Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2015.1046141

57 (2016) 11008–11018
May

Taylor & Francis
Taylor & Francis Group

Impact of modified starch on membrane fouling in MBRs

Jing Ji[a], Jianfeng Li[b], Yaozhong Li[c], Jiangping Qiu[a], Xudong Li[a,*]

[a]*School of Agriculture and Biology, Shanghai Jiaotong University, 800 Dongchuan Rd., Shanghai 200240, P.R. China, Tel. +86 34206142; emails: xiaoxiaohill@sjtu.edu.cn (J. Ji), jpq@sjtu.edu.cn (J. Qiu), Tel. +86 34206142, +86 13817065945; Fax: +86 21 34205877; email: lixudong@sjtu.edu.cn (X. Li)*
[b]*Institute of Resources and Environmental Engineering, Shanxi University, Taiyuan 030006, P.R. China, Tel. +86 13620612091; email: 63000808@qq.com*
[c]*Kemira APAC R&D Center, 4E, Block 10, Lianhang Road 1188, Minhang District, Shanghai 201112, P.R. China, Tel. +86 15821504285; email: lyzxjtu@hotmail.com*

Received 24 May 2014; Accepted 15 April 2015

ABSTRACT

The reduction of membrane fouling in membrane bioreactors (MBRs) by the addition of two modified starches (i.e. CGMS and MGMS) was investigated. The fouling rate in the CGMS-added MBR was approximately eight times and four times lower than that in the control MBR at fluxes of 40 L/m^2 h and 20 L/m^2 h, respectively. In contrast, the MBR with added MGMS demonstrated improved performance only in short-term filtration. Qualitative and quantitative analyses of membrane pore blocking, the gel layer and the cake layer were conducted. The results demonstrated that gel and cake resistance was reduced noticeably in starch-added MBRs. Compared to the control MBR, the concentration of macromolecules with MW ≧ 100 kDa in the supernatant of both CGMS- and MGMS-added MBRs was significantly lower. The CGMS-MBR demonstrated a higher porosity of fouling layers than the control and MGMS-MBRs, which was attributed to the bigger floc size and lower fractal dimension of the floc caused by the addition of CGMS. The detachment of large flocs from the membrane surface also contributed to the lower fouling rate in the CGMS-MBR.

Keywords: MBR; Filtration enhancement; Modified starch; Macromolecules; Porosity

1. Introduction

Membrane bioreactor (MBR) technology has been regarded as one of the most promising technologies for wastewater treatment and water reuse, as it offers many outstanding advantages over conventional activated sludge processes. However, membrane fouling is a major barrier that limits the wide application of this technology, as it increases operational cost and shortens membrane life. Therefore, it is necessary to develop effective and economical methods for preventing or retarding membrane fouling.

Various studies have been carried out to mitigate or eliminate membrane fouling through the addition of flocculants or coagulants, such as powdered activated carbon, metal salts (e.g. $AlCl_3$ and $FeCl_3$), inorganic polymeric substances (e.g. PACl and PFS), organic poly-electrolytes (e.g. MPL30, MPE50) and natural organics (chitosan and modified starches) [1–3]. However, it should be noted that some synthetic

*Corresponding author.

polymeric flocculants and metal salts may not be suitable for large-scale application. The addition of $FeCl_3$ and PACl has been found to be a factor that strongly affects the nitrification process [4]. It was also reported that some of the materials, including activated carbon and inorganic flocculants, had adverse impacts on nutrient removal in MBRs [5]. In addition, "secondary pollution" in the process of the flocculants degradation, which would be harmful to the environment and human health, presents another major concern for synthetic chemicals as filter aids [6]. Hence, biodegradable natural flocculants such as chitosan and modified starches, which have a lower ecological impact, have become more attractive in MBR applications.

The adoption of modified starches seems quite favourable because these materials are usually stable, cheap, minimally toxic and biodegradable. Recently, there have been a few studies on the addition of modified starches to MBR systems; however, the results were inconclusive and sometimes contrary to each other. Koseoglu et al. found that among seven different additives, the best performance in short-term filtration was achieved by starch [7]. However, Iversen et al. showed that the addition of starch has positive and negative impacts on filtration: it could eliminate some biopolymers and reduce CST, but at the same time, polysaccharide concentration increases in the supernatant, which could intensify membrane fouling processes in long-term filtration [5]. Therefore, a comprehensive assessment of the effects of modified starch on the enhancement of MBR filterability, including the effective times of different starches, would be very useful for further exploring appropriate fouling control strategies.

In our former study, it was found that the long-term filtration performance of modified starches was strongly correlated to their effect duration on SMP, dp and df [8], but the mechanism of fouling alleviation was not well explored yet. In this study, two modified starches, named CGMS and MGMS, respectively, were explored and tested in a lab-scale submerged membrane bioreactor. Previous investigations have focused on mixed liquor properties and fouling layer properties. Various analyses have been performed to understand membrane fouling mechanisms such as membrane pore blocking, removal of macromolecules, cake resistance and fouling layer porosity. The aims of this study were to assess the feasibility of modified starch as a filter aid in MBR operation and to explore how starches influence mixed liquor properties and thus alleviate membrane fouling.

2. Materials and methods

2.1. Experimental set-up and operating modes

2.1.1. Submerged MBR

Fig. 1 shows the schematic diagram of the submerged membrane bioreactors. Three identical reactors were operated simultaneously, with one reactor as the control (without adding a filter aid), and the other two reactors were supplemented with CGMS and MGMS, respectively, for comparison. All reactors were inoculated with the same activated sludge and operated in parallel under the same operating conditions.

The MBR systems were operated in constant flux mode, with 9 min of suction pumping followed by 1 min of relaxation. During operation, the flux and trans-membrane pressure data were recorded continuously every minute by SCADA and a PLC automatic control system. The working volume of each MBR is 5 L. A flat sheet membrane module (membrane material: hydrophilic Polyvinylidene Fluoride (PVDF); working membrane area: 0.05 m^2; membrane pore size: 0.22 μm; Millipore) was installed in each MBR. Compressed air with the airflow rate of 0.5 L/min was supplied continuously through a microporous aeration tube at the bottom of each reactor to provide dissolved oxygen for biomass growth and to create a turbulent flow along the membrane surface. Synthetic wastewater was prepared with the following composition and used to feed the MBRs: glucose (562.5 mg/L), NH_4Cl (114.5 mg/L), KH_2PO_4 (26.5 mg/L), $NaHCO_3$ (150.0 mg/L), peptone (50.0 mg/L) and yeast extract (20.0 mg/L) as macronutrients; and $MgSO_4{\cdot}7H_20$ (33.0 mg/L), $MnSO_4{\cdot}7H_20$ (3.0 mg/L) and $FeSO_4$ (0.2 mg/L) as trace elements.

