 7.75 and 12.23 ± 2.51 mg/L, respectively. On the other hand, EPS remained steady at 23.02 ± 7.22 mg/L during 60 days operation. During the operation, hydrolysis of bound EPS into small fractions and their subsequent dissolution into bulk solution could

lead to more SMP release and EPS reduction [31]. Thus, more serious fouling phenomenon was found in the CMBR. When compared to the CMBR, the MBR-G possessed less SMP (12.70 ± 4.07 mg/L) and higher total bound EPS in activated sludge (43.9 ± 16.2 mg/L), because SMP was adsorbed and/or entrapped onto the flocculated microbial flocs, thereby increasing EPS contents [16]. Furthermore, floc strength could be enhanced by EPS at high levels due to polymer entanglement, leading to better flocculation ability of sludge flocs and generation of larger flocs [28]. In addition, it has been reported that hydrophobicity and surface charge of sludge flocs depend on the ratio of proteins to polysaccharides in EPS (EPS_P/EPS_C) [32]. As shown in Fig. 4, the MBR-G exhibited higher EPS_P/EPS_C ratio (0.55–0.85) than that in the CMBR (0.32–0.52) during the operation period. Normally, amino acids with hydrophobic side groups can be resulted from higher EPS_P, thereby exhibiting higher RH of activated sludge. In addition, declining EPS_C also further reduced hydrophilic nature of sludge. Besides, higher zeta potential of sludge flocs obtained in the MBR-G also indicated that higher EPS_P reduced the surface charge of sludge flocs due to the fact that EPS_P containing amino groups carried positive charge, which neutralized sludge flocs having negative surface charge [27,32]. Overall, the improved aggregation ability of sludge flocs in the MBR-G was ascribed to increased EPS concentrations as well as EPS_P/EPS_C ratio. Hence, although activated sludge presented higher EPS concentrations, the MBR-G exhibited less membrane fouling propensity with lower fouling rate [23,33].

3.5. Membrane fouling behavior

Table 2 presents the fouling resistance for both MBRs after the experiments. It was observed that the total fouling resistances (R_T) of the CMBR and the MBR-G were 4.05×10^{12} m^{-1} and 3.54×10^{12} m^{-1}, respectively. The CMBR had about 2-time higher pore blocking resistance (R_P of 1.5×10^{11} m^{-1}) than the MBR-G. Cake layer resistance (R_C) of the CMBR (3.00×10^{12} m^{-1}) accounted for 74.1% of R_T, whereas R_C of the MBR-G was 1.94×10^{12} m^{-1}, corresponding to 54.8% of R_T. These results indicated that cake layer fouling played a significant role in membrane fouling of both MBRs. Additionally, Gemfloc® addition effectively alleviated membrane fouling due to the prevention of cake layer formation and pore blocking. Results reported by Hwang et al. [34] and Jamal Khan et al. [35] with addition of cationic polymer (MPE or MPE50) into MBR systems were consistent with the findings of this study. The reduction of R_C made a greater contribution to R_T decrease due to addition of cationic polymer.

