Effect of sludge characteristics on membrane fouling in membrane bioreactors

Jill Ruhsing Pan [a,*], Yu-Chun Su [b], Chihpin Huang [b], Hsin-Chieh Lee [b]

[a] Department of Biological Science and Technology, National Chiao Tung University, 300 Po-ai Street, Hsinchu 300, Taiwan, ROC
[b] Institute of Environmental Engineering, National Chiao Tung University, Hsinchu 300, Taiwan, ROC

ABSTRACT

In this study, the impact of sludge characteristics on membrane fouling in a submerged membrane bioreactor (MBR) was investigated. Bulking sludge due to excess growth of filamentous bacteria was changed to normal sludge by use of an aerobic selector. Excellent effluent quality was achieved in the MBR regardless of the quality of the sludge of the bioreactor. The removal rates of total organic carbon (TOC) and ammonia nitrogen were maintained at around 98 and 99%, respectively, during the entire experiment. However, serious fouling was observed during the occurrence of the bulking sludge despite having larger particle size distribution. Capillary suction time (CST) was found highly related to the amount of soluble microbial products (SMP) and membrane fouling. Therefore, it could be used as a simple indicator for SMP and fouling potential. Filamentous bacteria were found to produce more SMP including soluble polysaccharides and soluble proteins in the mixed liquor, which resulted in severe fouling. In particular, the release of high concentration of soluble polysaccharides resulted in serious fouling in bulking sludge. Bound EPS which was found similar in the normal sludge and bulking sludge was not the main cause for membrane fouling. In conclusion, solutes in mixed liquor such as SMP are responsible for membrane fouling, which cannot be prevented by increasing shear stress.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Nowadays, membrane technology has been extensively applied to wastewater treatment due to its high effluent quality to meet the requirement by strict legislations and the rapid development in membrane technology. Membrane bioreactor (MBR) has attracted a lot of attention because of the many advantages over the conventional activated sludge process, including excellent treated water quality, small footprint, less sludge production, and flexibility of operation [1,2]. However, membrane fouling results in increasing operation and maintenance costs, which has become one of the most significant factors hindering the widespread application of MBRs [3,4]. Feed water, biomass, membrane and membrane module, and operating conditions are important factors affecting membrane fouling in MBR [3,5]. Imposed flux was found to have great impact on membrane performance [6]. The concept of critical flux was first proposed by Field et al. [7] in 1995 that for microfiltration (MF) there was a flux below which the transmembrane pressure (TMP) would not increase with time of filtration. Therefore, MBR operation at constant flux under a critical value has been recommended for fouling control. Choi and Dempsey [8] proposed that critical flux test should be routinely performed for membrane filtration operation as an operational equivalent of jar testing in conventional water treatment plants.

Extracellular polymeric substances (EPSs) are considered key foulants in MBRs by many researchers [9–12]. EPS is a complex mixture of macromolecular polyelectrolytes including polysaccharides, protein, nucleic acids, and humic compounds. EPS is 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) [13]. According to Laspidou and Rittmann [13] soluble EPS is the same as soluble microbial products (SMP) which is defined as the pool of organic compounds that are released into solution from substrate metabolism and biomass decay [14]. Although EPS has been widely accepted as a major foulant in MBRs, contradictions exist between different laboratories. Some investigations have pointed out that polysaccharides in soluble EPS are the major foulant in MBRs [9,12,15,16]. On the contrary, it has been found that proteins in soluble EPS are the key factor affecting membrane performance [17,18]. In addition, Nagaoka et al. [11] and Nuengjamnong et al. [19] have reported that bound EPS is directly related to membrane fouling. The production of EPS is highly related to operation condition such as sludge retention time (SRT), organic loading rate (OLR), substrate, and temperature [14]. Therefore, it is reasonable to assume that sludge of different characterstics will produce EPS in various quantity and quality which in turn will affect membrane performance in MBRs.

* Corresponding author. Tel.: +886 3 5712121x56977; fax: +886 3 5726463.
E-mail address: jrpan@mail.nctu.edu.tw (J.R. Pan).

In conventional activated sludge processes, the effluent quality is significantly affected by the settleability of sludge. Wastewater with high contents of soluble readily degradable organic materials such as pulp and paper industrial wastewater is more likely to have sludge separation problem because of sludge bulking [20]. Although studies have shown that these sludge separation problems are caused by a variety of filamentous bacteria, there is no general consensus in regard to the occurrence of filamentous overgrowth. Jenkins et al. [21] indicated that factors such as F/M, aeration basin configuration, DO concentration, pH, nutrient concentration influence the occurrence of filamentous bacteria in activated sludge. The most accepted theories for the overgrowth of filamentous bacteria are [20]:

(1) The surface/volume theory: filamentous bacteria have easier access to substrate, oxygen and nutrients than floc-forming bacteria owing to the long filaments.
(2) The kinetic theory: filamentous and floc-forming bacteria have different maximum growth rates.
(3) The accumulation/regeneration theory: floc-forming bacteria have greater capacity of energy storage.
(4) The starvation theory: organisms with higher storage capacity are more resilient under limited substrate conditions.

To control sludge bulking problem several methods have been proposed, including adjustments in sludge return and wastewater feeding points, addition of polymer and coagulant, addition of toxicants [21], and improving reactor design such as plug flow configuration [22] and incorporation of a selector [20,23]. Among them selector has been successfully used to control activated sludge bulking caused by the proliferation of filamentous bacteria. A selector is a separate mixing zone upstream of the aerobic basin in which the recycled activated sludge and influent wastewater are mixed. Three types of selectors are used in dealing with filamentous bulking: aerobic, anoxic and anaerobic. The key in preventing filamentous bulking by selector is the substrate utilization characteristics of the bacteria [24]. Filamentous bacteria have lower half-saturation constant (K_s) and maximum growth rate (μ_{max}) than floc-forming bacteria, which therefore is the main theory of aerobic selector.