2.1.2. Filtration cycle and addition of modified starches

In this study, the filtration cycle refers to the process in which TMP increased from the initial value to 45 kPa, above which irreversible membrane fouling/deterioration will be caused. After each filtration cycle, the membrane module was removed from the MBR and replaced with a cleaned membrane. The filtration time spent before TMP reached 45 kPa was defined as $\mathbf{\Gamma}_{45}$.

The experiments were conducted under different fluxes. In the first stage, the permeate flux was fixed at 40 L/m^2 h. Relatively short test periods were applied to minimise variations in the characteristics of

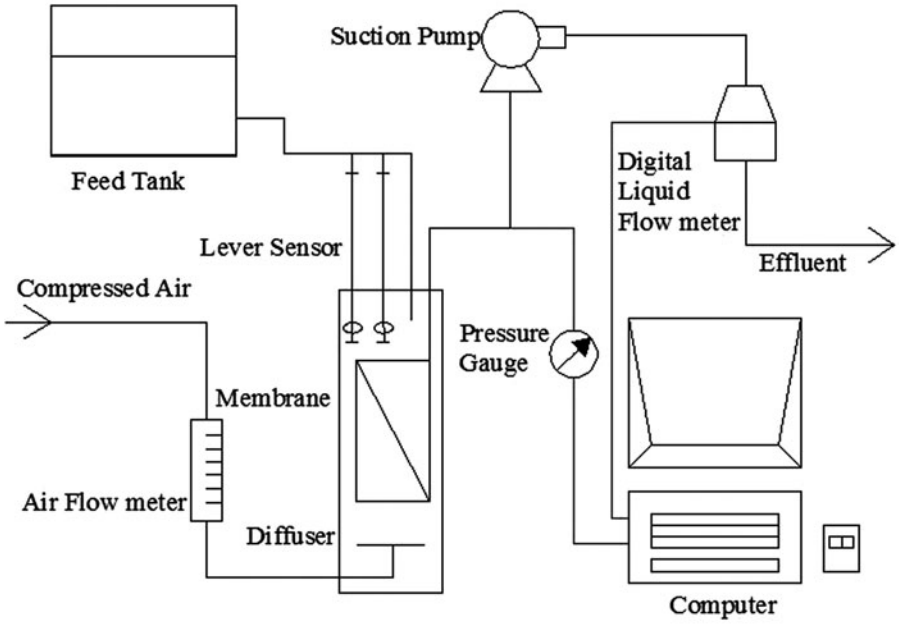

Fig. 1. Schematic diagram of the submerged membrane bioreactor.

the mixed liquors. In the second stage, a constant flux of 20 L/m^2 h was applied to study membrane fouling under long-term sustainable operation (critical flux was approximately 30 L/m^2 h). All MBRs were operated continuously for more than 6 months. The operating conditions of the MBRs in the two stages are summarised in Table 1.

Before MBR filtration experiments, a batch filtration test was conducted in a dead-end microfiltration cell at various CGMS and MGMS dosages to determine their effects on specific cake resistance (α_c) [9]. The dosage which provided the lowest (α_c) was chosen as the optimum concentration. The applied CGMS and MGMS dosages were 600 mg/L and 1,000 mg/L, respectively. At the very beginning of each cycle, modified starches were added to the MBRs and mixed for 20 min. Afterwards, no more filter aids were added during each filtration cycle; thus, the evolution of floc morphology in the MBR could be monitored.

Table 1
Operating conditions of the MBRs

Items	High flux	Sustainable flux
Membrane module	Polyvinylidene fluoride flat sheet	
Membrane surface area (m^2)	0.05	
Membrane type	hydrophilic PVDF (Millipore, Belgium)	
Pore size (μm)	0.22	
Effective volume (L)	6	
SRT (d)	30	
HRT (h)	3	6
Permeate flux (LMH)	40	20
MLSS (g L^{-1})	6.93 ± 1.73 g	6.42 ± 0.85 g

2.2. Membrane resistance analysis

The membrane resistance distribution in different MBRs was determined under constant flux according to a resistances-in-series model. All the MBRs were operated under identical operating conditions. Two rounds of filtration tests were conducted; in the first round, all the membrane modules were removed from MBRs for cleaning once the TMP in the control MBR reached 45 kPa (approximately 7 d). In the second round of filtration, the membrane modules were taken out when each MBR's TMP reached 45 kPa (this required 7, 8 and 36 d, respectively, for the control, MGMS- and CGMS-added MBR). The total resistance (R_t) was calculated from the final flux and TMP according to Darcy's law. Subsequently, the fouled membrane modules were rinsed with deionised water and then cleaned with a sponge to remove the attached fouling layers. The flux with deionised water was determined to obtain the combined membrane resistance and resistance due to pore blockage ($R_m + R_b$).

The membrane resistance (R_m) was determined by comparing the clean membrane flux with the deionised water flux. Because it is difficult to calculate the resistance of gel and cake layer (R_g and R_c) independently, R_c was defined as the sum of R_g and R_c. Thus, R_c was calculated as $R_c = R_t - R_b - R_m$ [1].

2.3. Analysis of mixed liquor and permeate

The profiles of mixed liquor properties such as specific cake resistance (α_c), mean floc size (dp), fractal dimension (df), and supernatant TOC in all MBRs were investigated. The (α_c) was determined using the dead-end filtration system as mentioned above. The dead-end filtration cell, driven by a vacuum pump and regulated by a vacuum valve, was operated under constant pressure at 86 kPa. If operated under constant pressure, Darcy's law can be transformed as follows [10]:

$$\frac{t}{V} = \frac{\mu\alpha_c C}{2A^2\Delta P}V + \frac{\mu R_m}{A\Delta P} \quad (1)$$

where V is the permeate volume, t is the filtration time and P is the applied pressure. Thus, the specific resistances of cakes can be determined from the slope of the straight line by plotting t/V vs. V.