Since no sludge was withdrawn from MBRs in this study, higher MLSS concentration and sludge viscosity induced the deposition of sludge flocs and higher R_C in the CMBR causing by the sticky cake layer also formed on membrane surface [36–38]. As the cake layer represented the significant fraction of the total fouling resistance, the compositions of EPS, SMP and BPC in cake layer were further analyzed and are shown in Fig. 5. EPS_C concentration of the cake layer presented minor difference for both MBRs. However, higher concentration of EPS_P (2.83 mg/g cake layer) was observed in the CMBR than that in the MBR-G (1.42 mg/g cake layer). The cake layer in the CMBR exhibited higher SMP_C and SMP_P concentrations of 0.63 and 0.58 mg/g cake layer, respectively, comparing to lower values for the MBR-G (0.41 and 0.12 mg/g cake layer, respectively). In addition, the CMBR possessed higher concentrations of BPC_P and BPC_C (by 16.94 and 3.13 times, respectively) comparing with the MBR-G. These results implied that EPS_P, SMP (SMP_C and SMP_P) and BPC (BPC_C and BPC_P) on membrane surface contributed to higher R_C in the CMBR. At higher TMP, the drag force from the permeate pump could promote cake layer formation by aggravating the deposition of EPS_P, SMP_C and SMP_P on membrane surface [39]. More sludge cake on membrane surface could cause
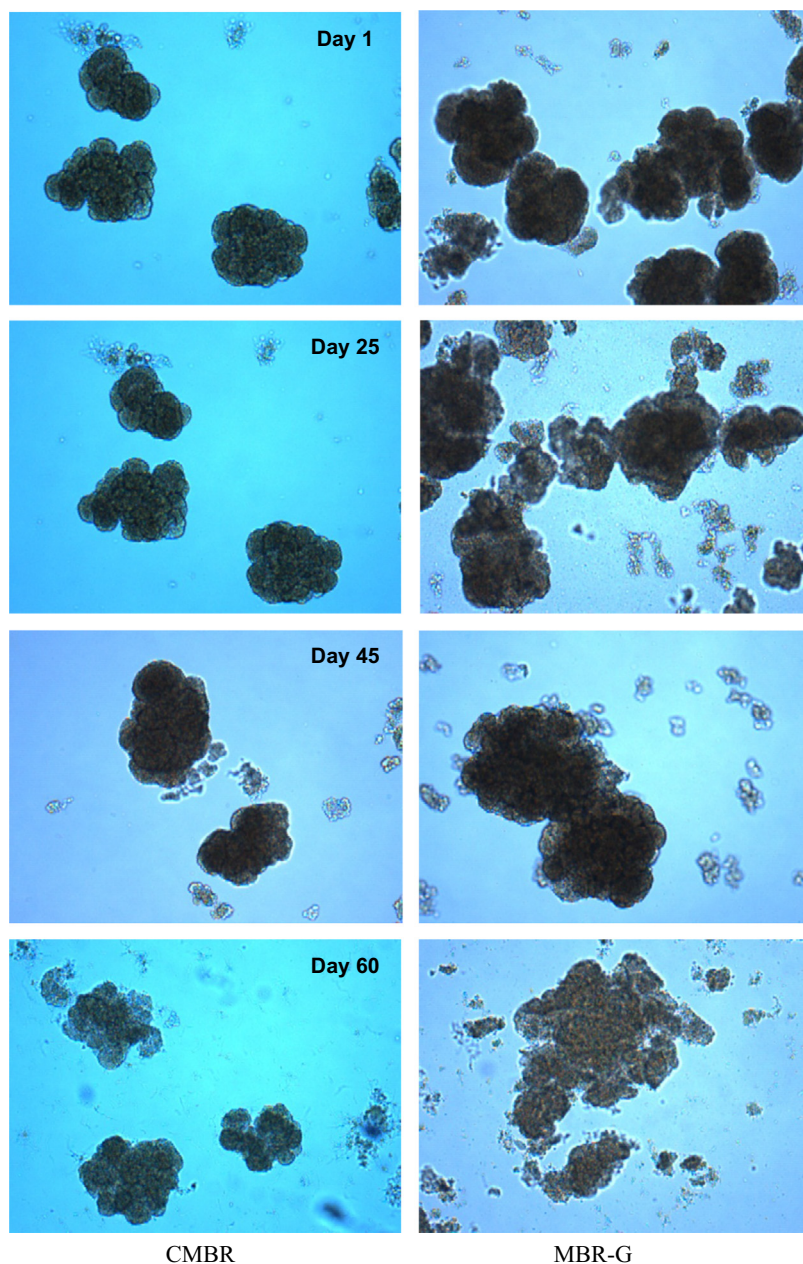
Fig. 2. Microscopic images of the sludge flocs in mixed liquor in the MBR-G and the CMBR (100×).

endogenous decay or cell lysis at the bottom layer, which led to release of more EPS_P and SMP [40,41]. Furthermore, the continuous accumulation of SMP in the sludge layer generated more BPC on membrane surface, which accelerated the formation and attachment of a sticky and impermeable sludge cake on the membrane surface [7,24]. On contrary, in the MBR-G, Gemfloc® addition not only reduced deposition of EPS_P by lowering TMP development, but also adsorbed SMP_P and SMP_C, resulting in less retention of BPC_P and BPC_C in the sludge cake.