By theory, all the biomass in MBRs can be retained by the membrane unit to maintain an excellent effluent quality regardless of the sludge settleability. However, recent researches have demonstrated that bulking sludge caused by overgrowth of filamentous bacteria results in deterioration of membrane performance in MBRs [25–27]. Meng et al. [25] reported that the excess growth of filamentous bacteria formed a non-porous cake layer on the membrane surface which interfered with the membrane filtration. These authors [26,27] further suggested that bulking sludge caused the formation of a dense cake layer on the membrane surface due to the fixation of filamentous bacteria. Chang et al. [28] also reported that bulking sludge has a higher fouling tendency than normal sludge and pinpoint sludge. However, Li et al. [29] had found the opposite that filamentous bacteria had negligible effect on membrane fouling. In most of these studies, the sludge samples in test were taken from different MBR reactors operated under different operation conditions while the filtration resistance tests were performed under constant TMP operation in short filtration duration (4 h) [25–27]. It has been well accepted that sludge from different influent wastewater and different processes (e.g. A/O MBR and sequencing batch MBR) possesses different characteristics, resulting in controversial results as reported in another study [29]. In this study, the sludge for filtration tests was obtained from the MBR unit under long-term operation. The objective of this study is to evaluate the effect of different sludge characteristics (filamentous bacteria and floc-forming bacteria) on membrane fouling under long-term and subcritical flux operation. To examine the fouling tendency and
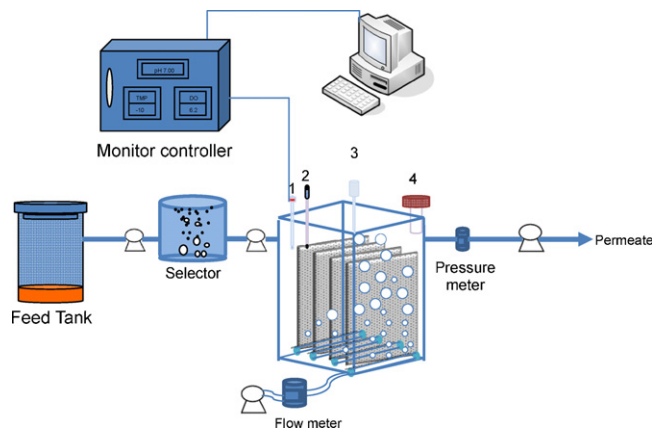

Fig. 1. Schematic of the membrane bioreactor system with an aerobic selector: (1) pH meter; (2) thermometer; (3) DO meter; (4) level sensor.

the fouling mechanism of bulking sludge and normal sludge, an aerobic selector ahead of the MBR unit was installed to shift the bacteria community from filamentous bacteria dominant to floc-forming bacteria dominant. Except the selector all other operation conditions were the same.

2. Materials and methods

2.1. Membrane bioreactor and operation

The experimental MBR system comprised a 30-L aerated tank as the bioreactor with a submerged flat sheet module (Kubota, Japan), which is shown in Fig. 1. The MF membrane is a hydrophilic polypropylene membrane with a mean pore size of 0.4 μm. The synthetic wastewater we used in this study was modified from Ng and Hermanowicz [30]. Although the synthetic wastewater is likely to be more readily biodegradable than the real wastewater, it should not affect the result of our study. Many other researchers have used synthetic wastewater in similar studies based on the same reason [25,29]. The composition of the synthetic wastewater is given in Table 1. The concentrated synthetic municipal wastewater was pumped into the bioreactor continuously at a constant rate to maintain a fixed organic load rate (1.2 kg TOC/m^3 day) to the MBR. Tap water was added to the bioreactor so that the feed flow rate matched the permeate flow rate. The concentrated sewage was diluted sixfold and the chemical oxygen demand (COD) concentration of the final feed was 400 ± 10 mg/L. The seed for the MBR was obtained from a wastewater treatment plant in National Chiao Tung University, Taiwan. An ADAMview software and a Programmable

Table 1
Composition of the synthesized wastewater.

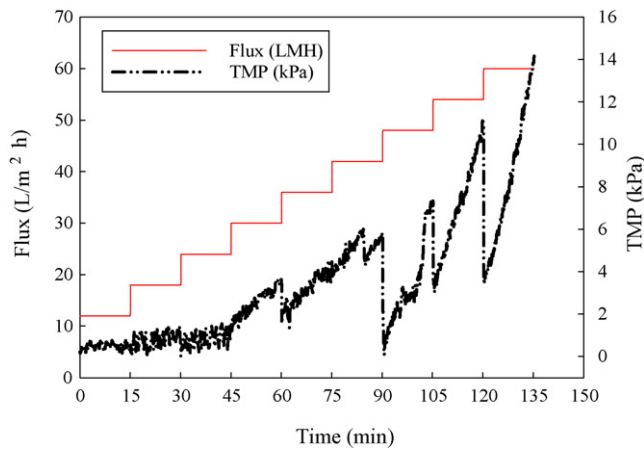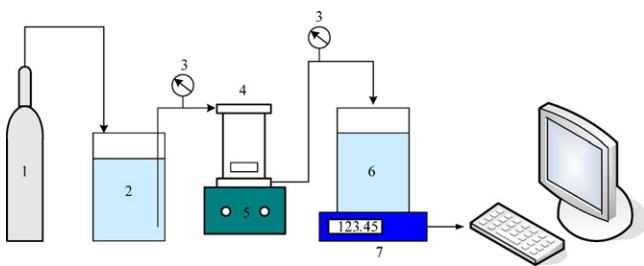| Component	Concentration (mg/L)
Sodium acetate	2527
Starch	150
Beef extract	250
NH_4Cl	670
KH_2PO_4	154
$MgSO_4 \cdot 7H_2O$	355
$CaCl_2$	73
$FeSO_4 \cdot 7H_2O$	87
$CuCl_2 \cdot 2H_2O$	0.35
$MnCl_2 \cdot 4H_2O$	0.63
$ZnSO_4 \cdot 7H_2O$	0.66
$CoCl_2 \cdot 6H_2O$	0.15
$Na_2MoO_4 \cdot 2H_2O$	0.08
H_3BO_3	0.124
KI	0.166

Fig. 2. Critical flux determination by flux-step method.

Fig. 3. Dead-end stirred cell set-up: (1) nitrogen cylinder; (2) pressure meter; (4) stirred cell; (5) magnetic stirrer; (6) permeate vessel; (7) electronic balance.

Logic Controller were used to adjust the flux by feedback control. A desired flow rate was first set. When the flow rate was detected by the permeate flow meter, a signal was sent to the computer and the pump speed was adjusted accordingly to keep the flow rate constant. The pH of the sludge suspension was adjusted to around 7.0 by adding hydrate chloride and sodium hydroxide. In this study all the experiments were carried out after the MBR was acclimated for 3 SRT to ensure the stability of the sludge characteristics. The SRT of the MBR was maintained at 10 days and the mixed liquid of suspended solids (MLSS) stabilized at around 3000 mg/L. After 3 SRT, the critical flux was measured by flux-step method [31]. Step duration and height at 15 min and 6 L/m h were chosen in this study. The initial flux was set at 12 L/m h. After operating for 15 min at the constant flux, the flux was increased by 6 L/m h and operated for another 15 min. The procedure was continued until it reached 60 L/m h. As suggested in Fig. 2, the critical flux was around 24 L/m h, over which TMP apparently increased. To maintain a subcritical operation in this study, the imposed flux used was set at 16 L/m h.