A Mastersizer/E (Malvern, UK) was used to measure the floc size distribution in the bulk solution as well as to calculate the sludge fractal dimension by means of forward scattered light analysis. The total organic carbon (TOC) concentration in the supernatant of MBR was measured by a TOC analyser (Shimadzu, Japan). The preparation of the supernatant was made according to the following procedures. First, a mixed liquor sample was centrifuged at 4,000 rpm for 10 min. Next, the sludge pellet was removed and the supernatant pH value was adjusted to 3–4. Finally, ionic carbon was removed by nitrogen gas stripping.

Analysis of the supernatant and permeate molecular weight distributions was made by means of gel permeation chromatography (Waters, USA) equipped with an ultrahydrogel linear column (MW ranges: 103–107, Waters, USA) and a refractive index detector (RID, Waters 2414, USA). Degassed deionised water was used as the mobile phase at a flow rate of 0.75 ml/min. Supernatant and permeate samples were passed through a 0.45 μm filter before injection. The injection volume was 100 μl, and the column was maintained at 30˚C. A series of standard samples (Pullulan P-82 and P-1, Showa Denko, Japan) with molecular weights from 1.3 kDa to 788 kDa were applied for standard curve calculation.

The membrane surface and foulant layer were observed by means of SEM (JSM-5,310 LV, JEOL Ltd, Japan). The membrane specimens (1 cm × 1 cm) were first cut from membrane modules and washed three times with milli-Q water. Subsequently, the membrane specimens were soaked in 2% glutaraldehyde for 4 h to fix the microbial cell and cake structure. The fixed samples were then washed three times with a 0.1 M sodium cacodylate buffer to remove glutaraldehyde. Next, the membrane specimens were dehydrated by a series of 10 min washes conducted in 50, 70, 85 and 95% ethanol, respectively, and then stored in 100% ethanol. The water molecules in the samples were gradually replaced by ethanol molecules. Finally, the dehydrated membrane samples were dried with CO_2 at the critical point and then sputter-coated with Au–Pd.

2.4. Preparation and physical parameters of modified starches

Corn starch was used in the synthesis of a series of modified starch flocculants through different methods with different types of reagents. The preparation process of the two modified starches is shown in Fig. 2. The physical parameters of CGMS and MGMS are shown in Table 2.

3. Results and discussion

3.1. Filtration performance of MBRs with addition of modified starches

The filtration performance of the control MBR and the two flocculant-added MBRs was investigated. Fig. 3(a) shows the TMP profiles of different MBRs at the flux of 40 L/m^2 h. According to the $\mathbf{\Gamma}_{45}$ of different MBRs, the membrane fouling rate was in the order of Control MBR > MGMS-added MBR > CGMS-added MBR, with respective $\mathbf{\Gamma}_{45}$ values of 13, 63 and 100 h. In contrast, long-term sustainable filtration was measured for all MBRs at the constant operating flux of 20 L/m^2 h. As shown in Fig. 3(b), the $\mathbf{\Gamma}_{45}$ values of the control MBR, MGMS-added MBR and CGMS-added MBR were 8, 9 and 36 d, respectively.

The fouling rate in the CGMS-added MBR was approximately eight times and four times lower than that in the control MBR at a constant operating flux of 40 L/m^2 h and 20 L/m^2 h, respectively, which indicated the effectiveness of CGMS as a membrane fouling reducer. However, compared to the CGMS-MBR, the MGMS-added MBR showed only a slight improvement at a flux of 20 L/m^2 h. This may be due to different physical and chemical properties of the two modified starches. The grafting ratio, relative viscosity

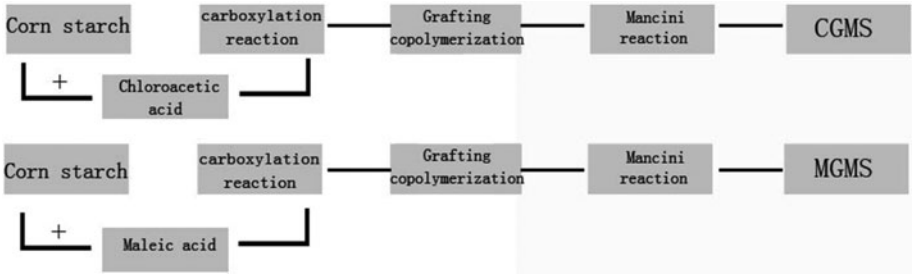

Fig. 2. Preparation process of the two modified starches.

Table 2
Physical parameters of CGMS and MGMS

Modified starch	Viscosity (mPa s)	Substitution (%)	Isoelectric point	Grafting ratio (%)
CGMS	6.9752	0.952	6.78	94
MGMS	3.9821	1.045	7.02	82

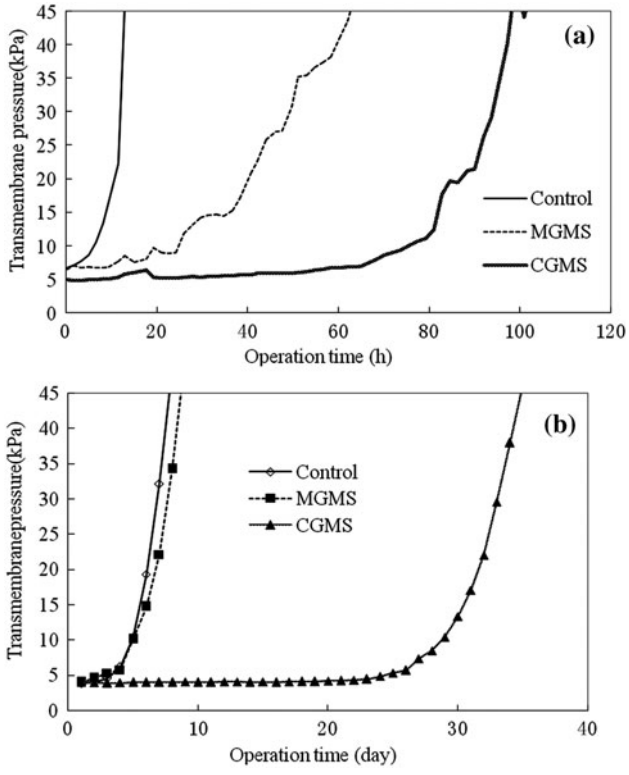

Fig. 3. (a) TMP profiles of different MBR systems at 40 L/m^2 h. (b) TMP profiles of different MBR systems at 20 L/m^2 h (filter aids added before filtration).

and molecular weight of CGMS are higher than those of MGMS, which indicates that CGMS has a long chain branched structure which favours the capture and sweeping of flocs. As shown in Table 2, the isoelectric point of CGMS and MGMS were 6.87 and 7.02 respectively, since the feed pH was slightly lower than 7, the CGMS demonstrated higher cationic charge density, which also contributed to the enhancement of the flocculation ability.