Since the CMBR demonstrated faster TMP development (Fig. 1) and smaller sludge flocs (Fig. 2), the obtained higher R_C and R_P values indicated that the presence of smaller flocs could block membrane pore as well as reduce the porosity of cake layer [10,42]. On contrary, lower membrane fouling propensity of the MBR-G was due to formation of more porous and permeable cake layer caused by the deposition of larger and looser sludge flocs on membrane surface [16]. Previous studies have suggested that SMP induces

internal fouling and decreases filterability since SMP can not only block membrane pores, but also block the pores and spaces between particles in the cake layer [29,43–45]. Moreover, SMP_C possessing partially hydrophilic nature could cause irreversible fouling by forming a thin gel layer on membrane compared to SMP_P [6,46–48]. In addition, high portion of SMP_P content in SMP could also cause the cake layer formation due to their stickiness [49]. Therefore, SMP played an important role in membrane fouling as well as contributed to the increased R_C and R_P in the CMBR.

3.6. Modeling of membrane fouling in the MBR-G and the CMBR

A modified resistance-in-series model was employed for quantitatively estimating membrane fouling behavior through the TMP evolution and quantifying the increase of filtration resistance in both MBRs. The model is based on the basic resistance-in-series model as shown in Section 2.3, which integrates membrane fouling
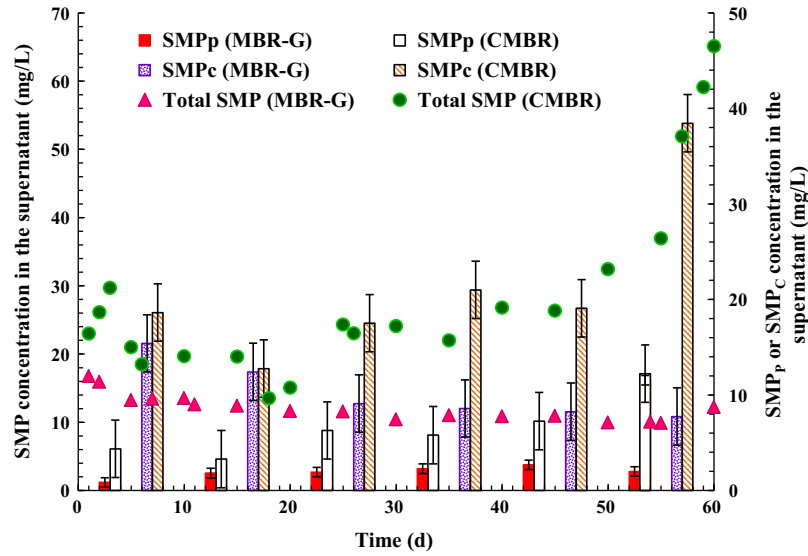
Fig. 3. Variations of SMP (including SMP_P and SMP_C) concentrations in the supernatant in the MBR-G and the CMBR.
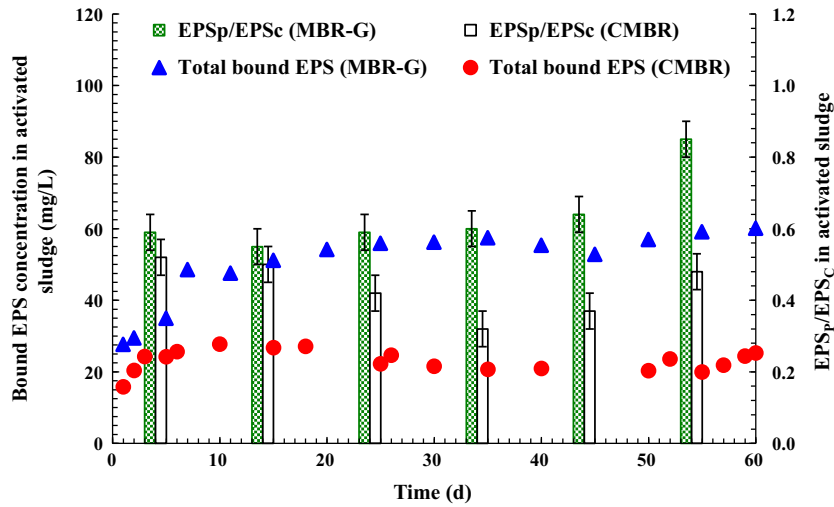

Fig. 4. Variations of EPS concentrations and EPS_P/EPS_C ratio in activated sludge in the MBR-G and the CMBR.

Table 2
Fouling resistance distribution in the MBR-G and the CMBR.

