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博士論文

生物薄膜系統中污泥特性對薄膜積垢之影響及二氧化鈦複合薄膜減緩積垢之研究

Effect of sludge characteristics on membrane fouling in MBRs and fouling mitigation by TiO_2-composite membrane

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摘要

生物薄膜程序為近年廢水生物處理程序中一嶄新之研究，由於利用薄膜單元取代傳統的沉澱池，使其具有較小的佔地面積、較少的汙泥產量及優良的出流水質等優勢。然而，生物薄膜中薄膜的阻塞卻限制其廣泛的應用，因為薄膜的阻塞會導致出水通量衰減、增加薄膜的清洗和更換次數，使操作成本增加。儘管已有許多研究針對薄膜積垢的機制及預防進行廣泛地探討，但其研究結果卻往往顯示出不同的結果。因為污泥及進流水的複雜特性及來源不同，或是不相同的薄膜模組及操作情況往往會導致此不一致的結論。薄膜積垢肇因於污泥和薄膜間的交互作用而導致汙泥中不同的成份吸附或沉積於薄膜表面。因此，汙泥的特性、薄膜的特性及其水力情況往往為導致薄膜積垢的關鍵因素。

因此，本研究主要針對不同的污泥特性對薄膜積垢進行探討。研究利用一好氧性選種槽將污泥中的主要菌相由絲狀菌轉變為膠羽形成菌，藉此探討其不同污泥特性下的薄膜過濾特性。結果顯示，儘管污泥膨化嚴重，生物薄膜系統仍可維持優良的出流水水質。實驗過程中，總有機碳和氨氮的去除率皆分別維持 98% 和 99%的高去除率。然而，即使絲狀菌比膠羽形成菌有較大的粒徑分布，當絲狀菌大量增生而導致污泥膨化時，薄膜積垢情況嚴重。研究發現，當絲狀菌大量增生時，污泥中的溶解性微生物產物大量增加，尤其是當中的多醣類含量。由傅立葉紅外線光譜結果顯示，溶解性微生物產物中的多醣類和蛋白質為導致此嚴重積垢發生的主因。污泥膠羽上的胞外聚合物並非造成此嚴重積垢的原因。

污泥停留時間的不同導致不同的污泥特性，進而對薄膜積垢造成重要的影響。本研究將污泥停留時間設定為 10、30 及 60 天，發現污泥停留時間越短薄膜積垢越嚴重。污泥停留時間為 10 天的生物薄膜系統，其薄膜積垢遠比操作於 30 及 60 天的嚴重許多，主要因為污泥於污泥停留時間為 10 天的生物薄膜分泌較多的溶解性微生物產物。然而，污泥停留時間 30 及 60 天的生物薄膜系統，其不同的積垢程度主要是因為膠羽中的胞外聚合物不同所導致。溶解性微生物產物於較短的污泥停留時間中，有較大的分子量分布。動態膜在過濾開始的 1 小時內便穩定形成於薄膜表面，進而過濾篩除污泥中的較大分子量的溶解性物質。而此形成於薄膜表面的動態膜並不會造成明顯的積垢現象。泥停留時間為 10 天的生物薄

膜系統中，溶解性微生物產物多為親水性物質，且大部分被薄膜截留於反應槽中。此親水性物質多為多醣類，並為主要的積垢物。

為了減緩薄膜積垢的發生，本研究利用二氧化鈦合成複合薄膜，用以降低薄膜積垢的速率。研究以低溫中性共沉澱凝膠法方式合成奈米級二氧化鈦，並利用含浸法合成二氧化鈦複合薄膜。此外，並利用文獻中所採用的酸性二氧化鈦溶液來合成二氧化鈦複合薄膜，探討並比較以此方法所合成之複合薄膜的抗積垢能力。結果顯示，不管以何種二氧化鈦合成之複合薄膜皆可降低薄膜積垢速率，主要原因為增加薄膜表面的親水性。適當的二氧化鈦含量對複合薄膜的抗積垢能力有很大的影響，雖然較多的二氧化鈦可以增加薄膜的親水性，但過多的二氧化鈦卻會導致薄膜孔洞的堵塞，增加過濾的阻抗。由超音波清洗薄膜的結果顯示，此複合薄膜的二氧化鈦可牢固的附著於薄膜表面，不會因清洗而大量流失二氧化鈦。

關鍵字：胞外聚合物、積垢、生物薄膜、溶解性微生物產物、二氧化鈦。

Effect of sludge characteristics on membrane fouling in MBRs and fouling mitigation by TiO_2-composite membrane

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Abstract

Membrane bioreactor (MBR) processes, in which membrane filtration is combined with biological degradation for biomass separation, have attracted great attention recently because of their advantages over conventional activated sludge processes, including a smaller footprint, less sludge production and superior effluent quality. However, their wide applications have been hindered by their excessive operation cost due to membrane fouling. Membrane fouling reduces water production and membrane lifespan, thereby, increasing operation and maintenance costs. Many studies have been devoted to exam the mechanisms of fouling and fouling mitigation in MBRs. Despite such intensive efforts, no conclusion on the cause of MBR fouling has been agreed upon, which may be due to the complication of mixed liquor and influent, module design and operation conditions implemented in various studies. Membrane fouling is the interaction between sludge and membrane, which results in adsorption or deposition of components in sludge on membrane surface. As a result, characteristics of sludge and membrane and hydrodynamic conditions are vital factors affecting membrane fouling in MBRs.

In this study, the impact of sludge characteristics on membrane fouling in a submerged MBR was investigated. Bulking sludge due to excessive 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. However, serious fouling was observed when bulking sludge occurred and filamentous bacteria were found dominant in the reactor despite the larger particle size distribution of the sludge. Filamentous bacteria were found to produce more SMP including soluble polysaccharides and soluble proteins in the mixed liquor, which contributed to severe fouling in bulking sludge, in particular, the release of high concentration of soluble polysaccharides. Bound extracellular bound substances (EPS) which was found similar in the normal sludge and bulking sludge

was not the cause for membrane fouling in this case.

Sludge retention time (SRT) has been found to alter sludge characteristics and therefore, have significant impact on membrane fouling. Shorter SRT (10 days) resulted in higher fouling propensity most likely due to higher SMP in the mixed liquor. Despite the similar amount of SMP in mixed liquor, fouling rate at SRT 30 days was higher than SRT 60 days. This may be due to the higher content of bound EPS in sludge flocs at SRT 30 days, resulting in higher specific cake resistance. SMP was found to have larger molecular weight at shorter SRT. Dynamic membranes which can reject small components such as solutes in mixed liquor were formed on the membrane in the beginning of the filtration. The dynamic membrane would not cause apparent membrane fouling but improved membrane rejection instead. Hydrophilic fraction which was accumulated in the mixed liquor was the dominant species in SMP. Hydrophilic carbohydrates were most likely the major foulants at SRT 10 days .

To reduce membrane fouling, titanium dioxide (TiO_2) composite membranes were prepared. A chemical copreciptization-peptization method was used to produce TiO_2 nanoparticles in neutral sol. The composite membranes were prepared by dip-coating the membrane in the neutral TiO_2 sol and also in acidic TiO_2 suspension. Filtration tests showed that membrane fouling was reduced in both cases possibly due to the increase in hydrophilicity of the membrane. Results showed that optimal amount of coating is important in fouling mitigation. Too much TiO_2 on membrane surface deteriorated membrane filtration due to the blocking of membrane pores. The ultrasonic washing test showed that most TiO_2 particles were firmly coated on the surface of the TiO_2 composite membrane.

Keywords: Extracellular polymeric substances (EPS), Fouling, Membrane Bioreactor (MBR), Soluble microbial products (SMP), Titanium dioxide (TiO_2)

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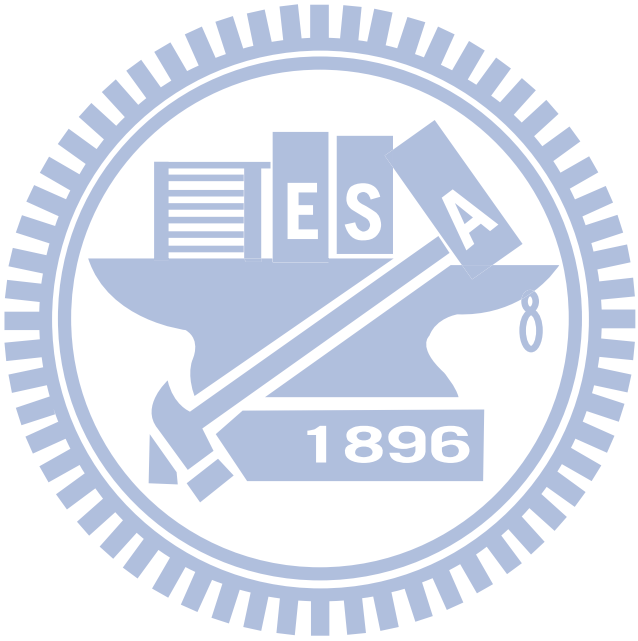

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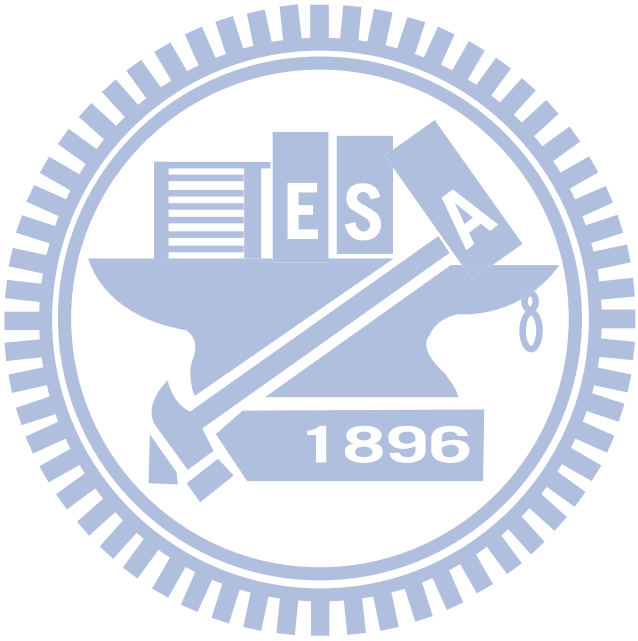


Chapter 1

Introduction

1.1 Background

Nowadays, membrane technology has been extensively applied to wastewater treatment due to its excellent effluent quality to meet the requirement by increasingly stricter regulations and its rapid development. 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. However, MBRs operation is commonly challenged by membrane fouling resulting in tremendous increase in costs, which has hindered its widespread application. Feed water, biomass, membrane and membrane module, and operating conditions are important factors affecting membrane fouling in MBR. Fouling in submerged MBRs can be significantly reduced by proper aeration and by operating at constant flux under a critical value, namely, critical flux.

Despite operation under subcritical flux, membrane fouling is inevitable. Many studies have been devoted to exam the mechanism of fouling and to search for the means for fouling mitigation in MBRs; however, there has not been a conclusion on the cause of MBR fouling, which may be due to the complication of mixed liquor and influent, different modules and different operation conditions implemented in the study. As a result, a comprehensive investigation of membrane fouling in MBRs is needed to facilitate proper fouling control in MBRs. Because fouling is the result of the interaction between sludge and membrane, sludge characteristics play important roles on membrane fouling.

The objective of this study is to investigate the effect of sludge characteristics on membrane fouling under long-term subcritical flux operation. Moreover, fouling mitigation by coating TiO_2 on membrane surface was also explored to evaluate the feasibility of TiO_2 composite membranes in MBRs.