3.2. Role of modified starches addition in reducing filtration resistance

It is widely accepted that, in the filtration process, the total permeability of membrane is dependent on both the membrane itself and the attached fouling layers. In the course of membrane fouling, pore blocking and the formation of gel and cake layers could create an additional barrier to membrane filtration. As a result, the permeability of the fouled membrane was far less than that of the clean membrane. To investigate the effect of additives on resistance distribution, two rounds of filtration tests were conducted. The first round was designed to investigate the filtration resistance in different MBRs for the same permeate volume. The MBRs were operated for 7 d at a constant flux of 20 L/m^2 h. The values of R_m, R_b and R_c and their relative percentages (with respect to R_t) of different MBRs are presented in Table 3.

From Table 3, it can be seen that when the same permeate volume was applied, the total filtration resistance in the CGMS-added MBR was only approximately 10% of that in the control MBR, and the R_c in the CGMS-MBR was less than 10% of that in the control MBR. Because the membrane module and operating conditions in both MBRs were identical, it is believed that the significant improved filtration performance

Table 3
Resistance analysis of MBRs

	Round 1				Round 2			
	R_t ($\times 10^{12}$)	R_m ($\times 10^{12}$) (%)	R_b ($\times 10^{12}$) (%)	R_c ($\times 10^{12}$) (%)	R_t ($\times 10^{12}$)	R_m ($\times 10^{12}$) (%)	R_b ($\times 10^{12}$) (%)	R_c ($\times 10^{12}$) (%)
CTR	8.109	0.059(0.73%)	0.090(1.11%)	7.953(98.16%)	8.106	0.059(0.73%)	0.090(1.11%)	7.953(98.16%)
CGMS	0.854	0.059(6.94%)	0.041(4.80%)	0.755(88.26%)	8.087	0.059(0.73%)	0.173(2.13%)	7.871(97.14%)
MGMS	5.836	0.059(1.02%)	0.044(0.76%)	5.672(98.22%)	8.113	0.059(0.73%)	0.043(0.53%)	7.942(98.74%)

Table 4
Relative peak area compared to control MBR

	CTR	MGMS	CGMS
Total peak area	1	0.726	0.551
Grey zone area	0.197	0.109	0.034

observed in CGMS-added MBRs was mainly caused by the lower gel and cake resistance (Table 4).

In contrast, the effect of MGMS was not satisfactory. The reduction of R_b was quite significant, but the R_c remained high compared to the CGMS MBR. Fig. 4 shows the SEM images of fouled membrane samples taken from the three MBRs. It was observed that part of the membrane surface in the CGMS-MBR was visibly cleaner (membrane pores could be seen clearly), indicating that the foulants deposited on the membrane surface decreased as large flocs were detached by air scouring. This suggested that the larger flocs present in the CGMS-MBR could enhance membrane filtration as a result of floc detachment. In contrast, in the MGMS-MBR, most of the membrane pores have been covered with gel layer attached to the membrane surface, and it was more colloidal and smooth compared to the CGMS-MBR (Fig. 4). It seemed that detachment of flocs from the membrane surface was not as good as in the CGMS-MBR.

The relative percentages of R_m, R_b and R_c with relation to R_t when TMP reached 45 kPa in the MBRs were investigated, with the results presented in Table 3—round 2 (the TMPs in the CTR, MGMS- and CGMS-MBRs took approximately 7, 8 and 36 d to reach 45 kPa, respectively). It is observed that in the CGMS-MBR, the relative percentage of R_b was significantly higher than that in the other two MBRs, indicating that more large molecules passed through the deposited cake and gel layers and entered membrane pores. Compared to the CGMS-MBR, the permeability of deposited layers in the MGMS-MBR was much lower; the colloidal and smooth cake/gel layers intercepted more macromolecules, small flocs and free MGMS molecules on the membrane surface.

3.3. Effect of modified starches on soluble and colloidal foulants

As indicated in Section 3.2, the addition of modified starches can effectively reduce filtration resistance. The concentration of soluble and colloidal foulants in MBR supernatant was reported to be one of the main contributors to fouling in a number of studies [11,12]. In our former studies, it was found that there is a significant difference between the fouling trends of different organic fractions in the supernatant of MBRs. If the molecules are far smaller than the membrane pores, they would be less likely to block membrane pores or deposit on the membrane surface. Only macromolecules rejected by the membrane could induce membrane fouling, including pore blocking and cake deposition. In this section, the effect of modified starches on the removal of various fractions of soluble and colloidal foulants was investigated.

3.3.1. The concentration of soluble and colloidal foulants in different MBRs

The effect of modified starches on soluble and colloidal foulants in the MBRs was investigated using TOC concentration as an index of macromolecular substances [13]. The profiles of the supernatant TOC concentrations in both MBRs at a flux of 40 L/m^2 h are presented in Fig. 5(a). With the addition of flocculants, significantly low levels of SMP were achieved, and colloidal foulants became large floc aggregates [9,13]. The highest elimination of TOC (85%) was achieved 2 h after the addition of modified starches in the CGMS-MBR. Subsequently, TOC concentration was maintained at a low level for more than 60 h. With regard to the MGMS-added mixed liquor, a 35% decrease in TOC was observed 4 h after the addition of modified starches, followed by a gradual increase to a plateau. The increase was probably caused by deflocculation of the flocs, suggesting that the CGMS reached equilibrium faster than the MGMS. In addition, the flocculated macromolecules and colloidal foulants remained stable for more than 60 h without