Resistance distribution	MBR-G		CMBR	
	m^{-1}	% of R_T[a]	m^{-1}	% of R_T[a]
Total	3.54×10^{12}		4.05×10^{12}	
Cake layer	1.94×10^{12}	54.8	3.00×10^{12}	74.1
Pore blocking	0.70×10^{11}	19.8	1.50×10^{11}	3.7
Clean membrane	9.00×10^{11}	25.4	9.00×10^{11}	22.2

[a] R_T = total fouling resistance.

Fig. 5. Compositions of bound EPS, SMP and BPC in cake layer in the MBR-G and the CMBR.

behavior with sludge properties. It can provide a rational and fundamental framework for understanding membrane fouling process and predicting impacts of sludge characteristics on fouling behavior. As suggested in Section 3.5, SMP and MLSS concentrations were important aspects influencing pore blocking and cake layer formation on membrane surface. Therefore, R_P and R_C can be simulated according to the profiles of SMP and MLSS, respectively.

It can be seen from Fig. 6 that the modeled SMP results are reasonably matched up with the experimental results. The simulated
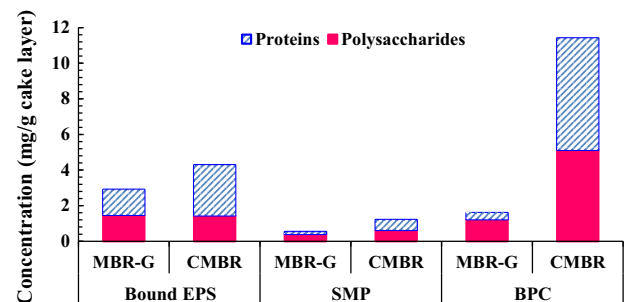
data shows a dramatic accumulation of SMP after 50 days in the CMBR, and the CMBR possessed more SMP than the MBR-G during the entire operation period. Regarding pore fouling, Zuthi [50] has proposed modeling related to pore fouling of the membrane (R_P) in a submerged MBR with membrane pore size of 0.1 μm (Eq. (5)).
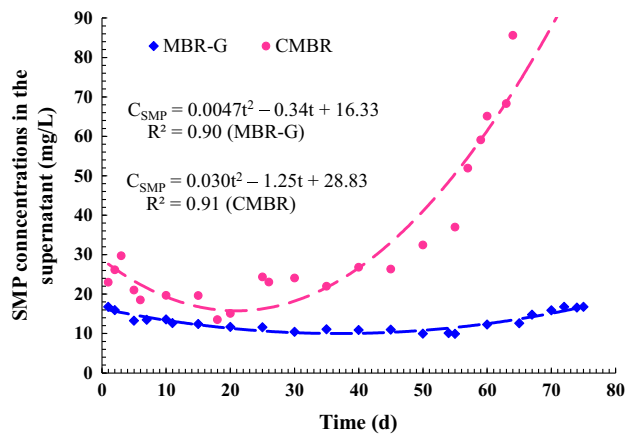
Fig. 6. SMP profile of the supernatant in the MBR-G and the CMBR.

Fig. 7. R_P profile drawn for the MBR-G and the CMBR with the modified equation (Eq. (6)).

However, in this study, the profile of R_P from trial simulation was not satisfactory even with the significant change of the pore fouling factor n_p and initial porosity. Further reduction or increase of the trial values of the unknowns still could not match the experimental value of R_P for both MBRs. Thus, according to the different membrane pore size (0.2 μm) used in this study, an empirical factor (($d_{p,used}$/0.1)^4) was assigned to Eq. (5). The modified equation of R_P is given in Eq. (6). Table 3 gives the values of coefficients and constants used for modeling. Plotting of R_P versus the operation time (Fig. 7) revealed that the simulation results were in good agreement with the experimental data ($R^2 > 0.9$). R_P in the CMBR showed a gradual increase before 50 days and a significant rise afterward, while the MBR-G presented much lower R_P even after 50 days. These results elucidated that the proposed models can explain the important influence of increase in SMP concentration on pore blocking.

$$\text{MBR-G}: \ C_{SMP}(t) = 0.0047t^2 - 0.34t + 16.33 \tag{3}$$

$$\text{CMBR}: \ C_{SMP}(t) = 0.030t^2 - 1.25t + 28.83 \tag{4}$$

$$R_P = \exp(n_p t)8h_m/fr_p^2 \tag{5}$$

$$R_P = \exp(n_p t)8h_m/(d_{p,used}/0.1)^4 fr_p^2 \tag{6}$$

where C_{SMP} is the time-dependent concentration of soluble particles entering the pores; t is the filtration time; the pore fouling factor n_p is to explain the typically observed exponential rise of TMP due to the pore fouling resistance especially at the final stage of operation of an MBR system; h_m is the membrane's effective thickness; f is the membrane's porosity (variable) and r_p is the membrane pore radius

Table 3
Values of coefficients and constants used to simulate the model.