An aerobic selector of 1-L working volume was installed when sludge bulking became serious to change the sludge characteristics. As shown in Fig. 1, the aerobic selector was set up ahead of the MBR. The simulated sewage was fed into the aerobic selector and then, pumped to the MBR.

A dead-end stirred cell system, as shown in Fig. 3, was used to analyze the filtration resistance contributed by individual sludge component as well as the contribution distribution. Sludge was filtered through the membrane by the pressure from a nitrogen cylinder. Permeate was continuously collected until a stable resistance was attained. The feed vessel in Fig. 3 was replenished with clean water to maintain a fixed volume of 200 mL during the filtration. The diameter and the height of the stirred cell are 5.6 and 10 cm, respectively. A stirrer, which is 4.5 cm in length, is suspended

above the membrane to generate shear rate by stirring. Two stirring rates, 400 and 1000 rpm, were selected in this study, to investigate the effect of shear rate on membrane fouling by sludge components. The effective area of the membrane is 24.63 cm^2 and the working volume is 200 mL.

2.2. Analytic methods

2.2.1. Extraction of EPS

Many methods have been proposed for EPS extraction, including heating [32], cation exchange [26], and extraction by EDTA chelating [33] and formaldehyde–NaOH [34]. The formaldehyde–NaOH extraction method was selected in this study since Liu and Fang [34] have indicated that it is most effective and does not cause cell lysis. Ten milliliters of mixed liquor was sampled and centrifuged for 10 min at 4000 rpm at 4 °C (U-320R Boeco, Germany), and then the supernatant was filtered through a 0.45 μm membrane filter (Mixed cellulose ester, Adventec). The permeate contained soluble EPS. The residual pellets were resuspended to 10 mL by using Milli-Q water, followed by the addition of 0.06 mL formaldehyde (63.5%). The suspension was refrigerated at 4 °C for 1 h and then 4 mL of 1N NaOH was added into the suspension. The suspension was refrigerated again at 4 °C for 3 h. The suspension was centrifuged at 20 000 × g for 20 min at 4 °C and then filtered through 0.2 μm filter (Mixed cellulose ester, Adventec) to obtain the bound EPS. The supernatant was further purified by dialysis through a membrane of 3500 molecular weight cut-off at 4 °C for 2 days to remove the extractant.

2.2.2. Analysis of EPS

EPS is a complex mixture of macromolecules including polysaccharides, proteins, nucleic acids, humic acids, etc. In this study, the total EPS is defined as the sum of carbohydrates and proteins because they are the main components of EPS [34]. A phenol–sulfuric acid method [35] was used to quantify polysaccharides in which glucose was the standard. Protein was measured using Bradford protein assay (Bradford, Sigma) according to the manufacturer's protocol, with bovine serum albumin (BSA, Sigma) as the standard.

2.2.3. Determination of particle size distribution of sludge

Particle size distributions of sludge were determined by Mastersizer 2000 particle size analyzer (Malvern, UK) which is based on laser diffraction scattering. The particle size analyzer can measure particles from 0.02 to 2000 μm which meets the requirement of this study. Each sample was measured three times with a standard deviation of less than 3%.

#### 2.2.4. Determination of filtration resistance

Resistance-in-series model was used to measure the resistance. In this study, sludge was separated into suspended solids, colloids and solutes. It was assumed that there was no interaction among these three parts and the total resistance was the sum of the three resistances. Sludge was centrifuged (4000 rpm) at 4 °C and the supernatant was considered to contain colloids and solutes. The supernatant was then filtered through a 0.45 μm membrane (mixed cellulose ester, Advantech) to obtain the solutes. The resistance of individual sludge component was determined by the following equations:

$$R_t = \frac{\Delta P_T}{\mu J_{as}} \tag{1}$$

$$R_m = \frac{\Delta P_T}{\mu J_{iw}} \tag{2}$$

$$R_{as} = R_{ss} + R_{col} + R_{sol} \tag{3}$$
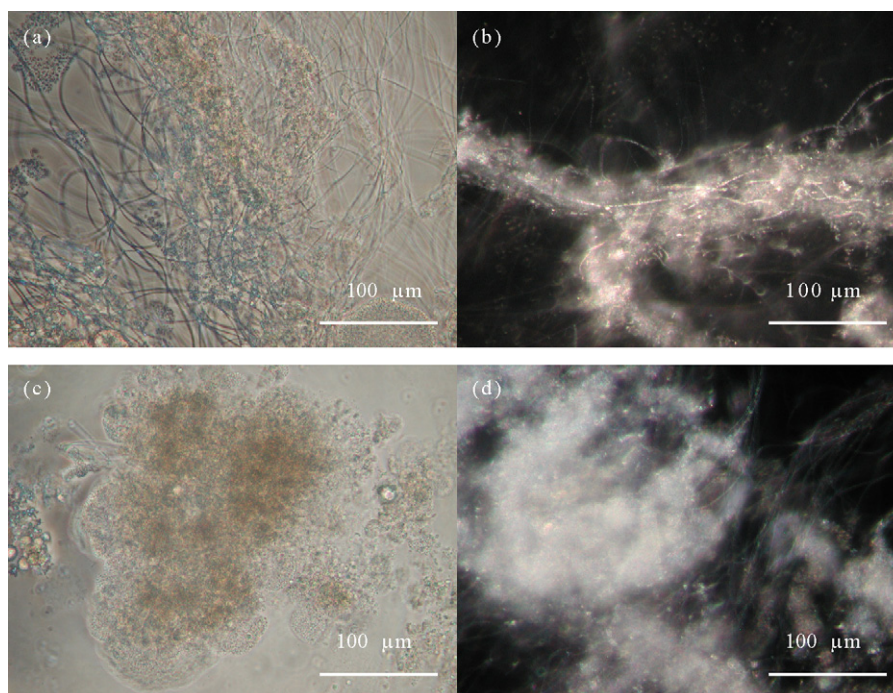
Fig. 4. Microscopic images of sludge flocs: (a) and (b) overgrowth of filamentous bacteria without installation of the selector; (c) and (d) floc-forming bacteria after installation of the selector.

$$R_{as} = R_t - R_m = \frac{\Delta P_T}{\mu J_{as}} = R_m \tag{4}$$

$$R_{col+sol} = \frac{\Delta P_T}{\mu J_{sup}} - R_m \tag{5}$$

$$R_{sol} = \frac{\Delta P_T}{\mu J_{sol}} - R_m \tag{6}$$

where ΔP_T is TMP (Pa), μ is permeate viscosity (Pa s), R_t is total resistance (m^{-1}), R_m is resistance caused by membrane itself (m^{-1}), R_{as} is resistance by sludge (m^{-1}), R_{ss} is resistance by suspended solids (m^{-1}), R_{col} is resistance by colloids (m^{-1}), R_{sol} is resistance by solutes (m^{-1}), J_{iw} is stable flux by filtering Milli-Q water (clean water flux), J_{as} is flux by filtering sludge, J_{sup} is flux by filtering supernatant and J_{sol} is flux by filtering solutes.