1.2 Outlines

In this study, the impact of sludge characteristics on membrane fouling in a submerged MBR was investigated. The cause for membrane fouling and the fouling tendency in bulking and normal sludge were investigated. To examine the fouling tendency and the fouling mechanism of bulking sludge and normal sludge, an aerobic selector was installed before the MBR unit to shift the bacteria community from filamentous bacteria dominant to floc-forming bacteria dominant. And, the MBRs were

operated at SRT 10, 30 and 60 days to evaluate the effect of SRT on sludge characteristics and membrane fouling. Sludge properties at three SRTs, including MLSS, specific cake resistance, EPS, SMP and particle size distribution, were investigated to evaluate their impact on membrane fouling.

For fouling mitigation, a TiO_2 composite membrane was prepared. A neutral sol containing 1% of TiO_2 nanoparticles was prepared by chemical copreciptization-peptization. Membranes were dip-coated with the neutral sol to form the TiO_2 composite membranes which were characterized by X-ray photoelectron spectroscopy (XPS). The fouling mitigations of the TiO_2 composite membranes made from acidic TiO_2 suspension and neutral TiO_2 sol were compared. The fouling mitigation was explored on two kinds of membranes, cellulose acetate (CA) and mixed cellulose ester (MCE). Finally, ultrasonic washing was performed to evaluate the stability of TiO_2 composite membranes. The schematic diagram of this study is illustrated in Figure 1.1.

Chapter 2 reviews literatures related to this study. It includes membrane fouling and mitigation of fouling in MBRs. For membrane fouling in MBRs, the effects of membrane characteristics, sludge characteristics, and environmental and operational conditions on membrane fouling are examined. For mitigation of membrane fouling in MBRs, modification of membrane characteristics is reviewed.

Chapter 3 describes the material and analytical methods used in this study.

Chapter 4 and 5 show the experimental results and discussion. In chapter 4, performance and fouling characteristics of MBR under different sludge characteristics (filamentous and floc-forming sludge) are presented along with the effect of SRT on sludge characteristics and membrane fouling.

Chapter 5 states the results concerning antifouling ability of TiO_2 composite membranes for MBRs. The preparation and characterization of TiO_2 composite membranes as well as the stability of TiO_2 nanoparticles on composite membranes are included.

Finally, the conclusions and recommendation are provided in Chapter 6.

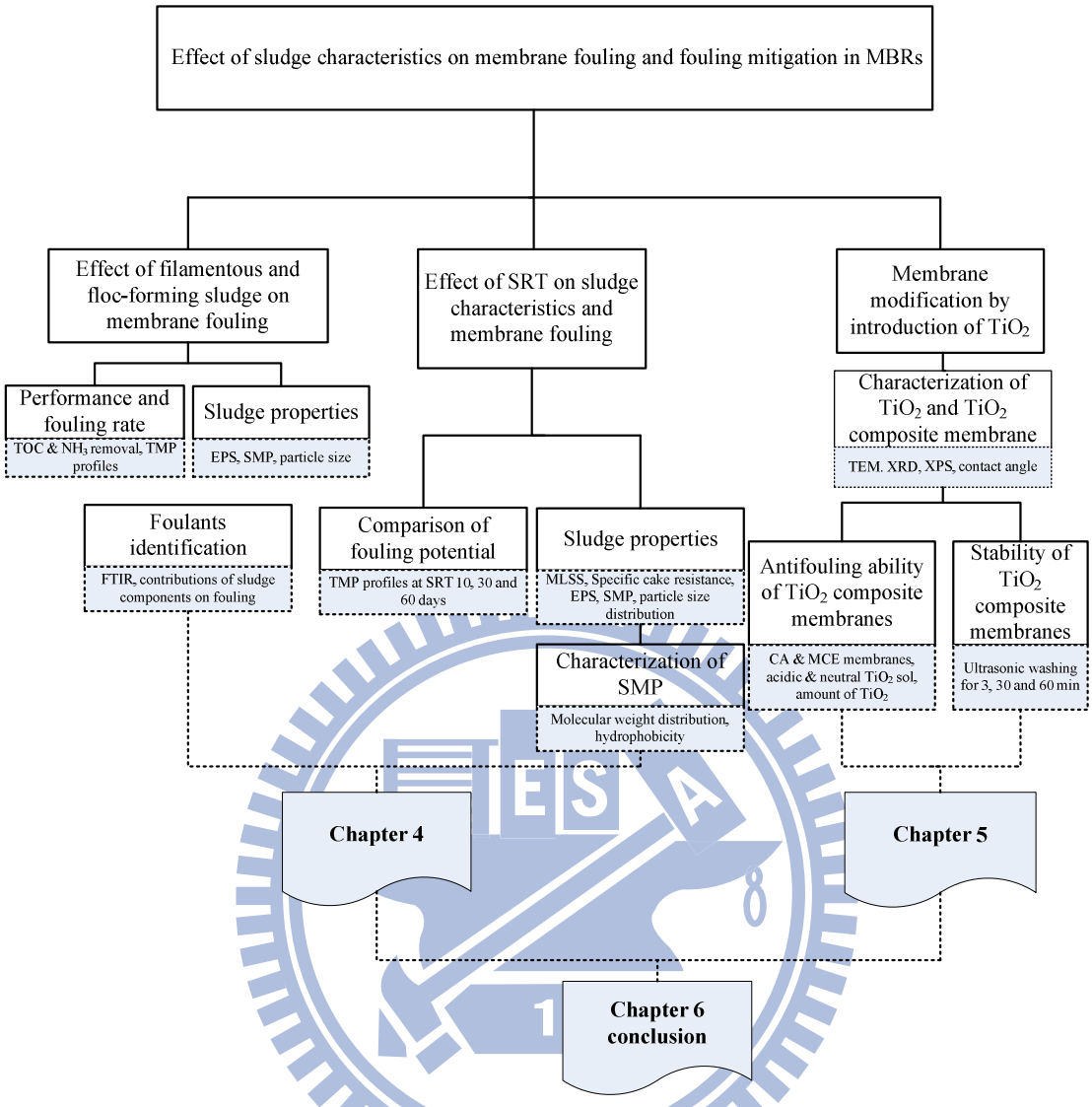


Figure 1.1. Schematic diagram of this study.

Chapter 2

Literature review

Membrane bioreactors (MBRs) have attracted a lot of attention in the last decade because of their advantages over conventional activated sludge processes. However, membrane fouling resulting in increase of operation and maintenance costs has become one of the most significant factors hindering the widespread application of MBRs. In this study, references considering membrane fouling in MBRs and the strategies to mitigate membrane fouling in MBRs are reviewed.

2.1 Membrane fouling in MBRs

Membrane fouling in MBRs is due to the deposition of materials into/onto the membrane, which is attributed to the interactions of membranes and activated sludge. Membrane fouling depends on nature of feed, sludge characteristics, operation conditions, etc. Although many investigations concerning fouling in MBRs have been performed, inconsistent results are usually observed in studies (as shown in Table 2.1) due to the complication of mixed liquor and influent, different modules and different operation conditions implemented in studies. Table 2.1 shows that most studies identified extracellular polymeric substances (EPS), especially the carbohydrates fraction, as the main foulant in MBRs (Cho & Fane, 2002; Kimura *et al*., 2005; Rosenberger *et al*., 2006). However, as shown in Table 2.1, some studies pointed out that other materials like biopolymer cluster, smaller particles or fatty acids were the major foulants on membranes (Bai & Leow, 2002; Wang & Li, 2008; Al-Halbouni *et al*., 2009).

According to Chang *et al* (2002), membrane, biomass, and operating conditions are three key factors influencing membrane fouling in MBRs. Recently, Liao *et al* (2004) also proposed four main parameters which have significant impact on membrane fouling in MBRs (as shown in Figure 2.1). Although some of these parameters in Figure 2.1 directly influence membrane fouling, others interact with other parameters and subsequently influence membrane fouling indirectly. Due to the complex interaction of parameters affecting membrane fouling, a comprehensive understanding and investigation of membrane fouling in MBRs should be provided to properly control fouling in MBRs. Some important factors affecting membrane fouling in MBRs are reviewed as follows.

Table 2.1. Membrane fouling in MBRs.

Influent	Pore size (μm)	Membrane configuration	Major foulants	Test duration	Other	References
UASB effluent	0.22	Flat sheet, Hydrophilised PVDF	EPS (presented as carbohydrates)	450 days	-	Cho & Fane (2002)
Synthetic wastewater	0.1	Hollow fiber, PVDF (Pall)	Smaller particles in MLSS	250 mins	-	Bai & Leow (2002)
Municipal wastewater	0.2	Hollow fiber, polyethylene (Mitsubishi Rayon)	Carbohydrates	120 days	-	Kimura *et al.* (2005)
Municipal wastewater	0.1-0.2	Hollow fiber	Polysaccharides fraction	1 year	Pre-denitrification and post-denitrification in MBR	Rosenberger *et al.* (2006)
Municipal wastewater	0.04	Hollow fiber, PVDF (Zenon)	Soluble humic substances and carbohydrates in complex with metal cations	2 years	Pre-denitrification in MBR	Lyko *et al.* (2007)
Synthetic wastewater	0.4	Flat sheet, Polyethylene	Soluble microbial products	50 days	10-min-operation and 5-min-off	Jeong *et al.* (2007)

Table 2.1. Membrane fouling in MBRs (continued)

Influent	Pore size (μm)	Membrane configuration	Major foulants	Test duration	Other	References
Municipal wastewater	0.2	Hollow fiber, PVDF (Zizheng, China)	Not only EPS but also other organic substances	160 days	Pre-denitrification in MBR	Wang *et al.* (2008)
Synthetic wastewater	0.4	Hollow fiber, (Mitsubishi Rayon)	Biopolymer clusters	28 days	18-min-operation and 2-min-off	Wang & Li (2008)
Municipal wastewater	0.04	Hollow fiber, PVDF (Zenon)	Fatty acids	3 years	-	Al-Halbouni *et al.* (2009)

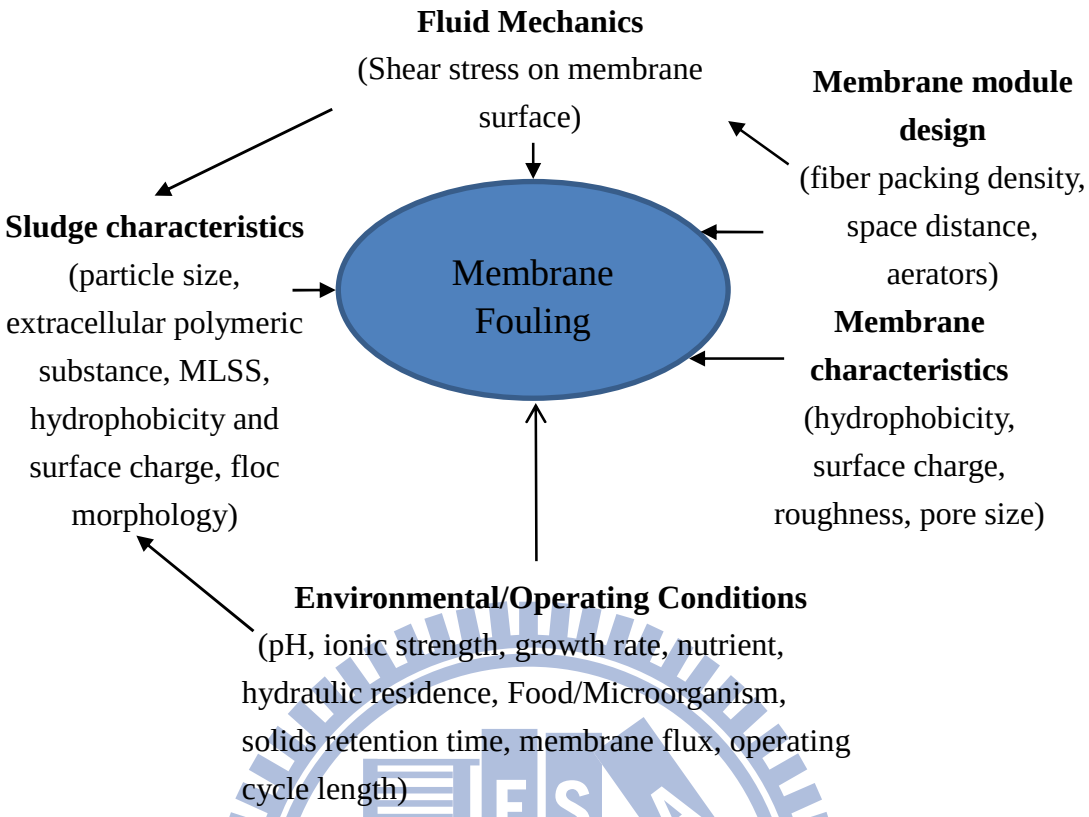


Figure 2.1. Factors affecting membrane fouling in MBRs. (adapted from Liao *et al.*, 2004)

2.1.1 Membrane characteristics

Membrane characteristics, such as roughness, pore size, porosity, surface charge, and hydrophobicity have impact on membrane fouling.