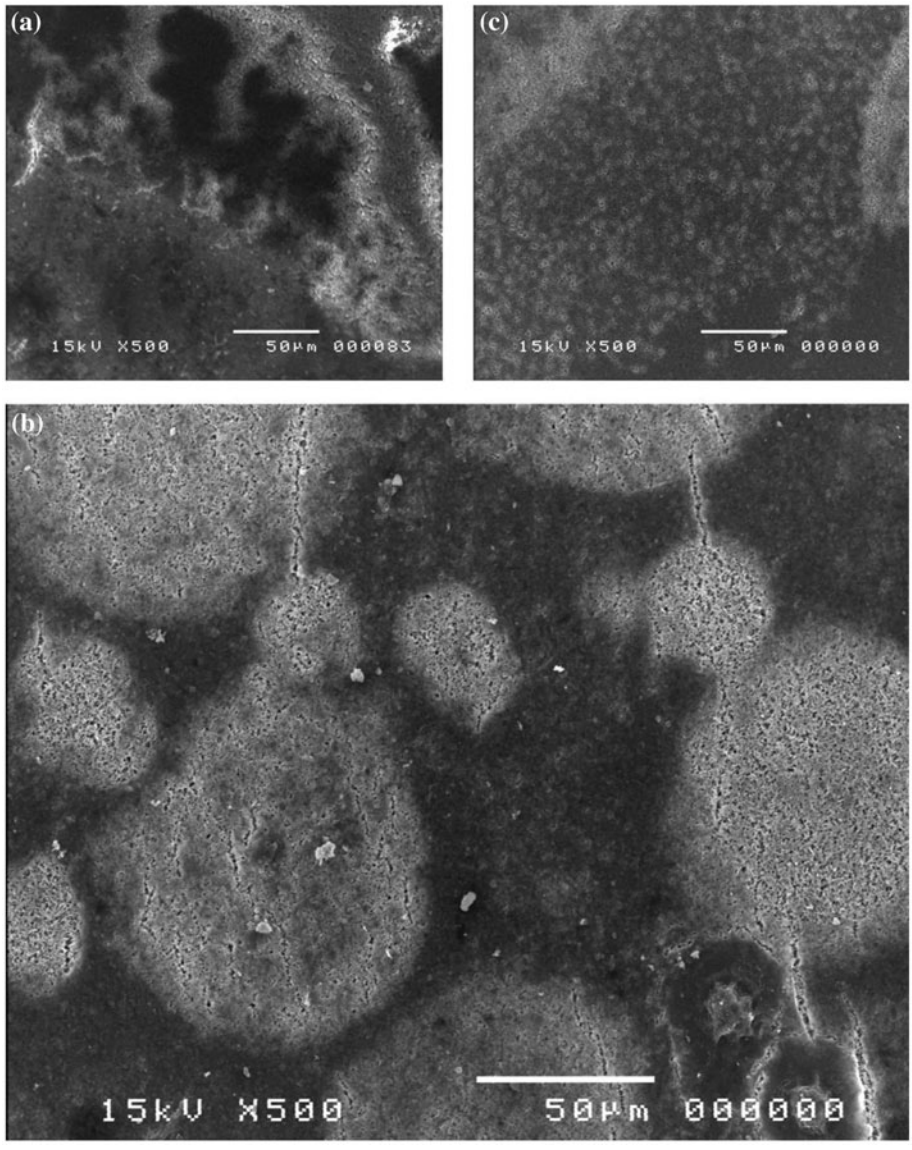

Fig. 4. SEM image of the surface of the fouled membrane from the control MBR. (a) Control MBR; (b) CGMS-added MBR; (c) MGMS-added MBR.

replenishing in the CGMS-MBR, which is much longer than in the MGMS-MBR. The effectiveness of flocculants as filter aids was determined by the performance of fouling control and the optimum dosage, thus the long flocculation duration of CGMS has an important significance in industrial applications.

The average TOC concentrations of the supernatants at a constant flux of 20 L/m^2 h of each MBR were 29.25, 28.87 and 7.03 mg/L for CTR, CGMS and MGMS added MBR, respectively. In long-term operation, the TOC in the supernatant of the MGMS-added MBR was not decreased significantly. This was due to the short flocculation duration of the MGMS. However, more than 75% of the TOC was eliminated in the supernatant of CGMS-added MBRs. The difference in TOC removal can be explained by the characteristics of the two starches. The grafting ratio and relative viscosity of CGMS were higher than those of MGMS, leading to a longer chain and branched structure in CGMS, which is more effective in capturing macromolecules and flocs. Furthermore, CGMS demonstrated a higher charge density (CD) than MGMS [8]. With more charges generated from flocculant hydrolysis, negative charges on the surface of the biomass were neutralised more easily, which in turn helps to produce strong and stable flocs.

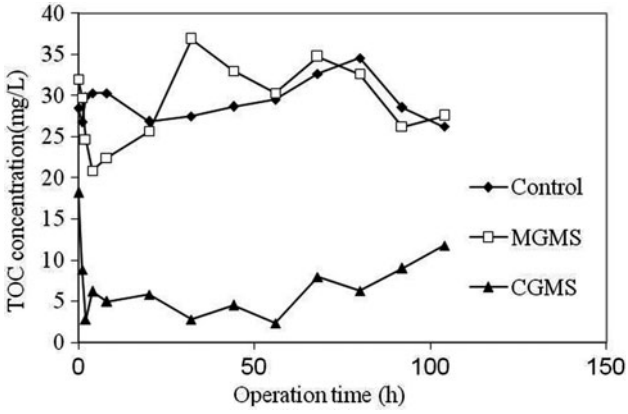

Fig. 5. TOC profiles in one filtration cycle (under a constant flux of 40 L/m^2 h).

As presented in Fig. 3(a), although the average TOC removal of MGMS was not significant, the fouling rate in MGMS-added MBRs was approximately 4.8 times lower than that in the control MBR. It should be noted that TOC only gives us an indication of the total amount of organic carbon, but not all the organic content in the MBR supernatant would lead to membrane fouling.

3.3.2. Molecular weight distribution of soluble and colloidal foulants

To further explore the mechanism of membrane fouling, the molecular weight distribution of macromolecules in the supernatant was investigated using GPC. The average pore size of the PVDF membrane in this study is 0.22 μm, which approximately corresponds to the molecular weight (MW) range of 100–1,000 kDa, according to the Filtration and Separation Spectrum from OSMONICS [14]. In our former studies, it was demonstrated that most molecules smaller than 100 kDa could pass through membrane pores and the cake layer; only soluble and colloidal substances with a molecular weight above 100 kDa would be rejected by membrane or fouling layers [15].