First, the Milli-Q water was filtered through the membrane to determine R_m by using Eq. (2). Sludge was then filtered to determine R_{as} by using Eq. (4) after a stable flux was reached. Supernatant and solutes were filtered through and the $R_{col+sol}$ and R_{sol} were determined by using Eqs. (5) and (6), respectively. The difference between $R_{col+sol}$ and R_{sol} was R_{col} (subtract Eq. (6) from Eq. (5)). Once R_{sol} and R_{col} are known, R_{ss} can be calculated by Eq. (3).

2.2.5. Fourier-transform infrared spectrometer (FTIR)

Attenuated total reflectance–FTIR (ATR–FTIR) (Bomem DA8.3, Canada) was used to characterize foulant on the membrane surface. Samples were prepared in $2\,cm \times 2\,cm$ rectangles and dried at a vacuum box overnight. Samples were examined to a resolution of $4\,cm^{-1}$.

2.2.6. Analysis of other parameters

MLSS was measured following the standard method [36]. TOC was measured using a TOC analyzer (TOC-5000A, Shimadzu). Each TOC sample was measured at least two times with a standard deviation of less than 5%. Ammonia nitrogen was measured using a spectrophotometer (DR/4000U, Hach) according to salicylate method (method 10031). All the samples for TOC and ammonia nitrogen measurements were filtered through a 0.45 μm mem-

brane filter first (mixed cellulose ester, Adventec). Capillary suction time was determined to evaluate the filterability of sludge. Five milliliters of sludge was sampled from the bioreactor and the CST (304B CST, Triton) was measured immediately. Each CST measurement was performed at least three times with a standard deviation of less than 5%.

3. Results and discussion

3.1. Performance of membrane bioreactor treatment under different sludge condition

In the beginning of the MBR operation, sludge bulking due to overgrowth of filamentous bacteria was observed. The excessive growth of filamentous bacteria when sludge bulking became serious was clearly shown in Fig. 4a and b. Ideally, the sludge contains both filamentous bacteria and floc-forming bacteria. When the two are in balance, the filamentous bacteria act as the backbone of activated sludge flocs without causing sludge bulking [21]. Since the majority of the nutrient compounds in the simulated feed are readily biodegradable, which are much more readily accessible to the filamentous bacteria. As a result, the filamentous bacteria became the dominant species. To correct this problem an aerobic selector was installed. In this way the sludge was successfully shifted from filamentous bacteria to floc-forming bacteria as seen in Fig. 4c and d.

In conventional activated sludge process, sludge settleability is the key factor in maintaining effluent quality. Sludge bulking which is usually due to overgrowth of filamentous bacteria often deteriorates the performance of activated sludge. Fig. 5 shows the removal of TOC and ammonia nitrogen. The selector was installed after the MBR was operated for 20 days. Despite the serious sludge bulking caused by overgrowth of filamentous bacteria, the effluent quality remained the same, as shown in Fig. 5a and b. The average TOC and NH_3-N in the MBR influent was 158 ± 20.0 and 32.0 ± 0.67 mg/L, respectively, over the entire period of operation. Nearly 98% of the organics were removed by the MBR treatment
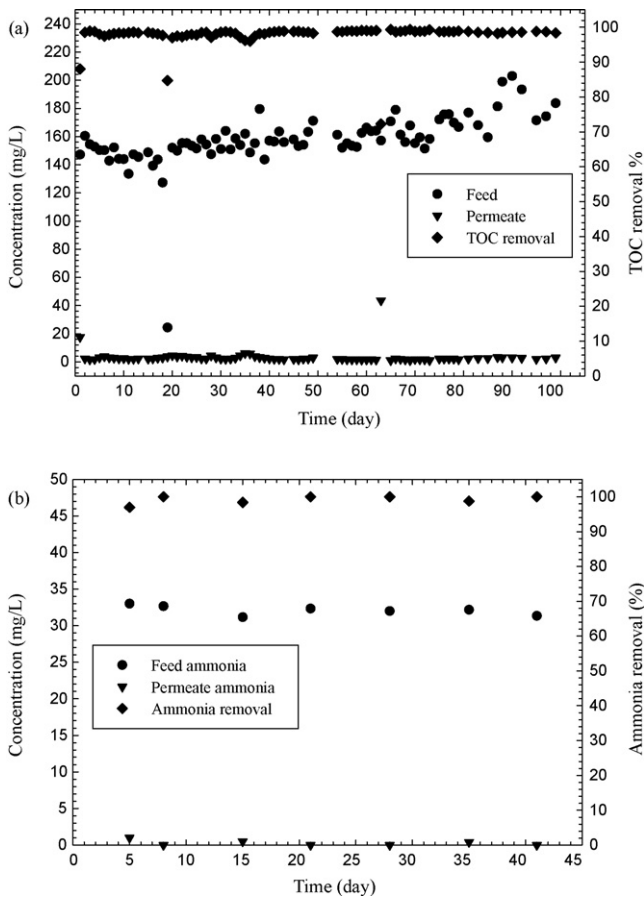
Fig. 5. (a) TOC and (b) ammonia nitrogen removals by MBR treatment in bulking sludge and normal sludge.

regardless of the sludge characteristics (Fig. 5a). Biological nitrification was also excellent. Almost 99% of ammonia nitrogen was nitrified during the experiment. The NH$_3$-N of the effluent was reduced to 0.24 ± 0.37 mg/L even when sludge bulking occurred (Fig. 5b). The result indicates that membrane bioreactor is a reliable wastewater treatment process. The excellent pollutant removal renders MBR a promising process for wastewater reuse as well as treatment of polluted surface water for drinking water supplies [37].