2.1.1.1 Roughness

Membrane roughness has been reported to have direct impact on membrane fouling. In general, studies revealed that the rougher membrane surface is, the more serious fouling is. Elimelech and his co-workers published a series of experimental results on effects of membrane morphology on membrane fouling (Elimelech *et al*., 1997). They first compared the fouling rate of cellulose acetate and aromatic polyamide thin-film composite reverse osmosis membranes (RO), and concluded that surface roughness increased membrane fouling by increasing the rate of colloid attachment onto the membrane surface. In the consequent study, similar results were discovered in RO and nanofiltration (NF) membranes that rough membranes had higher fouling propensity because particles preferentially accumulated in the "valleys" of rough membranes, resulting in "valley clogging" which caused more severe flux decline (Vrijenhoek *et al*., 2001). He *et al* (2005) used a series of polyethersulfone (PES) UF membranes of various molecular weight cutoff (MWCO) and roughness to evaluate the effect of MWCO and membrane roughness on flux decline in an anaerobic MBR. They found that smoother membranes had less permeate flux decline because foulants found fewer crevices to fill in and to buildup the fouling layer. Recently, Choi & Ng (2008) also concluded that in a submerged MBR phase-inversed polytetrafluorethylene (PTFE) membranes had higher total filtration resistance than track-etched polycarbonate (PCTE) and track-etched polyester (PETE) membranes due to its higher degree of roughness.

2.1.1.2 Hydrophobicity and hydrophilicity

For membrane, hydrophilicity affects its wettability and the pressure to drive the liquid through the membrane. It also influences the adhesion characteristics of contaminants to the membrane materials. In most cases, membranes with hydrophobic characteristics have been found more prone to membrane fouling because of the hydrophobic-hydrophobic interaction between solutes, microbial cells and membrane materials (Madaeni *et al*., 1999; Choi *et al*., 2002; Yu *et al*., 2005). However, Maximous *et al* (2009) observed that hydrophilic membranes did not benefit membrane flux although hydrophilic membranes did show better reversibility in cake resistance. This result is consistent with the finding observed by Parsmore *et al* (2002) that young biofilms attached on the hydrophilic membranes are more facile to be removed than hydrophobic

membranes. Nevertheless, it is difficult to show the correlation between membrane hydrophilicity and fouling, because membrane hydrophilicity usually accompanied by the changing of other membrane characteristics such as roughness. For example, Zhang *et al* (2008), reported that PES membranes fouled more easily than polyacrylonitrile (PAN) and polyvinylidene fluoride (PVDF) membranes due to higher degree of roughness and hydrophilicity.

2.1.1.3 Pore structure and size

Pore structure of membranes is also one of the important membrane characteristics affecting membrane fouling. Ho & Zydney (1999) filtered protein with various membranes such as track-etched, isotropic, and asymmetric microfiltration (MF) membranes. The result showed that membranes with interconnected pores fouled more slowly since the fluid could flow around the blocked pores. Hwang & Lin (2002) have shown that membranes with cylindrical pore structures had better filtration than those with sponge pore structures for filtration of suspension containing polymethyl methacrylate (PMMA) spherical particles. Fang & Shi (2005) also demonstrated that PES membrane which has the sponge-like microstructure with large pore openings had the highest pore resistance for filtration of activated sludge due to its large pore openings (18-20 μm). As a result, MBR system should use cake-resistance-dominant membranes, such as track-etched polycarbonate (PC), PVDF and mixed cellulose esters (MCE) rather than pore-resistance-dominant membranes like PES.

Choo & Lee (1996) proposed that MF membranes with 0.1 μm had minimal fouling tendency compared to membranes with 0.02, 0.5, and 1 μm. However, researchers have found that membrane pore size have no significant impact on critical flux (Madaeni *et al*., 1999; Le-Clech *et al*., 2003b). Critical flux was affected only when membranes with small pore size and in low concentration of mixed liquor suspended solids. As a result, the effect of membrane pore size on membrane fouling may depend on both particle size of sludge and membrane.

2.1.1.4 Surface charge

Surface charge of the membrane is critical to membrane fouling because the interaction between organic compounds and membranes depends on membrane surface charge. Surface charge of the membrane can attract or repel charged species in water. It is generally accepted that negatively charged membrane is preferable in MBR operation since natural particles and bacteria are usually negative charged. Repulsive electrostatic double layer interaction would develop between negatively charged particles and membrane surface. Not only the MWCO but also the surface charge was found to have significant impact on membrane performance because both

greatly affect the adsorption of effluent organic matters [Jarusutthirak & Amy, 2001]. Pasmore *et al* (2002) reported that biofilm attached on the membrane surface was easier to be removed when membrane surfaces bear neutral or slight negative charges.

2.1.2 Sludge characteristics

Sludge characteristics of MBRs directly relate to the feed characteristics and the environmental/operational conditions as illustrated in Figure 2.1. Different feed characteristics and the environmental/operating conditions result in different sludge characteristics. Membrane fouling is due to the interaction between sludge and membranes, and, therefore, sludge characteristics play a vital role in membrane fouling in MBRs.

2.1.2.1 Particle size

Sludge was generally divided into three components, suspended solids, colloids and solutes, by size to investigate their contributions on membrane fouling in MBRs. Table 2.2 compares the results concerning the contribution of sludge components on membrane fouling in various studies. Inconsistent results were observed in these published studies. Wisniewski & Grasmick (1998) showed that solutes were the main causes for membrane fouling. Others showed that suspended solids were the main contributor for membrane fouling [Defrance *et al*., 2000; Lee *et al*., 2003; Bae & Tak, 2005a]. Bouhabila *et al* (2001), on the other hand, found that colloids were the major component for membrane fouling. These contradictory findings may be caused by the differentce in operational conditions, sludge properties, methods of sludge separation and others.

In order to mitigate membrane fouling in MBRs, shear stresses along membranes are created by aeration in submerged MBRs or tangential flows in side-stream MBRs. Therefore, activated sludge usually contains larger flocs, while MBR sludge contains primarily small flocs due to higher shear stress. High shear stress could break and sludge flocs and reduce their size, resulting in serious fouling [Wisniewski & Grasmick, 1998; Cicek *et al*., 1999]. Chang & Kim (2005) compared the filtration performance of a submerged MBR and a tertiary treatment plant with membrane unit. They found that the tertiary treatment plant with membrane unit had worse filtration performance due to the small particle size in the secondary effluent. Bae & Tak (2005a) further fractionated the MBR sludge into solutes, colloids and suspended solids, and concluded that the fouling contribution of each sludge fraction was strongly related to particle size because both permeation drag and back transport velocity are particle size-related functions. Therefore, it is important to control the operational conditions to avoid breaking sludge flocs and simultaneously provide suitable shear stress for membranes filtration.

Table 2.2. Relative Contribution of sludge components on membrane fouling (%)

Fraction	Wisniewski & Grasmick (1998)	Defrance *et al*. (2000)	Bouhabila *et al*. (2001)	Lee *et al*. (2003)	Bae & Tak (2005a)
Suspended solids	24	65	24	63-72	72-83
Colloids	24	30	50	28-37[a]	4-14
Solutes	52	5	26		13-14

[a] supernatant

2.1.2.2 Extracellular polymeric substances

As mentioned in 2.1, EPS is the most commonly discussed foulant in studies. Extracellular polymeric substances is a complex mixture of macromolecular polyelectrolytes including polysaccharides, protein, nucleic acids, and humic compounds. It is generally subdivided into two categories: (1) bound or extractable EPS (sheaths, capsular polymers, condensed gel, loosely bound polymers, and attached organic material) and (2) soluble EPS (soluble macromolecules, colloids, and slimes) (Laspidou & Rittmann, 2002; Rosenberger & Kraume, 2002). According to Laspidou & Rittmann (2002) 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 (Barker & Stuckey, 1999). However, Ramesh *et al* (2006) compared the physiochemical characteristics of soluble EPS and SMP and concluded that soluble EPS and SMP were not identical. Furthermore, since there is no standard extraction method of EPS, contradicting results were found in studies concerning fouling caused by EPS and SMP, which were listed in Table 2.3. Although different foulants were identified, recent studied have suggested that soluble fraction (soluble EPS and SMP), especially the carbohydrates, is the major foulants in MBRs (Table 2.3).

Not only the quantity of EPS or SMP, but also the composition of EPS or SMP is critical for membrane fouling in MBRs (Mukai *et al*., 2000). Carbohydrates and proteins are the most abundant components in EPS or SMP. Therefore, studies have focused on the effect of protein and carbohydrate ratio (protein/carbohydrate) on membrane fouling. Preferential adsorption of solutes and sludge particles on membranes was observed when protein/carbohydrate ratios were high by Ji & Zhou (2006) and Choi *et al* (2009). They found that gradually increase the protein/carbohydrate ratio in bound EPS was likely to increase fouling propensity. Moreover, Kim & Nakhla (2009) reported that the higher protein/carbohydrate ratio in SMP was related with higher fouling rate. In summary, higher protein/carbohydrate ratio is associated with membrane fouling, whether they are SMP or bound EPS.

Table 2.3. EPS and SMP on membrane fouling.