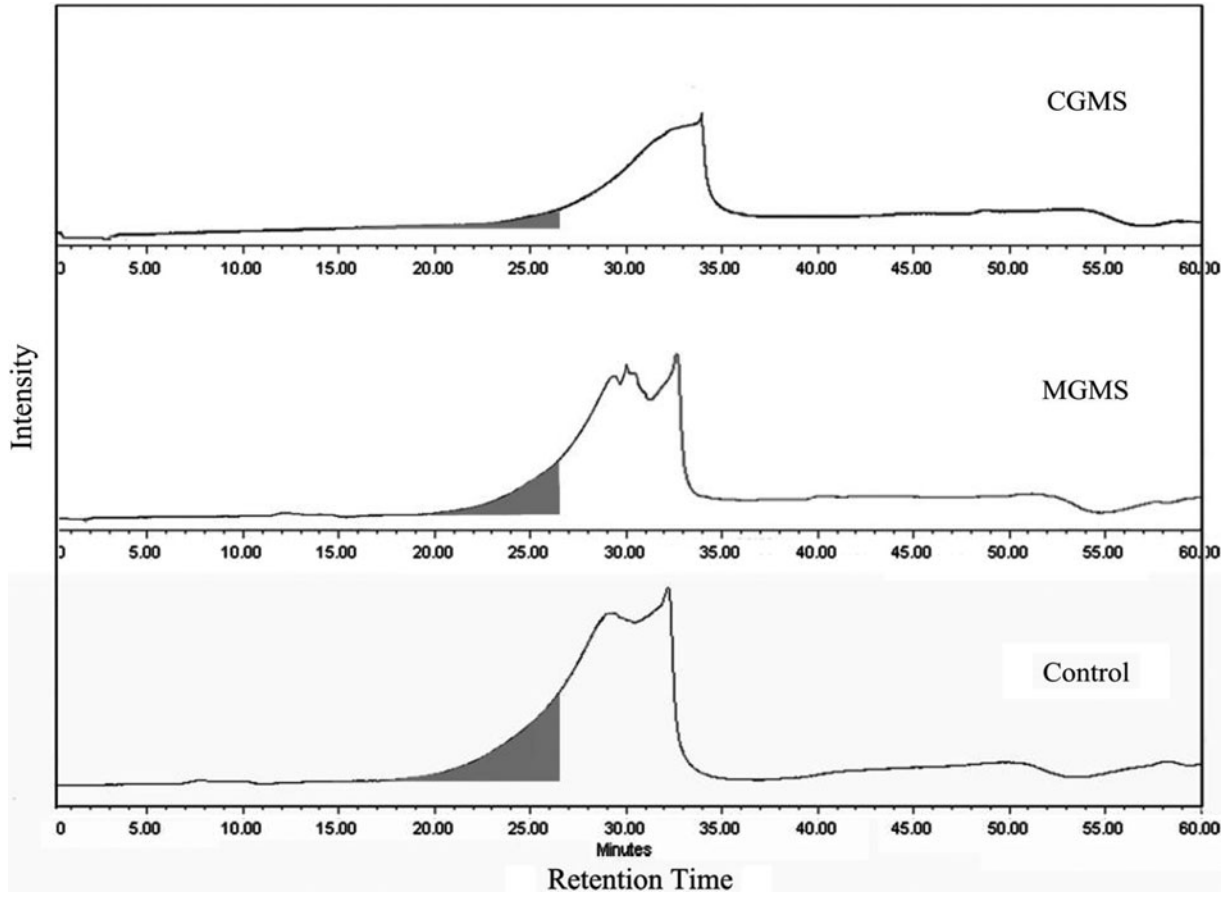

Fig. 6. GPC spectra of the MBR supernatants under a constant flux of 20 L/m^2 h (retention time from 0 to 26.6 min corresponds to MW ≧ 100 kDa).

In the GPC chromatograms of the supernatants from different MBRs, the total area of the peaks indicates the total concentration of soluble and colloidal substances, while the concentration of the fraction of foulants with MW ≧ 100 kDa could be estimated by comparing the corresponding peak area to total area of peaks. To visually show the effect of filter aids, the data were converted according to Eq. (2).

$$y = \frac{x}{\mathrm{TA}^{\mathrm{CTR}}} \tag{2}$$

where x is the calculated peak area corresponding to the fraction of foulants with MW ≧ 100 kDa in different MBRs (grey zone in Fig. 6), $\mathrm{TA}^{\mathrm{CTR}}$ represents the total peak area in CTR chromatograms, and y represents the relative area compared to $\mathrm{TA}^{\mathrm{CTR}}$.

As shown in Table 3, in the CGMS-added MBR, the soluble and colloidal foulants, especially macromolecules, were largely removed through either adsorption or aggregation. This was one of the main reasons behind the significant improvement of permeability at fluxes of 40 L/m^2 h and 20 L/m^2 h. However, flocculation by MGMS was weak, requiring frequent replenishing to maintain. Although the total foulant removal efficiency was not satisfying, the MSGS-MBR demonstrated a smaller grey zone than the control MBR, suggesting that macromolecules falling in the range of >100 kDa were partially eliminated. This could explain the lower fouling rate in the MGMS-added MBR operated at flux of 40 L/m^2 h, which was approximately 4.8 times lower than that in the control MBR (Fig. 3).

3.4. Effect of modified starches on floc morphology and fouling layer porosity

3.4.1. Effect of modified starch on floc foulants

As shown in Table 3, in all MBRs, the gel and cake layers contributed more than 85% of the total resistance. In this study, it was observed that in the control MBR, the flocs quickly deposited onto gel like "footprints", and the formation of the gel layer and cake layer was almost simultaneous. In the CGMS-added MBR, the deposition of flocs onto the membrane surface was not significant in the sustainable filtration period, but at the end of each operation cycle, flocs deposited onto the gel layer resulted in a quick increase in TMP from 10–45 kPa. It is accepted that gel layer resistance is mainly caused by soluble and colloidal substances, while cake resistance is mainly due to the deposition of flocs [16,17]. Thus, the cake resistance was determined by the properties of flocs.