3.2. Effect of sludge properties on membrane fouling

Bulking sludge, on the other hand, had significant impact on membrane fouling, as illustrated in Fig. 6a. In the initial period of operation, the TMP profile exhibited a typical two-stage pattern under subcritical flux operation when filamentous bacteria started to become dominant. A slow and progressive membrane fouling was observed in the initial 100 h followed by a sudden TMP increase. After the TMP reached −60 kPa, the membrane was chemically cleaned by 0.5% sodium hypochlorite for 2 h. However, the membrane fouled right after the membrane cleaning with a fouling rate of up to 28.7 kPa/h. Therefore, frequent membrane cleaning was performed afterwards. The TMP profile of the MBR after the aerobic selector was installed was shown in Fig. 6b. Membrane fouling decreased gradually and the TMP profile changed completely when floc-forming bacteria were dominant in the bioreactor. The TMP profile changed to a typical two-stage pattern in subcritical flux operation. The first stage of slow fouling rate lasted for about 200 h before the second stage of TMP jump appeared. The fouling rate was greatly reduced to 0.03 kPa/h in the progressive and slow
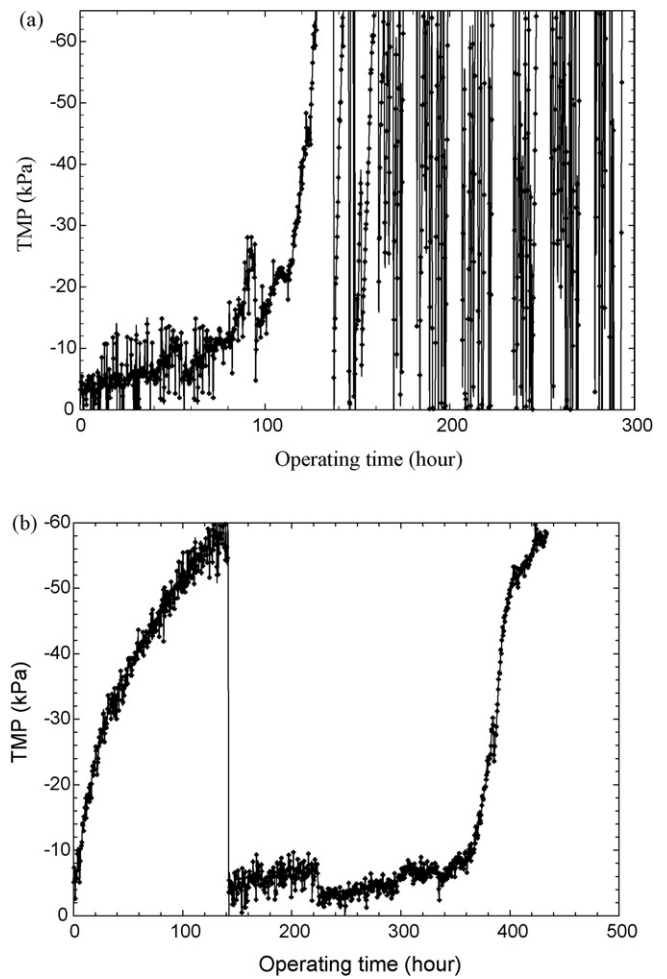

Fig. 6. TMP profiles of different sludge properties: (a) filamentous bacteria and (b) floc-forming bacteria.

fouling stage. After the floc-forming bacteria stabilized and became steadily dominant in the bioreactor, the fouling rate became steady and relatively slow.

Particle size distributions of normal sludge and bulking sludge are shown in Fig. 7, in which the flocs of normal sludge are obviously larger than that of bulking sludge. The D (4,3) volume weighted
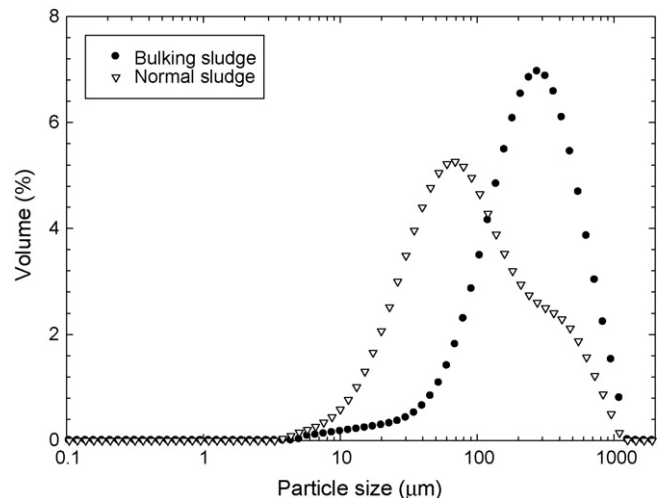

Fig. 7. Particle size distribution of normal sludge and bulking sludge.

Table 2
Comparison of sludge characteristics between normal sludge and bulking sludge.

	Supernatant TOC (mg/L)	CST (s)	Soluble EPS[a] (mg/L)	Cell-bound EPS[a] (mg/g MLSS)
Normal sludge	5 ± 2	16 ± 2	25 ± 16	130 ± 13
Bulking sludge	66 ± 9	30 ± 28	145 ± 37	133 ± 20

[a] The concentration of EPS is expressed as the sum of proteins and polysaccharides as BSA and glucose, respectively.

mean of bulking sludge and normal sludge was 326 and 164 μm, respectively. The result is consistent with the findings of other studies [25,27,29], all of them reported that bulking sludge caused by overgrowth of filamentous bacteria had larger particle size distribution. It contradicts the common knowledge that smaller particles are generally more easily to deteriorate membrane filtration [5,38]. Therefore, the severe fouling in bulking sludge cannot be explained by particle size alone.

The distinct TMP profiles of normal sludge (floc-forming bacteria) and bulking sludge (filamentous bacteria) must be answered by the difference in sludge characteristics, which is summarized in Table 2. The supernatant TOC, representing SMP in mixed liquor [38], was about 12 times higher than that of normal sludge. The soluble EPS of bulking sludge was about six times higher. It strongly implies that SMP or other organic compounds in bulking sludge might be responsible for the higher fouling rate. On the contrary, the concentrations of cell-bound EPS in normal sludge and bulking sludge were about the same. The detail will be discussed in the next section. The CST which is commonly used to represent the filterability of activated sludge. The CST of the bulking sludge was significantly larger than that of normal sludge, which echoes the findings by Wang et al. [39] and Wu et al. [40] that CST values are positively correlated to membrane fouling. Rosenberger and Kraume [41] have also reported that soluble EPS affected the filterability of activated sludge most significantly, in agreement with our result.