Influent	Membrane module	Details	Major foulants identified	References
Synthetic wastewater	Loop-type hollow fiber; polyethylene; 0.1 μm	-	Bound EPS	Nagaoka *et al.* (1996a)
Synthetic wastewater	Flat sheet; regenerated cellulose, acrylic copolymer, polysulfone (PS); 30k and 50k Da	-	Extractable EPS	Chang & Lee (1998)
Municipal wastewater	Hollow fiber; polyethylene with hydrophilic coating; 0.4 μm	SRT: 20, 50 and 100 days; HRT: 4 h; F/M: 0.1 and 1 kg COD/kg MLVSS	SMP	Cho *et al.* (2003)
-	-	-	SMP	Jefferson *et al.*(2004)
Synthetic wastewater	U-shaped hollow fiber; PS, 0.1 μm	Organic loading: 0.3-0.4 g COD/g MLSS/d	Soluble EPS	Hernandez Rojas *et al.* (2005)
Municipal effluent, municipal wastewater and Industrial wastewater	MF and UF	Six pilot cases in Europe	Polysaccharides, a part of bacterial EPS	Rosenberger *et al.* (2005)
Synthetic wastewater	Flat sheet; polyolefin with hydrophilic coating; 0.25 μm	SRT: 8, 20 and 80 days; F/M: 0.04-0.1 kg COD/kg MLSS/d HRT: 1.5-5.0 h	Extractable EPS directly related to membrane fouling	Nuengjamnong *et al.* (2005)

Table 2.3. EPS and SMP on membrane fouling (continued)

Influent	Membrane module	Details	Major foulants identified	References
Synthetic wastewater	Hollow fiber; 0.1μm	Constant pressure operation	Extractable EPS	Meng *et al.* (2006c)
Synthetic wastewater	Flat sheet; hydrophilic polypropylene; 0.2 μm	SRT: 10 and 30 days; TOC/m^3/day; Organic loading: 0.6-0.7 kg Constant flux operation	Polysaccharides in supernatant EPS (i.e. soluble EPS)	Zhang *et al.* (2006b)
Municipal wastewater	Hollow fiber (ZeeWeed 500); PVDF; 0.04 μm	SRT: 5 and 12 days; MLSS: 10.9 to 21.1 g/L; Constant flux operation	Soluble EPS (soluble carbohydrates and humic substances)	Fan *et al.* (2006)
Municipal wastewater (MBR for enhanced wastewater treatment involving nitrification, denitrification and advanced biological phosphorous removal)	Hollow fiber; 0.1-0.2 μm	SRT: 8, 8.6, 14.7 and 14.8 days; F/M: 0.13-0.21 kg COD/kg MLSS/d; Organic loading: 1.5-1.69 kg COD/m^3/d	Polysaccharide fraction of soluble EPS or SMP	Ronsenberger *et al.* (2006)
Municipal wastewater	Hollow fiber; 0.035 μm	Constant flux operation	SMP	Trussell *et al.* (2006)
Municipal wastewater	Hollow fiber; PVDF; 0.04 μm	SRT: 12 days;HRT: 7 and 10 h; Organic loading: 0.88 and 1.03 kg COD/m^3/d	Soluble EPS	Geng & Hall (2007)

Table 2.3. EPS and SMP on membrane fouling (continued)

Influent	Membrane module	Details	Major foulants identified	References
Synthetic wastewater	Flat sheet; polyethylene; 0.4 μm	HRT: 12 h; Organic loading: 0.36 and 0.9 kg TOC/m^3/d	SMP	Jeong *et al.* (2007)
Synthetic wastewater and domestic wastewater	Flat sheet; PAN and PES; UF	HRT: 12, 13 and 17 h; SRT: 22-31 days; F/M: 0.11-0.66 g COD/g VSS/d	SMP but only under certain conditions such as larger particle size and low sludge age	Drews *et al.* (2008)
Synthetic wastewater	Flat sheet; polypropylene; 0.1μm	Sequencing batch MBR; HRT: 12 h; SRT: 10, 20, 40 and 60 days	Carbohydrate in SMP	Dong & Jiang (2009)

2.1.2.3 Mixed liquor suspended solids

Concentration of mixed liquor suspended solids (MLSS) is considered to impact directly upon cake layer formation on the membrane surface. The deposited cake layer on the membrane surface can play an important role in flux decline or trans-membrane pressure (TMP) increase, although contradict results were observed in studies. Table 2.4 shows the effect of MLSS on membrane fouling. Nagaoka *et al* (1996a) found that higher MLSS in MBRs resulted in higher sludge viscosity which caused serious membrane fouling. The finding was in consistent with the result observed by Madaeni *et al* (1999). On the other hand, some studies reported that higher MLSS resulted in better filtration performance (Lee *et al*., 2001). Others have concluded that there was no significant impact of MLSS on membrane fouling or the impact depended on the concentration of MLSS (Defrance *et al*., 2000; Hong *et al*., 2002; Rosenberger & Kraume, 2002; Le-Clech *et al*., 2003b; Fan *et al*., 2006). This may be explained by the complex sludge composition. For example, sludge taken from different MBRs may possess different sludge properties such as particle size distribution and EPS, which are important in membrane fouling. Moreover, some studies evaluated the impact of MLSS on membrane fouling by settling sludge or diluting with saline solution, which neglected the non-settable fraction of sludge and small particles in sludge. Hence, the relationship between MLSS and membrane fouling is difficult to establish without considering other important factors.

Table 2.4. Relationship between MLSS and membrane fouling in MBRs.

Influent	Membrane module	MLSS (mg/L)	Effect of MLSS on fouling	Details	References
Synthetic wastewater	Polyethylene, 0.1 μm, loop-type hollow fiber	-	Increasing MLSS resulted in decreasing filterability due to higher sludge viscosity	-	Nagaoka *et al.* (1996a)
-	HVLP membrane (MIllipore), 0.45 μm	0 to 10,000	Critical flux was lower for higher concentration	Testing with batch a crossflow cell	Madaeni *et al.* (1999)
Domestic water (75%) and industrial wastewater (25%)	Ceramic membrane, 0.1 μm	2,000 to 6,000	No significant effect	Adjusted settling time to obtain required SS	Defrance *et al.* (2000)

Table 2.4. Relationship between MLSS and membrane fouling in MBRs (continued)

Influent	Membrane module	MLSS (mg/L)	Effect of MLSS on fouling	Details	References
Synthetic wastewater	Polyethylene, 0.1 μm, u-shaped hollow fiber	100 1,000 1,500 2,000 3,000 5,000	Increasing MLSS resulted in better membrane permeability	Attached growth vs. suspended growth microorganisms	Lee *et al*. (2001)
Municipal, domestic, fruit juice rinsing wastewater and wastewater containing surfactants	Zenon, Kubota, GKSS and X-flow	2,000 to 24,000	No effect	-	Rosenberger & Kraume (2002)
Synthetic wastewater	PS membrane, 0.1 μm, hollow fiber	3,600 6,800 8,400	No effect was observed	-	Hong *et al*. (2002)

Table 2.4. Relationship between MLSS and membrane fouling in MBRs (continued)

Influent	Membrane module	MLSS (mg/L)	Effect of MLSS on fouling	Details	References
-	200 kDa 0.1 μm 1 μm	4,000 8,000 12,000	Critical flux had no difference from 4 to 8 g/L, but critical flux significantly increased at 12 g/L	Changing SRT to obtain required MLSS	Le-Clech *et al.* (2003b)
Synthetic wastewater	PS membrane, 30 kDa,	90 190 250 1,100 1,900 2,900 3,700	Specific cake resistance increased with MLSS decreased; R_c decreased with MLSS decreased	Adjusted settling time and diluted with saline solution to obtain required MLSS	Chang & Kim (2005)
Municipal wastewater	PVDF membrane, 0.04 μm	10,000 to 21,000	Little impact was observed on critical flux	-	Fan *et al.* (2006)

2.1.2.4 Hydrophobicity and surface charge

Other sludge characteristics like hydrophobicity and surface charge of sludge also have significant impact on membrane fouling. Lee *et al* (2003) found that hydrophobicity and surface charge of flocs were closely related to composition and properties of EPS and were significantly related to composition and properties of EPS and could be used to estimate resistance caused by flocs. Arabi & Nakhla (2009) have reported that higher EPS concentration and relative hydrophobicity of flocs in nitrification and denitrification MBR resulted in increasing of cake resistance. Meng *et al* (2006b) concluded that higher hydrophobicity of flocs resulted from excess growth of filamentous bacteria would cause serious membrane fouling in MBRs. Ahn *et al* (2007) also found that severe fouling was due to the increased EPS and hydrophobicity of supernatant when using an anaerobic upflow bed filter combined with an aerobic MBR to treat high strength organic and nitrogen wastewater.

2.1.2.5 Floc morphology

By theory, all the biomass in MBRs can be retained by the membrane unit to maintain an excellent effluent quality regardless of the sludge seattleability. Hence, sludge bulking should not be a problem in MBRs. However, Chang & Lee (1998) reported that foaming sludge showed greater flux decline than the non-foaming sludge. Later, Chang *et al* (1999) also reported that bulking sludge had higher fouling tendency than normal sludge and pinpoint sludge. Among these three sludge morphologies, normal sludge had the least fouling tendency. More recently, studies have focused on the effect of filamentous bacteria on membrane fouling in MBRs. They have demonstrated that bulking sludge caused by overgrowth of filamentous bacteria resulted in deterioration of MBR performance (Meng *et al*., 2006a, 2006b, 2007). Meng *et al* (2006b) reported that the excess growth of filamentous bacteria formed a non-porous cake layer on the membrane surface which interfered with the membrane filtration. Meng *et al* (2006a, 2007) and Meng & Yang (2007) further suggested that bulking sludge caused the formation of a dense cake layer on the membrane surface due to the fixation of filamentous bacteria. You & Sue (2009) concluded that for relatively high hydrophobic membranes, foam-forming filamentous bacteria had negative effect on membrane fouling. On the other hand, for relatively low hydrophobic membranes foam-forming filamentous bacteria had no significant effect on membrane fouling. However, Li *et al* (2008) found an opposite result that filamentous bacteria had negligible effect on membrane fouling. In most of these studies, the sludge samples in test were taken from a different MBR reactor operated under different operation condition while the filtration resistance tests were performed under constant TMP operation in short filtration duration (4 hours) (Meng *et al*., 2006a, 2006b, 2007; Meng & Yang, 2007). 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, which may be the cause for such contradictory results.

2.1.3 Environmental and operational conditions

Environmental and operational conditions of MBRs directly alter the sludge characteristics and hydrodynamic conditions, which have important impact on membrane fouling. Sludge under different environmental and operational conditions will produce EPS in various quantity and quality which in turn will affect membrane performance in MBRs.

2.1.3.1 Sludge retention time

Sludge retention time which directly affects the properties of biomass and the concentration of MLSS is one of the most common operating conditions discussed in the studies. Due to the membrane unit applied in MBRs, SRT can be infinitely lengthened theoretically, which can reduce sludge production, tolerate unstable fluctuation of organic loading and reduce footprint of wastewater treatment plants. However, in order to avoid high sludge viscosity resulting from high MLSS concentration, most MBRs are operated at SRT from 10 to 60 days. Table 2.5 lists the studies concerning the effect of SRT on membrane fouling. Despite the decreased concentration of MLSS, most studies found that decreasing SRT resulted in deterioration of membrane fouling (Chang & Lee, 1998; Grelier *et al*., 2006; Ng *et al*., 2006; Zhang *et al*., 2006b; Ahmed *et al*., 2007; Holakoo *et al*., 2007; Liang *et al*., 2007; Al-Halbouni *et al*., 2008; Dong & Jiang, 2009). Some studies pointed out that higher fouling potential at shorter SRT is due to the higher concentration of SMP or EPS (Ng *et al*., 2006; Zhang *et al*., 2006b; Dong & Jiang, 2009). Other studies, however, showed contradictory result that longer SRT had higher fouling tendency (Rosenberger & Kraume, 2002; Lee *et al*., 2003). The ranges of SRTs used in these two studies were similar (5 to 60 days), totally opposite findings were observed. Therefore, a different approach must be taken to understand the effect of SRT on membrane fouling.

Table 2.5. Effect of SRT on membrane fouling.