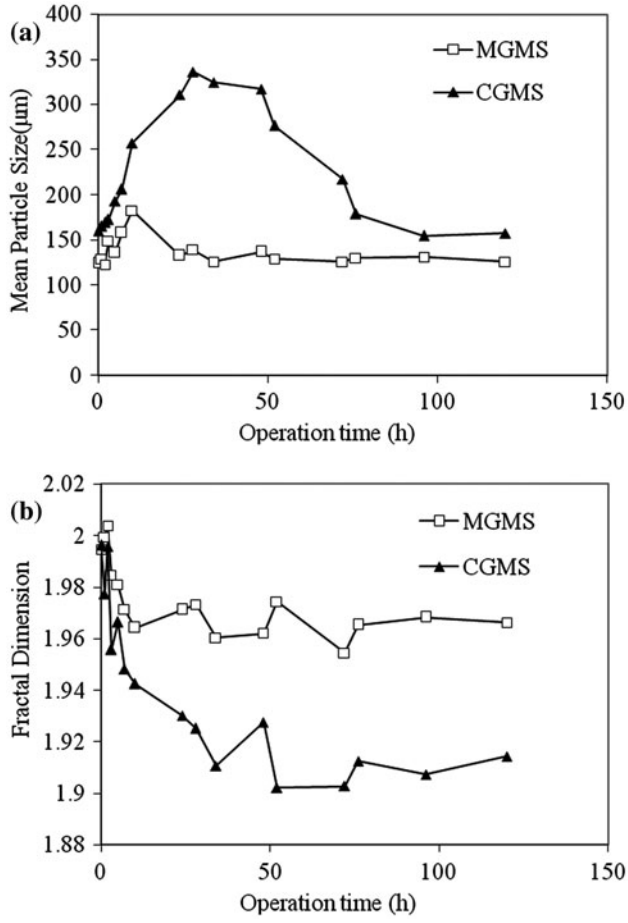

Fig. 7. (a) Profiles of mean particle size in one filtration cycle in filter aid-added MBRs. (b) Profiles of fractal dimension in one filtration cycle in filter aid-added MBRs.

It is frequently reported that the permeability and porosity of the cake layer deposited by flocs is mostly dependent on particle size and fractal dimension. Generally, a higher dp but lower df value indicates a higher porosity cake layer [10,18]. Fractal dimension is an index used to describe particle morphology. With regard to activated sludge flocs, the value of df is in the range of 1.8–2.4 [19]. A higher df value indicates spherical and compact aggregates, while a lower df is related to a loose and linear structure. Fig. 7 shows the profiles of mean floc size (dp) and fractal dimension (df) at the flux of 40 L/m^2 h. A sharp increase in floc size was observed in CGMS-MBRs; the mean floc size increased to approximately three times that of the blank sludge floc after 28 h of operation. Then, a gradual decline in mean floc size occurred with operation time. The flocculation of flocs lasted for more than 60 h. This is another main reason behind the significantly improved permeability in CGMS-MBRs. In comparison, although large aggregates were observed

in MGMS-MBRs, they existed only for several hours. The average floc size in the MGMS-MBR decreases to the same level as the control MBR after approximately 25 h of filtration. Combined with the discussion in Sections 3.3.1. and 3.3.2, it could be concluded that the performance and applicability of filter aids was mostly determined by their effective duration on soluble and floc foulants. Due to shear force and the degradation of the modified starches, the aggregate breakage is an irreversible process in MBRs [20]. Thus, the CGMS demonstrated better performance in short-term filtration than long-term filtration, and the short flocculation time of MGMS required frequent replenishing to maintain, which hindered its industrial MBR application.

3.4.2. The porosity of fouled membranes

It is reported that fouling layer porosity plays an important role in membrane permeability, but it is very difficult to determine the total porosity of fouled membranes. Some studies explain cake porosity by microscopy and image processing [21]. However, in this study, as shown in Fig. 4, the gel and cake layers were very heterogeneous; the porosity of several membrane specimens can hardly represent the total membrane permeability. Therefore, the molecular rejection of the fouled membranes was investigated using GPC to estimate the total effective porosity of the membranes.

Fig. 8 shows the molecular weight distribution of supernatant and permeate samples taken from each MBR simultaneously (all MBRs were operated at a constant flux of 20 L/m^2 h for 7 d). It has been suggested that a membrane with lower porosity would reject more macromolecules. As shown in Fig. 8, in the control MBR, the fouled membrane had almost no rejection of molecules with MW less than 100 kDa. For molecules with MW between 100 and 1,000 kDa, supernatant and permeate curves began to separate. The lower molecular concentration in permeates than in supernatants indicates that molecules with MW larger than 100 kDa could be rejected by the fouled membranes. On the other hand, in the CGMS-MBR, membrane rejection excluded molecules with MW larger than approximately 600 kDa, indicating that loss of membrane porosity is very slow in CGMS-MBR, as the clean membrane "MW cut-off" was also approximately 600 kDa. As for the MGMS-MBR, membrane rejection occurred to molecules with MW larger than approximately 400 kDa. The reduction of porosity was attributed to the cake layer on the membrane surface formed through deposition of larger flocs and/or macromolecules.

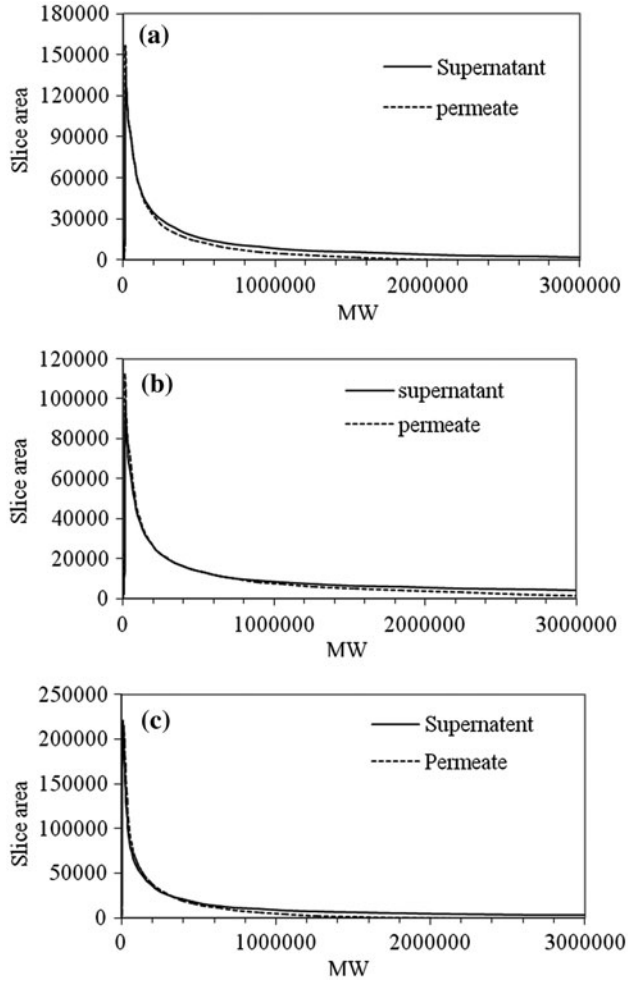

Fig. 8. MW distribution of supernatants and corresponding permeate samples in MBRs. (a) Control MBR; (b) CGMS-added MBR; (c) MGMS-added MBR.