3.3. Effect of sludge properties on EPS

Since EPS has been widely accepted as the major foulant in MBR [9–12], the EPS components in the mixed liquor were monitored and compared with the performance of the MBR operation for fouling study. Four components were monitored: soluble polysaccharides, soluble proteins, cell-bound polysaccharides and cell-bound proteins. In this study, total soluble EPS or SMP is the sum of soluble polysaccharides and soluble proteins. And the sum of cell-bound polysaccharides and cell-bound proteins represents the total cell-bound EPS. Fig. 8 compares the concentration of cell-bound and soluble EPS in various sludge conditions. There was no significant difference in the production of cell-bound EPS between bulking and normal sludge. On the other hand, much more soluble polysaccharides and soluble proteins were produced in bulking sludge, especially the soluble polysaccharides. Higher membrane fouling caused by overgrowth of filamentous bacteria seems to relate to the increased amount of SMP in bulking sludge, which echoes the observations by other researches that soluble polysaccharides and soluble proteins in SMP influence the membrane performance in MBR [9,12,15–18]. However, Meng et al. [25–27] later made an observation that contradicts our results. They concluded that severe membrane fouling caused by excessive growth of filamentous bacteria might be caused by the production of more cell-bound EPS. The result differed from our observation, possibly because that they obtained the sludges from different MBR processes. Lately, Li et al. [29] also reported that cell-bound EPS was the major contributor to membrane fouling. They pointed out that filamentous bacteria have no significant influence on membrane fouling. The contradicting findings could come from the difference in operation conditions or the difference in filamentous species. To

verify the cause for severe fouling associated with bulking sludge, the foulants on membrane surface were identified by FTIR. FTIR spectra of fresh and fouled membranes are shown in Fig. 9 to show the functional groups of the foulants on the membrane surface. The peaks at wave number 1647 and 1533 cm^{-1} are assigned to the amide-I and amide-II bands [9,42], respectively. The absorption band at 3286 cm^{-1} is N–H stretching. The peak at wave number 1041 cm^{-1} is assigned to bond vibrations of polysaccharides [43] and the peak at wave number 2925 cm^{-1} is also a character of polysaccharides. The result suggests that foulants on the membrane surface mainly consists of polysaccharides and proteins. The FTIR spectrum of the fouled membrane in this study is very similar to those of SMP-fouled membranes [40], which further confirms that severe fouling in bulking sludge caused by overgrowth of filamen-
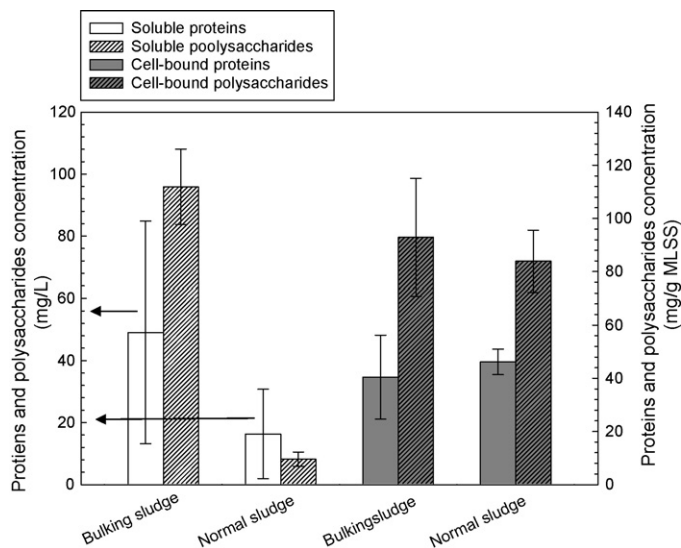
Fig. 8. Comparison of EPS components in filamentous bacteria and floc-forming bacteria.
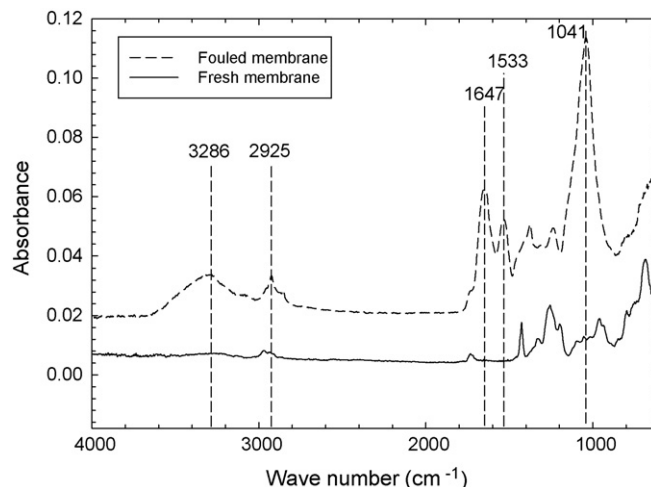
Fig. 9. FTIR spectra of fresh and fouled membranes.

Table 3
Contribution of sludge fraction to resistance at different stirring rate.

	Stirring rate (rpm)			
	400		1000	
	m^{-1}	%[a]	m^{-1}	%[a]
[b]R_{ss}	$4.60 \pm 0.04 \times 10^{11}$	27.33	0	0
[b]R_{col}	$6.15 \pm 0.02 \times 10^{11}$	36.52	$2.55 \pm 0.02 \times 10^{11}$	25.22
[b]R_{sol}	$6.09 \pm 0.14 \times 10^{11}$	36.15	$7.55 \pm 0.09 \times 10^{11}$	74.78

[a] Percentage in total resistance (%).
[b] Membrane resistance (R_{mem}) = $3.99 \pm 1.32 \times 10^{10}$.

tous bacteria is due to the attachment of SMP on the membrane surface.

3.4. Effect of sludge fractions on membrane fouling

To provide more information concerning the contradictory results among other studies [25–28] and ours, fouling by sludge components was also investigated. Sludge was separated into three fractions by particle size: suspended solids, colloids and solutes. The experiment was first operated at two stirring rates to create different shear forces for the evaluation of the contributions of different sludge fractions on membrane fouling. Table 3 illustrates the resistance of sludge fractions at different stirring rates. At low shear stress (stirring rate of 400 rpm), the major fouling contributors are colloids and solutes. The resistance contributed by colloids and solutes were 36.52 and 36.15%, respectively. When the stirring rate was increased to 1000 rpm, the resistance contributed by suspended solids disappeared completely while the majority of resistance came from the solutes. As shown in Table 3, increasing the stirring rate increased the contribution of solutes to fouling. The finding of this study also proved that different operation conditions might lead to different results, which might explain the disagreement between studies [44–47]. Defrance et al. [46] and Bae and Tak [47] concluded that suspended solids are the main contributor to membrane fouling because their systems were operated under relatively high flux and low crossflow. On the other hand, Wisniewski and Grasmick [45] reported differently, that solutes are the main contributor to membrane fouling since their system was operated under high crossflow, similar to our high shear stress conditions.