Influent	Detail	SRT	Effect of SRT on fouling	References
Synthetic wastewater	A stirred cell batch cell was used for filtration test; Membrane: regenerated cellulose with 30 kDa, acrylic copolymer with 50 kDa and PS with 30 kDa	3, 8, and 33 days	Fouling tendency increased as SRT decreased	Chang & Lee (1998)
Municipal wastewater, domestic wastewater and industrial wastewater	Filtration index was used to represent filterability using constant pressure operation and UF membranes	5, 10, 20, 40 and 80 days	A partial rise of filterability was observed as increasing SRT	Rosenberger & Kraume (2002)
Synthetic wastewater	Membrane: hollow fiber, hydrophilized polypropylene, 0.4 μm	20, 40, and 60 days	Fouling resistance increased as SRT prolonged	Lee *et al.* (2003)
Synthetic wastewater	HRT: 6 h; Organic loading: 0.6-0.7 kg TOC/m^3/d; Membrane: flat sheet, 0.2 μm	10 and 30 days	Short SRT had more severe fouling due to small particles and higher polysaccharides EPS in the supernatant	Zhang *et al.* (2006b)

Table 2.5. Effect of SRT on membrane fouling (continued)

Influent	Detail	SRT	Effect of SRT on fouling	References
Domestic wastewater	With a pre-anoxic zone; Membrane: flat sheet, polyolefin, 0.4 μm	3, 5, 10 and 20 days	Shorter SRT had severe membrane fouling due to the increase of SMP and EPS	Ng *et al.* (2006)
Municipal wastewater	HRT: 4.5, 6 and 12 h; Organic loading: 0.9, 1, 1.9 and 2 kg COD/kg MLSS/d; Membrane: hollow fiber, PVDF, 0.1-0.2 μm	8, 15 and 40 days	Worse membrane performance was obtained as SRT decreased due to higher solutes and colloids resistance	Grelier *et al.* (2006)
Synthetic wastewater	With simultaneous nitrification-denitrification; Membrane: hollow fiber, 0.04 μm	20 and 40 days	Low SRT had worse filterability	Holakoo *et al.* (2007)
Synthetic wastewater	Sequential anoxic/anaerobic MBR; HRT: 8 h; Membrane: 0.25μm	20, 40, 60 and 100 days	Specific cake resistance increased as SRT decreased	Ahmed *et al.* (2007)

Table 2.5. Effect of SRT on membrane fouling (continued)

Influent	Detail	SRT	Effect of SRT on fouling	References
Synthetic wastewater	HRT: 10 h; Membrane: flat sheet, polyolefin, 0.4 μm	10, 20, and 40 days	Shorter SRTs had high fouling potentials due to the hydrophilic neutrals of SMP	Liang *et al.* (2007)
Municipal wastewater	HRT: 12 and 9 h; F/M: 0.09 and 0.14 kg COD/kg MLSS/d; Membrane: hollow fiber, PES, 0.05 μm	23 and 40 days	Low SRT had worse filtration index due to higher concentration of bound EPS , but the permeability of membranes was similar in both SRTs	Al-Halbouni *et al.* (2008)
Synthetic wastewater	Sequencing batch MBR; HRT: 12 h; Membrane: flat sheet, polypropylene, 0.1 μm	10, 20, 40 and 60 days	Fouling increased as SRT decreased due to higher SMP	Dong & Jiang (2009)

2.1.3.2 Imposed flux

Among all operational parameters, such as organic loading rate, flux and shear stress, imposed flux was found to have the greatest impact on membrane performance (Nagaoka *et al*., 1996b). To prevent rapid membrane fouling, constant flux operation is preferable and sub-critical flux is frequently chosen for crossflow filtration. The concept of critical flux was first proposed by Field *et al* (1995) that for microfiltration there was a flux below which a decline of flux with time does not occur; above it fouling is observed. Critical flux depends on the hydrodynamic conditions and other variables. They further divided the concept of critical flux into two forms: (1) strong form: Permeability ($J/\Delta P_T$, K) is equivalent to the corresponding clean water permeability; (2) weak form: permeability is maintained at a constant. The latter is more practical for membrane filtration. Subsequently, different concepts of critical flux were proposed. Howell (1995) pointed out that under critical flux operation there is no membrane fouling by colloids and the value of critical flux is a function of particle size, hydrodynamics and membrane-colloid interactions. Chen *et al* (1997) proposed that under critical flux little (for MF) or negligible (for UF) hysteresis was observed. Li *et al* (2000) used direct observation through the membrane (DOTM) to identified critical flux as the start-up of the deposition of supermicron particles on MF membranes.

However, even under subcritical flux, membrane fouling is actually inevitable after operating for a period of time. Dramatic increase of TMP is eventually observed after a slow and progressive increase of TMP. The two-step TMP profile can be explained by the concept of local flux, proposed by Yu *et al* (2003) and Ognier *et al* (2004) when the MBR was operated under subcritical flux. At the state of filtration, the loss of effective filtration pores to the filtration occurs as a result of the deposit of macromolecules. Membrane pores for filtration will continue to be lost because of the gradual deposit of particles. Therefore, a slow and progressive increase in TMP will be observed on the initial period. The local flux of effective pores continuously increases in order to maintain the overall imposed flux. Once the loss of effective pores for filtration reaches a critical point, which means that the local flux is over the critical flux, a sudden TMP jump will be observed due to the formation of a cake layer. Despite the fact that membrane fouling still occurs, subcritical flux is usually practiced in MBRs to reducee the frequency of membrane cleaning. As a result, Choi and Dempsy (2005) 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.

Le-Clech *et al* (2003a) has reviewed several methods for critical flux determination including observation of TMP and flux behavior, hydraulic tests

(changes in TMP for several fluxes), determination of inertial lift velocity, DOTM, mass balance, flux-step method and stepwise increase of TMP. Among these methods, flux-step method is more convenient and practical. Although the flux-step determination of critical flux cannot be used to predict long-term TMP behavior in real MBRs, it provides useful data on comparative fouling propensity. Combing specific hydraulic parameters such as initial TMP increase, rate of TMP increase, membrane permeability and average TMP with flux-step method, critical flux can be more precisely defined.

2.2 Mitigation of membrane fouling in MBRs

To mitigate membrane fouling in MBRs, several strategies have been proposed, including physical or chemical cleaning, optimization of membrane characteristics, optimization of operating conditions and modification of biomass characteristics (Le-Clech *et al*., 2006).

2.2.1 Modification of membrane characteristics

In most cases, membranes with hydrophobic characteristics have been found more prone to membrane fouling because of the hydrophobic-hydrophobic interaction between solutes, microbial cells and membrane materials as mentioned in 2.1.1.2. Several methods in surface modification of membrane such as plasma treatment (Yu *et al*., 2005, 2008), graft polymerization (Yu *et al*., 2007), and TiO_2 modification (Bae & Tak, 2005b; Bae & Tak, 2005c; Bae *et al*., 2006) have been proven efficient in reducing membrane fouling in MBRs. Recently, membrane surface modification by adding TiO_2 onto membrane surface has attracted great attention due to its commercial availability and ease of preparation. Table 2.6 lists the studies which modified membrane surface by addition of TiO_2 onto membrane surface. The idea of introduction of TiO_2 onto membranes to mitigate membrane fouling was first proposed by Kwak and his coworkers (Kwak *et al*., 2001; Kim *et al*., 2003). They modified thin-film-composite (TFC) RO membranes by a coating of TiO_2 nanoparticles. The composite membrane showed substantial prevention against microbial fouling under UV illumination. Luo *et al* (2005) then used the same method to prepare the composite UF membranes. They found that the composite membranes not only had antifouling properties but also perform better when filtering PEG solution. For MBRs, Bae and his coworkers performed a series of experiments investigating the antifouling ability of TiO_2-entrapped membrane and TiO_2-deposited membrane (Bae & Tak, 2005b, 2005c; Bae *et al*., 2006). Both membranes reduced fouling in filtration of activated sludge. The TiO_2-deposited membrane had better antifouling ability than the entrapped one because larger amount of TiO_2 was located on the membrane surface. More recently, several researchers have applied the similar

membrane modification technology to reduce membrane fouling under UV or non-UV illumination (Choi *et al*., 2007; Madaeni & Ghaemi, 2007; Yang *et al*., 2007; Rahimpour *et al*., 2008). No matter what the TiO_2 composite membranes preparation is, all of the TiO_2 composite membranes provide good antifouling ability for filtration of activated sludge, BSA, whey and non-skim milk. However, it is noted that most of these studies synthesized the composite membranes by dip-coating in acidic TiO_2 solution (pH 1.5). This may have the risk of deteriorating membrane structure and shorting the lifespan of membranes.

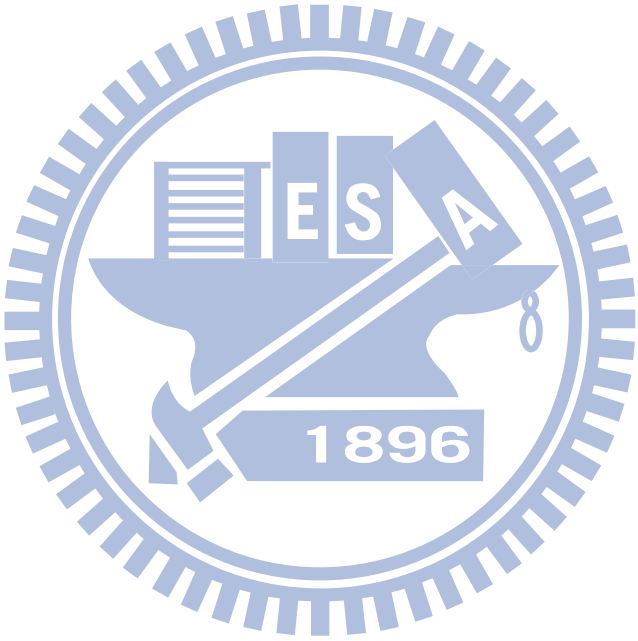


Table 2.6. Fouling mitigation by coating TiO_2 on membranes

Preparation of TiO_2	Membrane and Method of modification	Details	Results	References
Controlling of hydrolysis of titanium tetraisopropoxide, $Ti(OCH(CH_3)_2)_4$ under pH 1.5	TFC membranes (RO); Dip-coating in TiO_2 solution for 1h	*Escherichia coli* (*E. coli*) as a model bacterium	Antibacterial fouling was remarkably higher for the TiO_2 hybrid membrane under UV illumination	Kwak *et al.* (2001)
Controlling of hydrolysis of titanium tetraisopropoxide under pH 1.5	TFC membranes (RO); Dip-coating in TiO_2 solution for 1h	*Escherichia coli* as a model bacterium	The TiO_2 composite membrane showed substantial prevention against microbial fouling under UV illumination	Kim *et al.* (2003)
Controlling of hydrolysis of titanium tetraisopropoxide under pH 1.5	PES membrane (UF); Dip-coating in TiO_2 solution for 1h	Polyethylene glycol (PEG-500) solution was used for evaluation of the separation performance of the composite membrane	The composite membrane showed good separation performance and substantial prevention against hydrophobic substances	Luo *et al.* (2005)

Table 2.6. Fouling mitigation by coating TiO_2 on membranes (continued)

Preparation of TiO_2	Membrane and Method of modification	Details	Results	References
Commercial Degussa TiO_2	PS, PVDF and PAN (UF) membrane; addition of TiO_2 into casting solution (TiO_2-entrapped membrane) and dip-coating in TiO_2 solution for 1 min and pressuring at 400 kPa for 2 h (TiO_2-deposited membrane)	Activated sludge (MLSS: 7,000 mg/L) from a submerged MBR was used to evaluate the antifouling potential of the composite membrane	TiO_2 deposited membrane showed greater fouling mitigation than TiO_2 entrapped membrane	Bae & Tak (2005b)
Controlling of hydrolysis of titanium tetraisopropoxide under pH 1.5	PES membrane (MF); sulfonattion and dip-coating in TiO_2 solution for 10 min	Activated sludge (MLSS: 6,900 mg/L) from a submerged MBR was used to evaluate the antifouling potential of the composite membrane	Membrane fouling was greatly reduced by the immobilization of TiO_2 particles on the membrane surface	Bae & Tak (2005c)
Controlling of hydrolysis of titanium tetraisopropoxide under pH 1.5	PES membrane (UF); sulfonattion and dip-coating in TiO_2 solution for 10 min	Activated sludge (MLSS: 7,000 mg/L) from a submerged MBR was used to evaluate the antifouling potential of the composite membrane	The composite membrane showed less fouling propensity than the neat membrane	Bae *et al.* (2006)