Coefficient/constant[a]	MBR-G	CMBR
n_p	0.003	0.003
Constant for f	0.6	0.6
Constant for r_p	1.00×10^{-7}	1.07×10^{-7}
k	0.3	0.1
n_c	0.030	0.042
Constant for R_C	75	1000
$(d_{p,used}/0.1)^4$	16	16

[a] f = the membrane's porosity (variable), k = the factor representing the detachment of the cake layer from the membrane surface, n_p = pore fouling factor to explain the typically observed exponential rise of TMP due to the pore fouling resistance especially at the final stage of operation of an MBR system, n_c = cake fouling factor to explain the typically observed exponential rise of TMP due to the cake layer resistance especially at the final stage of operation of an MBR system, r_p = the membrane pore radius (variable).
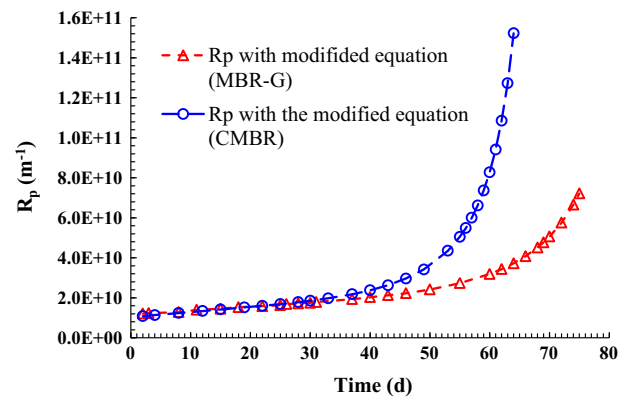
(variable); $d_{p,used}$ is the initial pore diameter of the membrane in μm (0.1 μm is the reference membrane pore size). f and r_p are the time-dependent parameters and are assumed to be affected by the dynamic changes of SMP concentration within the bioreactor. These two parameters (f and r_p) can be calculated according to the Eqs. (7) and (8) proposed by Busch et al. [51] and Giraldo and LeChevallier [52].

$$\rho_p df/dt = -4\eta_f J(t)C_{SMP}(t)m_{d,o}\Big/\Big((m_{d,o})^2 - (m_{d,i})^2\Big) \tag{7}$$

$$dr_p/dt = -\alpha_p C_{SMP}(t)J(t) \tag{8}$$

where ρ_p is the density of biomass; the constant related to the porosity (f) is the effective initial porosity of the membrane (60% in this study); η_f is the average fraction of soluble particles that accumulate in the pores taken as 0.2 from Busch et al. [51]; $m_{d,o}$ and $m_{d,i}$ are the outer and inner membrane diameter, (0.49×10^{-3} m and 0.35×10^{-3} m, respectively, in this study); α_p is pore size reduction coefficient (0.000943).

Fig. 8 displays experimental data vs. simulated results for the variation of MLSS concentration in activated sludge and shows good model fit. It could be referred that sludge concentration increased with filtration time in both MBRs, whereas higher MLSS concentration was obtained in the CMBR. After obtaining the Eqs. (9) and (10) from Fig. 8, R_C could be calculated using the Eqs. (11) and (12) which were proposed by Zuthi [50] to model the rise of TMP in a submerged MBR.
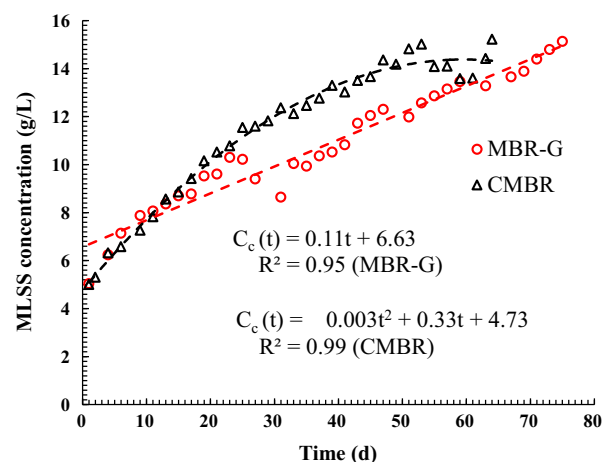