At high shear force, smaller components, namely, colloids and solutes, dictated the resistance. Back transport caused by Brownian diffusion is dominant for small particles and at low shear stress, while back transport caused by shear-induced diffusion and inertial lift increase with shear rate and is proportional to particle size [48]. As a result, the shear-induced diffusion and inertial lift of larger particles such as suspended solids and colloids keeps them away from the membrane, resulting in reduced resistance. In contrast, shear-induced diffusion and initial lift is negligible for small molecules. Back transport of small molecules is caused by Brownian diffusion. In membrane filtration when the drag force due to filtration balances the back transport, membranes are free of deposit. In subcritical flux, the back transport was equal or greater than the permeation drag, therefore, no sharp TMP increase would be observed. Table 3 implies that when the membrane was operated at subcritical flux, larger particles such as suspended solids would not deposit on the membrane to form a sludge cake. On the other hand, smaller particles such as soluble EPS and other macromolecules would be continuously attracted onto the membrane regardless of the strength of the shear force. TMP jump will be observed when local flux exceeds critical flux. The result is in agreement with the results in Section 3.3 that SMP dominated the membrane fouling in MBR, and, therefore, membrane fouling will occur eventually even though the MBR is operated under subcritical condition.

4. Conclusions

The effect of sludge characteristics of normal sludge and bulking sludge on membrane fouling in the MBR was investigated in this study. Overgrowth of filamentous bacteria was founded to be the main cause of sludge bulking. By use of an aerobic selector the sludge was successfully shifted from bulking sludge to normal sludge. The result showed that:

1. Even the MBR was operated under severely sludge bulking, the MBR could maintain excellent effluent. The removal rates of TOC and ammonia nitrogen were up to 98 and 99%, respectively, regardless of the changes of sludge characteristics.
2. Although the particle size distribution of the bulking sludge was higher than that of the normal sludge, the bulking sludge resulted in much more serious fouling in the MBR compared with the normal sludge. The higher membrane fouling caused by bulking sludge mainly resulted from the higher SMP released form filamentous bacteria. CST correlated well with SMP and it could be used as a good indicator of SMP and fouling potential.
3. The concentrations of cell-bound polysaccharides and cell-bound proteins were similar in bulking sludge and normal sludge. Bound EPS were not the main foulants of MBR in this study. In bulking sludge, filamentous bacteria were observed to release higher soluble polysaccharides and soluble proteins into the mixed liquor and induced the sever membrane fouling. Especially the high concentration of soluble polysaccharides was found to attach on the membrane surface and cause membrane fouling.
4. Shear force was found to only influence the attachment of larger particles on the membrane surface. Because increasing shear force on the membrane surface can increase the back transport. The back transport caused by shear-induced diffusion and inertial lift was proportional to particle size. However, the back transport would have limited effect for smaller particles such as smaller colloids and solutes in the mixed liquor when increasing shear force. This was the cause of importance of SMP for membrane fouling in MBR under subcritical flux operation.

Acknowledgements

References

[1] C. Visvanathan, R.B. Aim, K. Parameshwaran, Membrane separation bioreactors for wastewater treatment, Crit. Rev. Environ. Sci. Technol. 30 (2000) 1–48.
[2] T. Stephenson, S. Judd, B. Jefferson, K. Brindle, Membrane Bioreactors for Wastewater Treatment, IWA Publishing, London, 2000.
[3] P. Le-Clech, V. Chen, A.G. Fane, Fouling in membrane bioreactors used in wastewater treatment, J. Membr. Sci. 284 (2006) 17–53.
[4] W. Yang, N. Cicek, J. Ilg, State-of-the-art of membrane bioreactors: Worldwide research and commercial applications in North America, J. Membr. Sci. 270 (2006) 201–211.
[5] I.S. Chang, P. Le-Clech, B. Jefferson, S. Judd, Membrane fouling in MBRs for wastewater treatment, J. Environ. Eng. ASCE 128 (11) (2002) 1018–1029.
[6] H. Nagaoka, S. Yamanishi, A. Miya, Modeling of biofouling by extra-cellular polymers in a membrane separation activated sludge, Water Sci. Technol. 38 (4–5) (1998) 497–504.
[7] R.W. Field, D. Wu, J.A. Howell, B.B. Gupta, Critical flux concept for microfiltration fouling, J. Membr. Sci. 100 (1995) 259–272.
[8] K.Y.J. Choi, B.A. Dempsey, Bench-scale evaluation of critical flux and TMP in low-pressure membrane filtration, J. Am. Water Assoc. 97 (2005) 134–143.
[9] K. Kimura, N. Yamato, H. Yamamura, Y. Watanabe, Membrane fouling in pilot-scale membrane bioreactors (MBRs) treating municipal wastewater, Environ. Sci. Technol. 39 (2005) 6293–6299.
[10] B.D. Cho, A.G. Fane, Fouling transients in nominally sub-critical flux operation of a membrane bioreactor, J. Membr. Sci. 209 (2002) 391–403.