Table 2.6. Fouling mitigation by coating TiO_2 on membranes (continued)

Preparation of TiO_2	Membrane and Method of modification	Details	Results	References
Hydrolysis of titanium tetraisopropoxide in isopropanol with Tween 80 surfactant	Al_2O_3 membrane; Dip-coating in TiO_2 solution	Activated sludge was used to evaluate the antifouling potential of the TiO_2/Al_2O_3 membrane	The composite membrane exhibited less adsorption fouling tendency under UV illumination	Choi *et al.* (2007)
Commercial TiO_2 was added into sodium dodecylsulfone (SDS) solution to acquire TiO_2 powders	PS membrane; addition of TiO_2 into casting solution	1 % bovine serum album (BSA, 67 kDa) was used to evaluate the antifouling performance	At 2% TiO_2 content, the composite membrane exhibited good antifouling ability	Yang *et al.* (2007)
Commercial Degussa TiO_2	TFC membranes (RO); Dip-coating in 0.003% TiO_2 solution for 10 min	Whey was used to evaluate the antifouling performance	The composite membrane acquired self-cleaning property and higher flux under UV illumination, especially when incorporating SiO_2	Madaeni & Ghaemi (2007)

Table 2.6. Fouling mitigation by coating TiO_2 on membranes (continued)

Preparation of TiO_2	Membrane and Method of modification	Details	Results	References
Commercial Degussa TiO_2	PES membrane; addition of TiO_2 into casting solution (TiO_2-entrapped membrane) and dip-coating in TiO_2 solution for 15, 30 and 60 min (TiO_2-deposited membrane)	Non-skim milk was used to evaluate the antifouling performance at 50 psi and 4 h	Both TiO_2-entrapped and TiO_2-deposited membranes showed good antifouling properties under UV illumination but TiO_2-deposited membranes showed superior antifouling ability under UV illumination	Rahimpour *et al.* (2008)

Chapter 3

Experimental methods

3.1 Material

3.1.1 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 Figure 3.1. 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 (2005). Although the synthetic wastewater is likely to be more biodegradable than the real wastewater, the difference between synthetic and real wastewater should not affect our study. Many other researchers have used synthetic wastewater in similar studies based on the same reason (Meng *et al*., 2006b, 2006c; Li *et al*., 2008). The composition of the synthetic wastewater is given in Table 3.1. 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 six-fold 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 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 7.0±0.2 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 SRTs of the MBR were maintained at 10, 30 and 60 days, respectively. After 3 SRT, the critical flux was measured by flux-step method (Le-Clech *et al*., 2003a). The step duration and step height were chosen at 15 min and 6 L/m.h in this study, respectively. The initial flux was set at 12 L/m^2.h. Each constant flux was operated for 15 min. The flux was increased by 6 L/m^2.h at the end of each step until it reached 60 L/m^2.h. As shown in Figure 3.2, the critical flux was around 24 L/m^2.h over which TMP increased apparently. To maintain a subcritical operation, the imposed flux used in this study was set at 16 L/m^2.h.

An aerobic selector of 1-L working volume was installed when sludge bulking became serious to change the sludge characteristics. 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. The Membrane bioreactor system equipped with an aerobic selector is illustrated in Figure 3.3.

A dead-end stirred cell system, as shown in Figure 3.4, 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 Figure 3.4 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 cm 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 rpm and 1,000 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.

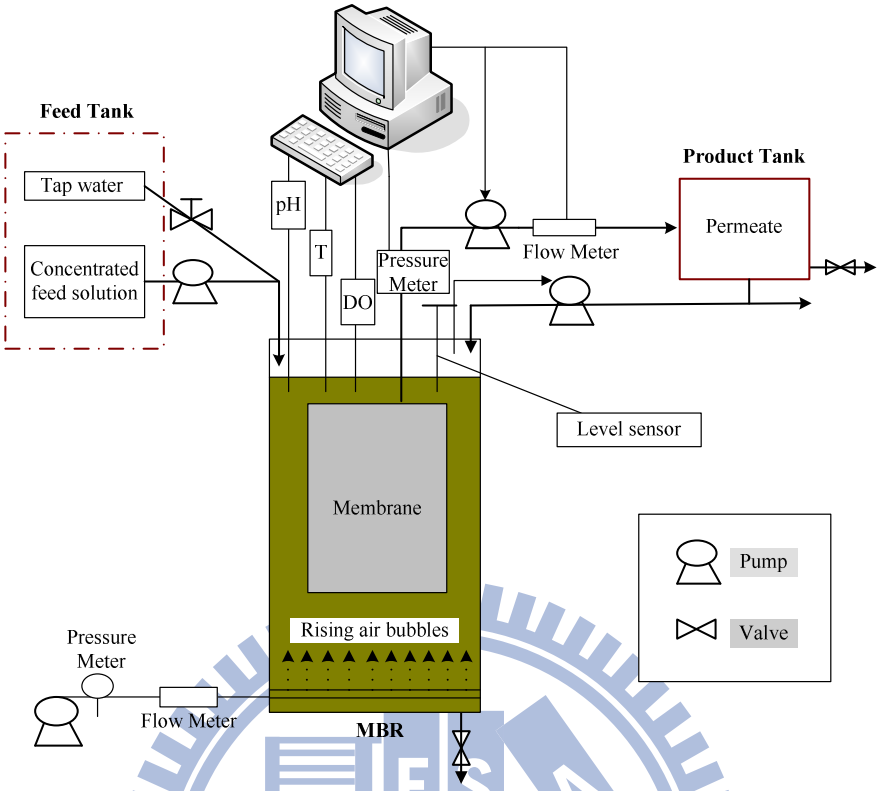


Figure 3.1. Schematic of the membrane bioreactor system.

Table 3.1. Composition of the synthesized wastewater. (adapted from Ng & Hermanowicz, 2005)

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

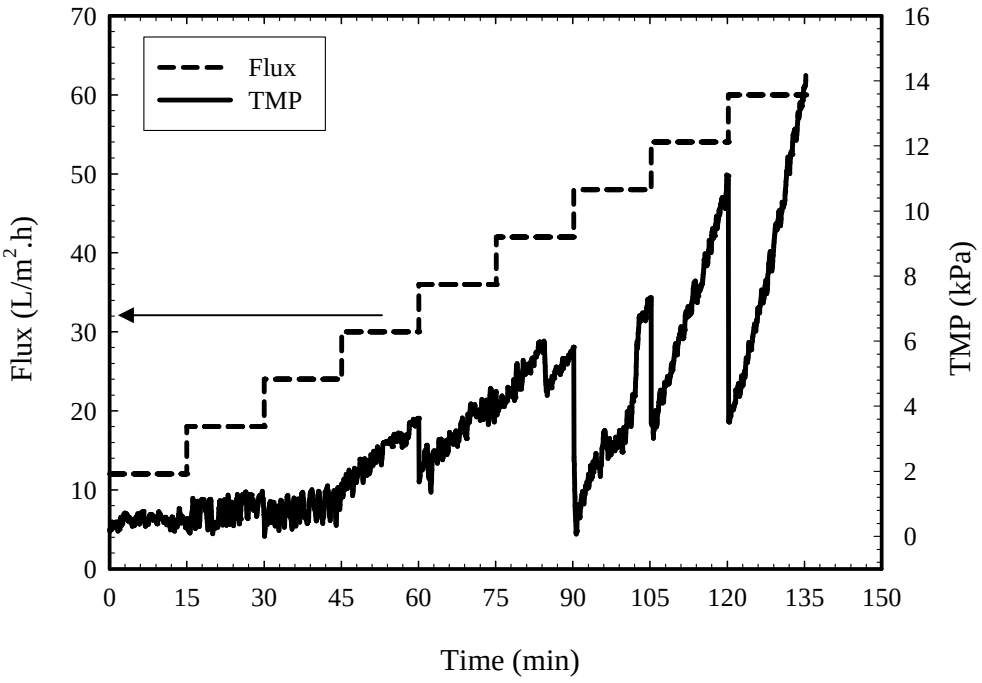


Figure 3.2. Critical flux determination by the flux-step method.

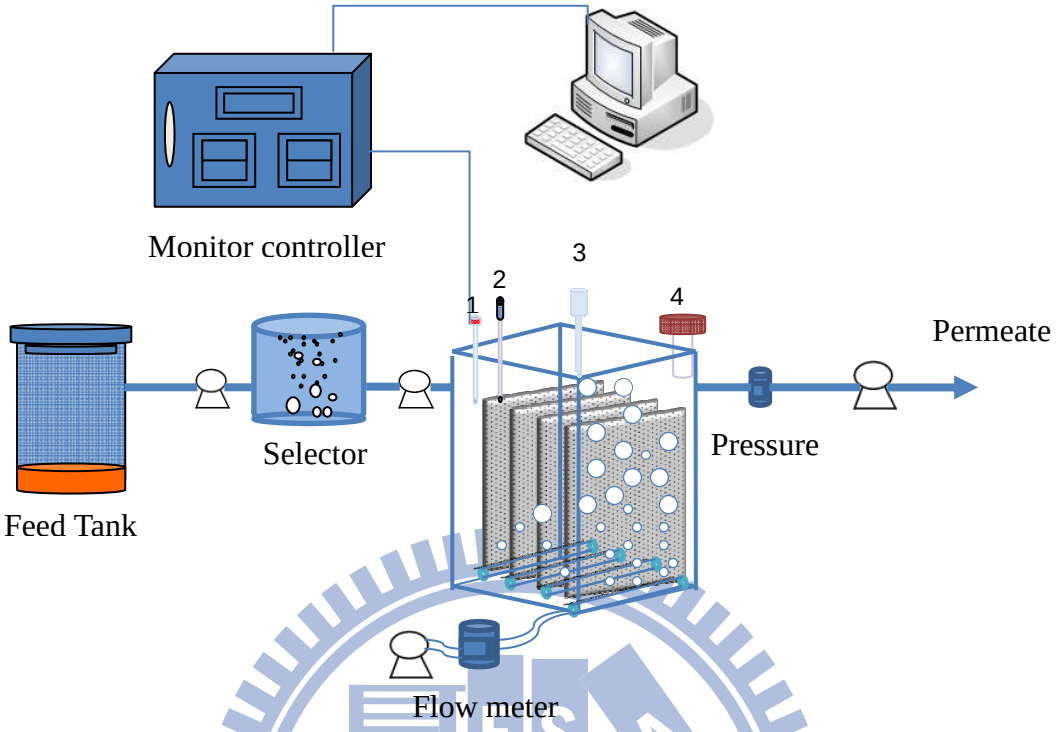


Figure 3.3. Schematic of the membrane bioreactor system with an aerobic selector: (1) pH meter; (2) thermometer; (3) DO meter and (4) level sensor.