4. Conclusions

The flux enhancement in MBRs with the addition of two starches has been investigated in this study. The main conclusions are as follows:

(1) Addition of modified starches (CGMS and MGMS) in MBRs could lead to reduction of the fouling rate, especially for CGMS. The fouling rate in the CGMS-added MBR was approximately eight times and four times lower than that in the control MBR at the constant operating fluxes of 40 and 20 L/m^2 h, respectively. The good performance of CGMS can be ascribed to the long duration of its effect on both soluble and floc foulants.
(2) The results of GPC and resistance-in-series analysis demonstrated that the filtration

resistance from pore blocking, gel layer and cake layer were all reduced in the filter aid-added MBRs. The reduction of R_b and R_g could be ascribed to the decline in the concentration of protein and polysaccharides (MW ≧ 100 kDa). The decrease in R_c was achieved by increasing dp and decreasing df of the flocs. The detachment of large flocs from the membrane surface in the CGMS-added MBR also helped to alleviate membrane fouling.

(3) When the same permeate volume was attained, the porosity of fouled membranes was in the order of CGMS-added MBR > MGMS-added MBR > Control MBR. The effectiveness of CGMS on fouling reduction seemed to prevent the blocking of membrane pores by soluble and colloidal macromolecules, as well as flocs.

Acknowledgments

This study was financially supported by China Postdoctoral Science Foundation (Grant No: 20110490723).

References

[1] N. Dizge, D.Y. Koseoglu-Imer, A. Karagunduz, B. Keskinler, Effects of cationic polyelectrolyte on filterability and fouling reduction of submerged membrane bioreactor (MBR), J. Membr. Sci. 377 (2011) 175–181.

[2] V. Iversen, L. Bonnet, A. Drews, B. Lesjean, M. Kraume, Can we control the fouling with flux enhancing chemicals, in: "EUROMBRA Workshop" Biofouling in Membrane Systems, Trondheim, 2006.

[3] J. Wu, F. Chen, X. Huang, W. Geng, X. Wen, Using inorganic coagulants to control membrane fouling in a submerged membrane bioreactor, Desalination 197 (2006) 124–136.

[4] W. Guo, H.-H. Ngo, S. Vigneswaran, F. Dharmawan, T.T. Nguyen, R. Aryal, Effect of different flocculants on short-term performance of submerged membrane bioreactor, Sep. Purif. Technol. 70 (2010) 274–279.

[5] V. Iversen, H. Koseoglu, N.O. Yigit, A. Drews, M. Kitis, B. Lesjean, M. Kraume, Impacts of membrane flux enhancers on activated sludge respiration and nutrient removal in MBRs, Water Res. 43 (2009) 822–830.

[6] I. Shih, Y. Van, L. Yeh, H. Lin, Y. Chang, Production of a biopolymer flocculant from *Bacillus licheniformis* and its flocculation properties, Bioresour. Technol. 78 (2001) 267–272.

[7] H. Koseoglu, N. Yigit, V. Iversen, A. Drews, M. Kitis, B. Lesjean, M. Kraume, Effects of several different flux enhancing chemicals on filterability and fouling reduction of membrane bioreactor (MBR) mixed liquors, J. Membr. Sci. 320 (2008) 57–64.

[8] J. Ji, J. Li, J. Qiu, X. Li, Polyacrylamide–starch composite flocculant as a membrane fouling reducer: Key factors of fouling reduction, Sep. Purif. Technol. 131 (2014) 1–7.

[9] J. Ji, J. Qiu, N. Wai, F.-S. Wong, Y. Li, Influence of organic and inorganic flocculants on physical–chemical properties of biomass and membrane-fouling rate, Water Res. 44 (2010) 1627–1635.

[10] S.A. Lee, A.G. Fane, T.D. Waite, Impact of natural organic matter on floc size and structure effects in membrane filtration, Environ. Sci. Technol. 39 (2005) 6477–6486.

[11] F. Meng, H. Zhang, F. Yang, S. Zhang, Y. Li, X. Zhang, Identification of activated sludge properties affecting membrane fouling in submerged membrane bioreactors, Sep. Purif. Technol. 51 (2006) 95–103.

[12] C. Ng, D. Sun, J. Zhang, H. Chua, W. Bing, S. Tay, A. Fane, Strategies to improve the sustainable operation of membrane bioreactors, in: Proceedings of the International Desalination Association Conference, Singapore, 2005.

[13] I.l. Roux, H. Krieg, C. Yeates, J. Breytenbach, Use of chitosan as an antifouling agent in a membrane bioreactor, J. Membr. Sci. 248 (2005) 127–136.

[14] Osmonics Filtration and Separation Spectrum, GE Power & Water, Technical Bulletin. Available from: www.gewater.com/kcpguest/document-library.

[15] J. Ji, J. Qiu, F.-S. Wong, Y. Li, Enhancement of filterability in MBR achieved by improvement of supernatant and floc characteristics via filter aids addition, Water Res. 42 (2008) 3611–3622.

[16] B. Cho, A. Fane, Fouling transients in nominally subcritical flux operation of a membrane bioreactor, J. Membr. Sci. 209 (2002) 391–403.

[17] K.-J. Hwang, C.-L. Hsueh, Dynamic analysis of cake properties in microfiltration of soft colloids, J. Membr. Sci. 214 (2003) 259–273.

[18] Q. Jiang, B.E. Logan, Fractal dimensions of aggregates determined from steady-state size distributions, Environ. Sci. Technol. 25 (1991) 2031–2038.

[19] T. Swaminathand, Effect of DO concentration on biofilm structure and membrane filterability in submerged membrane bioreactor, Water Res. 40 (2006) 2829–2836.

[20] M. Soos, A.S. Moussa, L. Ehrl, J. Sefcik, H. Wu, M. Morbidelli, Effect of shear rate on aggregate size and morphology investigated under turbulent conditions in stirred tank, J. Colloid Interface Sci. 319 (2008) 577–589.

[21] P.-K. Park, C.-H. Lee, S. Lee, Variation of specific cake resistance according to size and fractal dimension of chemical flocs in a coagulation-microfiltration process, Desalination 199 (2006) 213–215.