[11] H. Nagaoka, S. Ueda, A. Miya, Influence of bacterial extracellular polymers on the membrane separation activated sludge process, Water Sci. Technol. 34 (9) (1996) 165–172.
[12] J. Zhang, H.C. Chua, J. Zhou, A.G. Fane, Factors affecting the membrane performance in submerged membrane bioreactors, J. Membr. Sci. 284 (2006) 54–66.
[13] C.S. Laspidou, B.E. Rittmann, A unified theory for extracellular polymeric substances, soluble microbial products, and active and inert biomass, Water Res. 36 (2002) 2711–2720.
[14] D.J Barker, D.C. Stuckey, A review of soluble microbial products (SMP) in wastewater treatment systems, Water Res. 33 (1999) 3063–3082.
[15] S. Rosenberger, H. Evenblij, S. te Poele, T. Wintgens, C. Laabs, The importance of liquid phase analyses to understand fouling in membrane assisted activated sludge processes-six case studies of different European research groups, J. Membr. Sci. 263 (2005) 113–126.
[16] F. Fan, H. Zhou, H. Husain, Identification of wastewater sludge characteristics to predict critical flux for membrane bioreactor processes, Water Res. 40 (2006) 205–212.
[17] T. Mukai, K. Takimoto, T. Kohno, M. Okada, Ultrafiltration behaviour of extracellular and metabolic products in activated sludge system with UF separation process, Water Res. 34 (2000) 902–908.
[18] M.E. Hernandez Rojas, R. Van Kaam, S. Schetrite, C. Albasi, Role and variations of supernatant compounds in submerged membrane bioreactor fouling, Desalination 179 (2005) 95–107.
[19] C. Nuengjamnong, J.H. Kweon, J. Cho, C. Polprasert, K.H. Ahn, Membrane fouling caused by extracellular polymeric substances during microfiltration processes, Desalination 179 (2005) 117–124.
[20] E. Dalentoft, P. Thulin, The use of aerobic selectors in activated sludge systems for treatment of wastewater from the pulp and paper industry, Water Sci. Technol. 35 (2–3) (1997) 181–188.
[21] D. Jenkins, M.G. Richard, G.T. Daigger, Manual on the Causes and Control of Activated Sludge Bulking and Foaming, Second ed., Lewis publishers, Michigan, 1993.
[22] D. Mamais, A. Andreadakis, C. Noutsopoulos, C. Kalergis, Causes of, and control strategies for, *Microthrix parvicella* bulking and foaming in nutrient removal activated sludge systems, Water Sci. Technol. 37 (4–5) (1998) 9–17.
[23] L. Prendl, H. Kroiβ, Bulking sludge prevention by an aerobic selector, Water Sci. Technol. 38 (8–9) (1998) 19–27.
[24] Y.C. Tsai, C.M. Lee, Substrate utilization characteristics of the predominant filamentous and floc-forming bacteria isolated from a chemical fiber factory wastewater treatment plant, Water Sci. Technol. 37 (4–5) (1998) 291–295.
[25] F. Meng, H. Zhang, F. Yang, Y. Li, J. Xiao, X. Zhang, Effect of filamentous bacteria on membrane fouling in submerged membrane reactor, J. Membr. Sci. 272 (2006) 161–168.
[26] F. Meng, F. Yang, Fouling mechanisms of deflocculated sludge, normal sludge, and bulking sludge in membrane bioreactor, J. Membr. Sci. 305 (2007) 48–56.
[27] F. Meng, F. Yang, J. Xiao, H. Zhang, Z. Gong, A new insight into membrane fouling mechanism during membrane filtration of bulking and normal sludge suspension, J. Membr. Sci. 285 (2006) 159–165.
[28] I.S. Chang, C.H. Lee, K.H. Ahn, Membrane filtration characteristics in membrane-coupled activated sludge system: the effect of floc structure on membrane fouling, Sep. Sci. Technol. 34 (1999) 1743–1758.
[29] J. Li, Y. Li, D.G. Ohandja, F. Yang, F.S. Wong, H.C. Chua, Impact of filamentous bacteria on properties of activated sludge and membrane-fouling rate in a submerged MBR, Sep. Purif. Technol. 59 (2008) 238–243.
[30] H.Y. Ng, S.W. Hermanowicz, Membrane bioreactor operation at short solids retention times: performance and biomass characteristics, Water Res. 39 (2005) 981–992.
[31] P. Le-Clech, B. Jefferson, I.S. Chang, S.J. Judd, Critical flux determination by the flux-step method in a submerged membrane bioreactor, J. Membr. Sci. 227 (2003) 81–93.
[32] X.Y. Li, S.F. Yang, Influence of loosely bound extracellular polymeric substances (EPS) on the flocculation, sedimentation and dewaterability of activated sludge, Water Res. 41 (2007) 1022–1030.
[33] G.P. Sheng, H.Q. Yu, Z. Yu, Extraction of extracellular polymeric substances from the photosynthetic bacterium *Rhodopseudomonas acidophila*, Appl. Microbiol. Biotechnol. 67 (2005) 125–130.
[34] H. Liu, H.H.P. Fang, Extraction of extracellular polymeric substances (EPS) of sludges, J. Biotechnol. 95 (2002) 249–256.
[35] M. Dubois, K.A. Gilles, J.K. Hamilton, P.A. Rebers, F. Smith, Calorimetric method for determination of sugars and related substances, Anal. Chem. 28 (1956) 350–356.
[36] APHA, Standard Methods for the Examination of Water and Wastewater, 20th ed., American Public Health Association, Washington, DC, 1998.
[37] X.Y. Li, H.P. Chu, Membrane bioreactor for the drinking water treatment of polluted surface water supplies, Water Res. 37 (2003) 4781–4791.
[38] S. Liang, C. Liu, L. Song, Soluble microbial products in membrane bioreactor operation: behaviors, characteristics, and fouling potential, Water Res. 41 (2007) 95–101.
[39] Z. Wang, Z. Wu, G. Yu, J. Liu, Z. Zhou, Relationship between sludge characteristics and membrane flux determination in submerged membrane bioreactors, J. Membr. Sci. 284 (2006) 87–94.
[40] Z. Wu, Z. Wang, Z. Zhou, G. Yu, G. Gu, Sludge rheological and physiological characteristics in a pilot-scale submerged membrane bioreactor, Desalination 212 (2007) 152–164.
[41] S. Rosenberger, M. Kraume, Filterability of activated sludge in membrane bioreactors, Desalination 146 (2002) 373–379.
[42] C. Jarusutthirak, G. Amy, Role of soluble microbial products (SMP) in membrane fouling and flux decline, Environ. Sci. Technol. 40 (2006) 969–974.
[43] A. Omoike, J. Chorover, Spectroscopic study of extracellular polymeric substances form *Bacillus subtilis*: aqueous chemistry and absorption effects, Biomacromolecules 5 (2004) 1219–1230.
[44] E.H. Bouhabila, R.B. Aim, H. Buisson, Fouling characterisation in membrane bioreactors, Sep. Purif. Technol. 22–23 (2001) 123–132.
[45] C. Wisniewski, A. Grasmick, Floc size distribution in a membrane bioreactor and consequences for membrane fouling, Colloids Surf. A 138 (1998) 403–411.
[46] L. Defrance, M.Y. Jaffrin, B. Gupta, P. Paullier, V. Geaugey, Contribution of various constituents of activated sludge to membrane bioreactor fouling, Bioresour. Technol. 73 (2000) 105–112.
[47] T.H. Bae, T.M. Tak, Interpretation of fouling characteristics of ultrafiltration membranes during the filtration of membrane bioreactor mixed liquor, J. Membr. Sci. 264 (2005) 151–160.
[48] G. Belfort, R.H. Davis, A.L. Zydney, The behavior of suspensions and macromolecular solutions in crossflow microfiltration, J. Membr. Sci. 96 (1994) 1–58.