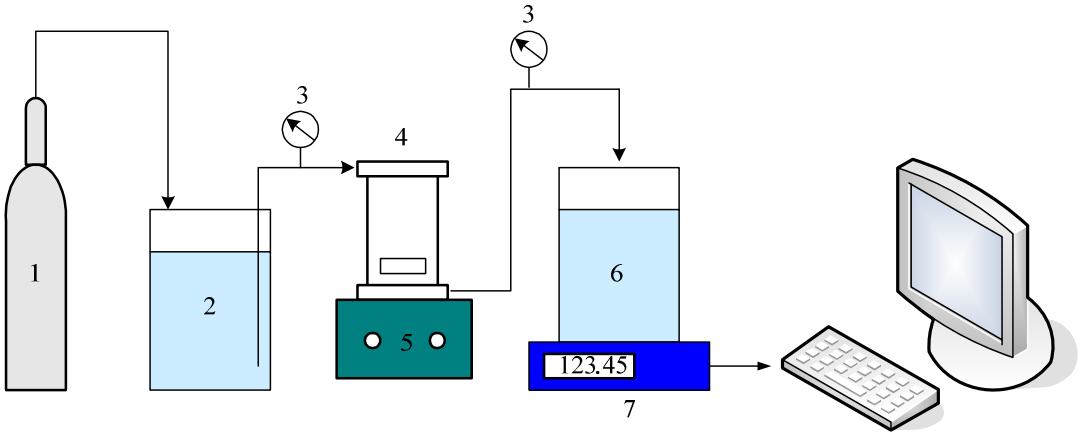


Figure 3.4. Dead-end stirred cell set-up: (1) nitrogen cylinder; (2) feed vessel; (3) pressure meter; (4) stirred cell; (5) magnetic stirrer; (6) permeate vessel and (7) electronic balance.

3.1.2 Preparation of nanosized TiO_2 particles

The neutral TiO_2 sol was prepared by a chemical coprecipitization-peptization method, as described in our previous study (Huang *et al.*, 2007). Ammonium hydroxide (NH_4OH) was dropped into a 1 M titanium tetrachloride ($TiCl_4$) solution to form $Ti(OH)_4$. The yellow transparent TiO_2 sol (1 wt% of TiO_2) was obtained after 2 h peptization with hydrogen peroxide (10 %) and 24 h heating at 95℃. The TiO_2 sol can remain homogeneous for a long period of time without any observable sedimentation.

The acidic TiO_2 colloidal solution was prepared from the controlled hydrolysis of titanium tetraisoproposide, $Ti(OCH(CH_3)_2)_4$ (Choi *et al.*, 1994). A sample of 1.25 ml $Ti(OCH(CH_3)_2)_4$ (Aldrich, 97%) was mixed with 25 ml of absolute ethanol. The solution was added drop by drop to 250 ml of distilled water (4℃), followed by pH adjustment to 1.5 with nitric acid. The mixture was stirred overnight until it was clear.

3.1.3 Preparation of TiO_2 composite membranes

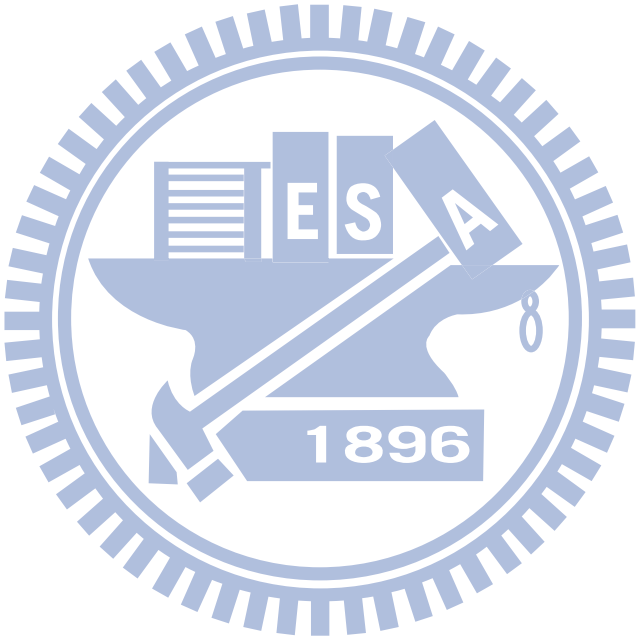
Two microfiltration (MF) membranes, cellulose acetate (CA) and mixed cellulose ester (MCE) membranes (Advantec MFS, Inc.), were used in this study. Both of them have nominal pore size of 0.2 μm and were cut into 24.63 cm^2 to fit the experimental device. The virgin membrane was dipped in the TiO_2 sol for one hour. After that, the membrane was washed with distilled water.

3.2 Analytical methods

3.2.1 Extraction of EPS

Many methods have been proposed for EPS extraction, including heating (Li *et al.*, 2007), cation exchange (Meng & Yang, 2007), and extraction by EDTA chelating (Sheng *et al.*, 2005) and formaldehyde-NaOH (Liu & Fane, 2002). The formaldehyde-NaOH extraction method was selected in this study since Liu and Fang (2002) have indicated that it is most effective and does not cause cell lysis. Extraction of EPS is illustrated in Figure 3.5. Ten milliliters of mixed liquor was sampled and centrifuged for 10 min at 4,000 rpm at 4℃ (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℃ for one hour and then 4 ml of 1 N NaOH was added into the suspension. The suspension was refrigerated again at 4℃ for 3 h. The suspension was centrifuged at 20,000 g for 20 min at 4℃ 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 3,500 molecular weight cut-off at 4℃ for two days to remove the extractant.



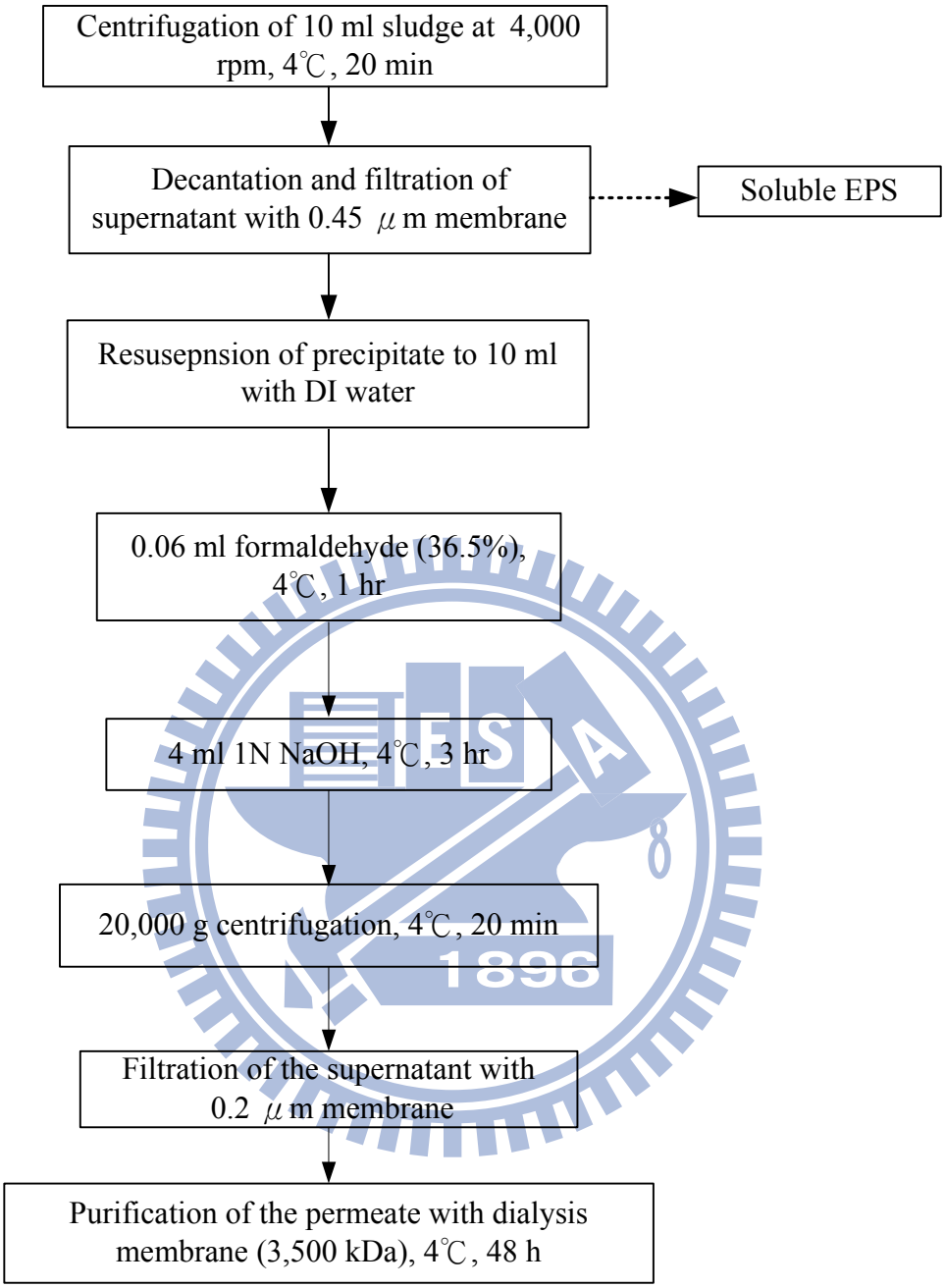


Figure 3.5. Extraction of EPS from sludge flocs.

3.2.2 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 (Liu & Fane, 2002). A phenol-sulfuric acid method (Dubois *et al.*, 1956) was used to quantify carbohydrates in which glucose was the standard (as shown in Figure 3.5). Protein was measured using Bradford protein assay (Bradford, Sigma) according to the manufacturer's protocol, with Bovine Serum Albumin (BSA, Sigma) as the standard. The measurements of polysaccharides and proteins are illustrated in Figure 3.6 and Figure 3.7, respectively.

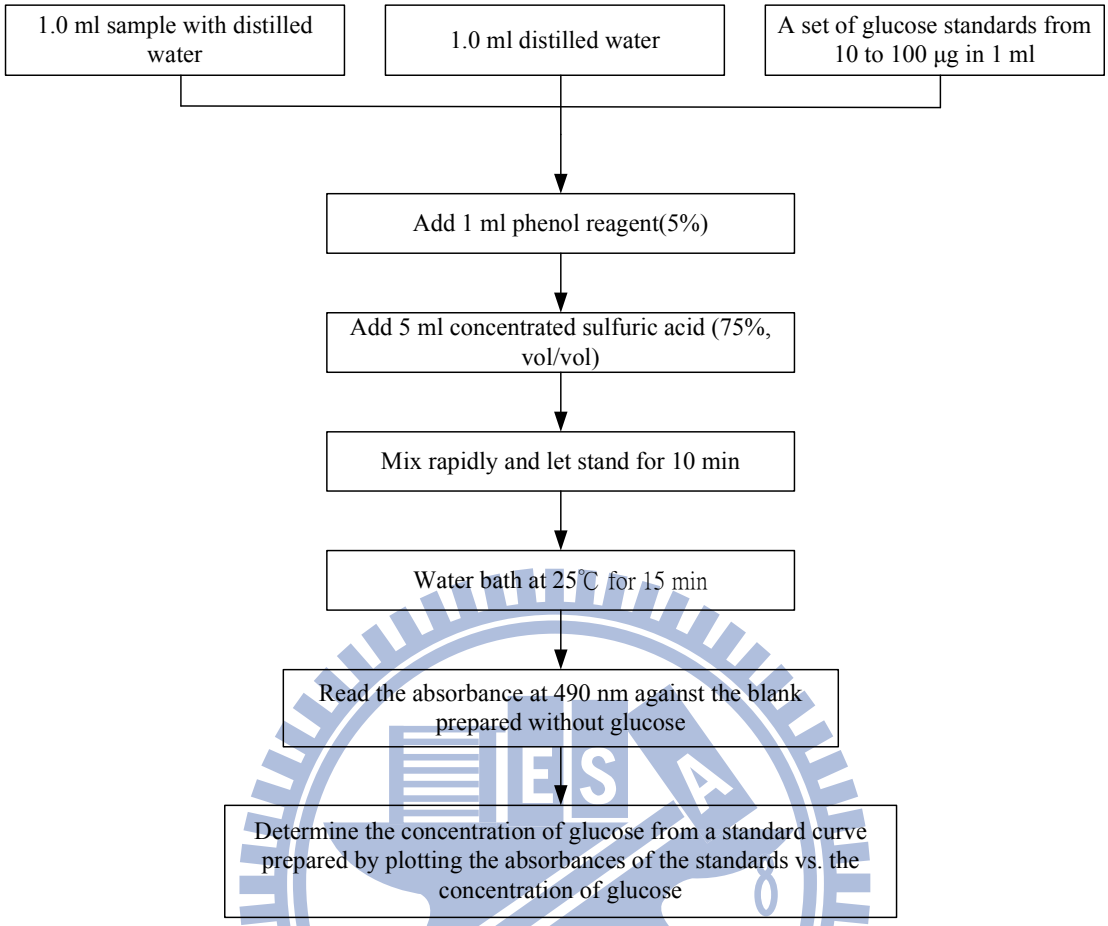


Figure 3.6. Procedure of measurement of carbohydrates in EPS and SMP.