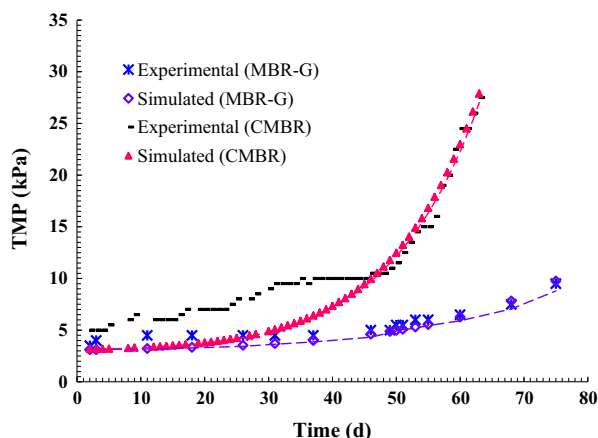**Fig. 8.** Variation of MLSS concentration in activated sludge in the MBR-G and the CMBR.

Fig. 9. TMP profile after model calibration for the MBR-G and the CMBR.

$$\text{MBR-G}: \quad C_c(t) = 0.11t + 6.63 \tag{9}$$

$$\text{CMBR}: \quad C_c(t) = -0.003t^2 + 0.33t + 4.73 \tag{10}$$

$$R_C = \alpha_c h_c(t) \rho_c \exp(n_c t) \tag{11}$$

$$\rho_c dh_c/dt = J \cdot (1-k) C_c(t) \tag{12}$$

where C_c is concentration of potential cake forming particles in the bulk liquid (e.g. MLSS) which typically varies over time in the MBR-G and the CMBR (Eqs. (9) and (10), respectively); α_c is specific resistance of the compressible cake layer; h_c is variable depth of the cake layer expressed as a first order differential function in time; ρ_c is density of the cake layer; the factor n_c is to explain the typically observed exponential rise of TMP due to the cake layer resistance especially at the final stage of operation of an MBR system (the MBR-G and the CMBR in this study); k is factor representing the detachment of the cake layer from the membrane surface.

Based on the calculated values of R_P and R_C as well as Eq. (1), the fouling propensity in both MBRs in terms of TMP development can be modeled. Fig. 9 shows actual TMP development during experiments and the simulated TMP versus filtration time. It can be observed that the simulated TMP fit well to the experimental TMP profile for both MBRs during the operation period. In addition, the sudden TMP increase recorded in the CMBR was also depicted and predicted by the models. Overall, the results implied that the proposed models in this study are capable of predicting the contributions of SMP and MLSS to membrane fouling as well as the TMP development during the operation. In real MBR applications, SMP and MLSS are common parameters and can be easily measured. Thus, by utilizing the profiles of SMP and MLSS, this model can provide an economic way to monitor membrane fouling behavior through simulation of R_P, R_C and TMP.

4. Conclusions

The effects of Gemfloc® addition on membrane fouling reduction in a SMBR were investigated in this study. Specific conclusions could be drawn as follows:

- Gemfloc® could contribute to membrane fouling alleviation in terms of reduced cake formation, retarded pore blocking and improved membrane filterability.
- Compared to the CMBR, activated sludge in the MBR-G contained less SMP but more EPS with higher EPS$_P$/EPS$_C$ ratio, which led to higher RH and zeta potential of activated sludge. The addition of Gemfloc® enhanced aggregation of sludge flocs and increased floc size.

- Compared to the CMBR, the MBR-G exhibited lower membrane fouling potential as well as lower R_P and R_C due to lower sludge growth rate and viscosity, less deposition of EPS$_P$ and SMP on membrane surface, as well as less retention of BPC in the cake layer.
- The proposed mathematical model could successfully simulate R_P, R_C and TMP development based on the profiles of SMP and MLSS during operation. Thus, this model can help to quantitatively understand the relationship between sludge properties and membrane fouling behavior in SMBR.

Acknowledgements

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