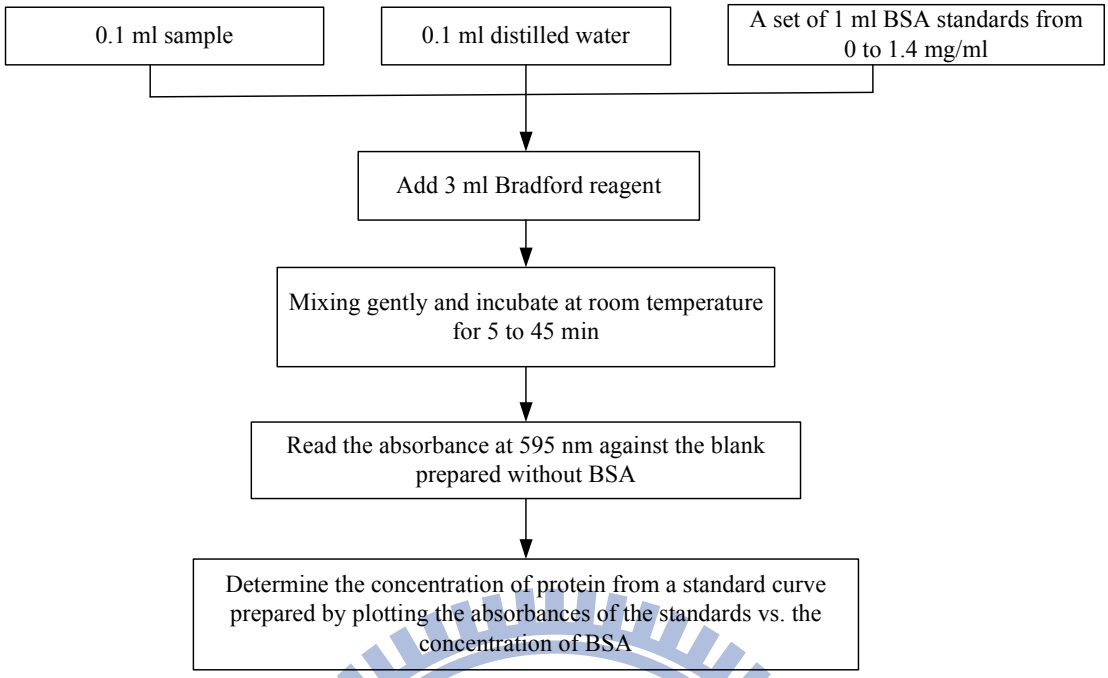


Figure 3.7. Procedure of measurement of proteins in EPS and SMP.

3.2.3 Measurement 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 2,000 μm which meets the requirement of this study. Each sample was measured three times with a standard deviation of less than 3%.

3.2.4 Measurement of molecular weight distribution of supernatant solutes

The apparent molecular weight distributions of supernatant solutes were determined using regenerated cellulose membranes in series with molecular weight cut-off (MWCO) of 5, 10, 30 kDa. (PXC005C50, PXC010C50 and PXC030C50, Pellion, Millipore Corp., USA). These hydrophilic membranes were used to minimize adsorption of organic matter. Samples were processed by passing aliquots through each membrane, yielding a retentate and corresponding permeate containing all molecular weight fractions below the indicated cutoff. The samples were at ambient pH and were not buffered. The actual pressure employed for a given membrane was based on the flow rate recommended by the manufacturer. The sample permeate and retentate were based on a concentration ratio of approximately 4:1. Both permeate and retentate were analyzed for TOC. The results of TOC balance generally indicated larger than 90% recovery of the introduced sample by the permeate and retentate.

3.2.5 Fractionation of supernatant solutes

Supelite DAX-8 and Amberlite XAD-4 resins were used to fractionate supernatant solutes into hydrophobic acids (HPO-A) and hydrophobic neutrals (HPO-N) adsorbing onto the DAX-8 resin, transphilic acids (TPI-A) and transphilic neutrals (TPI-N) absorbing onto the XAD-4 resin, and the hydrophilic faction which does not adsorb on either theDAX-8 or XAD-4 resin. Only the hydrophobic acids and the transphilic acids fractions were used in this study. However, the separation of the different organic matter fractions with XAD resins is not sharp, instead the fractions overlap to a certain degree (Aiken & Leenheer, 1993). It should be mentioned that the so-called hydrophobic fraction (adsorbing onto the DAX-8 resin) do not exhibit a truly hydrophobic character in chemistry. The organic matter found in the hydrophobic fraction merely exhibits a more hydrophobic character in comparison to the transphilic and the hydrophilic fractions.

3.2.6 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 (4,000 rpm) at 4℃ 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.

$$R_t = \frac{\Delta P_T}{\mu J_{as}} \quad (1)$$

$$R_m = \frac{\Delta P_T}{\mu J_{iw}} \quad (2)$$

$$R_{as} = R_{ss} + R_{col} + R_{sol} \quad (3)$$

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

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

$$R_{sol} = \frac{\Delta P_T}{\mu J_{sol}} - R_m \quad (6)$$

where $\triangle P_T$ is TMP (Pa), μ is permeate viscosity (Pa.s), R_t is total resistance (1/m), R_m is resistance caused by membrane itself (1/m), R_{as} is resistance by sludge (1/m), R_{ss} is resistance by suspended solids (1/m), R_{col} is resistance by colloids (1/m), R_{sol} is resistance by solutes (1/m), 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 equation 2. Sludge was then filtered to determine R_{as} by using equation 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 equation 5 and 6, respectively. The difference between $R_{col+sol}$ and R_{sol} was R_{col} (Subtract equation 6 from equation 5). Once R_{sol} and R_{col} are known, R_{ss} can be calculated by equation 3.

3.2.7 Specific cake resistance

Constant pressure filtration using the dead-end cell system under unstirred condition was used to calculate specific cake resistance (α). Plotting t/V vs. V, knowing other parameters, α can be calculated as follows:

$$\frac{t}{V} = \frac{\mu R_m}{A\Delta P} + \frac{\mu C \alpha}{2A^2 \Delta P} V \qquad (7)$$

Where t is operation time (s), V is volume of filtrate (m^3), A is the area of the membrane (m^2), C is concentration of MLSS and α is specific cake resistance (m/kg). t/V versus V plot is depicted linearly and the slope can be obtained by linear regression analysis. Then the specific resistance is calculated from the slop value.

3.2.8 Fourier-transform infrared spectrometer

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 × 2 cm rectangles and dried at a vacuum box overnight. Samples were examined to a resolution of 4 1/cm.

3.2.9 Characterization of nanosized TiO_2 particles

The crystal structure of TiO_2 particles was characterized by X-ray diffraction (XRD) with a Mac Science MXP-18 X-ray diffractometer using Cu K_α (voltage: 30 kV; current: 20mA; λ = 0.154056 nm) radiation. The particle size of TiO_2 was determined by a Philip transmission electron microscope (TEM, Philip CM-200 TWIN) at 200 kV. For TEM observation, TiO_2 suspension was dropped on a carbon-coated grid and then dried at room temperature. The particle size distribution of TiO_2 particles was also measured by a dynamic light scattering particle size distribution analyzer (Zetasizer Nano ZS, Malvern, UK).

3.2.10 Characterization of morphology and chemical composition of membrane surface

The surface topography of the TiO_2 composite membrane was observed by JEOL JSM-6700F field emission scanning electron microscopy (FE-SEM). For SEM observation, the membrane samples were cut into appropriate size and the surfaces were coated with gold by a sputter coating machine.

X-ray photoelectron spectroscopy (XPS) was conducted to determine the chemical composition of the membrane surface and the relative atomic concentrations of the individual element. The XPS was performed using an X-ray photoelectron spectrometer (Thermo VG-Scientific, UK), with a monochromatized Kα X-ray beam at 3.8 kW generated from an Al rotating anode.

The contact angle goniometer (MagicDroplet model 100, Future digital scientific, USA) was used to characterize the hydrophilicity of the composite membranes by sessile drop method. The contact angles were determined by taking the average of three measurements.

3.2.11 Fouling test of composite membranes

The membrane fouling test of the composites membranes were conducted using a stirred cell system, as shown in Figure 3.4. The activated sludge used as the feed of the fouling test was taken from a 30-L submerged MBR system with synthetic influent. The samples in the filtration cell were stirred at a constant stirring rate over the entire experiment and all the data were automatically logged in a computer. All the experiments were carried out at 0.5 bar constant pressure by using a nitrogen cylinder. Resistance-in-series model was used to assess the degree of membrane fouling:

$$J = \frac{\Delta P_T}{\mu R t} \tag{8}$$

where J is the permeate flux ($m^3/m^2.s$), $\triangle P_T$ the trans-membrane pressure (Pa), μ the viscosity of the permeate (Pa.s), and R_t the total filtration resistance (1/m).

3.2.12 Ultrasonic wash of the TiO_2 composite membrane

To evaluate the fixation of TiO_2 coating on membrane, ultrasonic washing (40 KHz) was applied. The relative atomic concentrations of elements on the membrane surface were quantified by XPS. The relative atomic concentrations of the individual elements can be calculated:

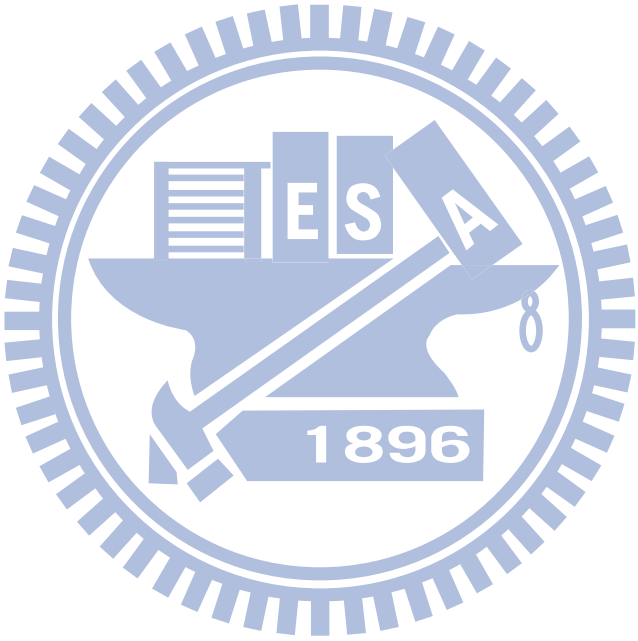
$$C_i = \frac{A_i / S_i}{\sum_j^m A_j / S_j} \tag{9}$$

where A_i is the photoelectron peak area of the element *i*, S_i is the sensitivity factor for the element *i*, and *m* is the number of the elements in the sample.

3.2.13 Other analytical methods

MLSS was measured following the standard method (APHA, 1998). 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 membrane filter first (Mixed cellulose ester, Adventec). Capillary suction time (CST) 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%.



Chapter 4

Effect of sludge characteristics on membrane fouling in MBRs

4.1 Performance and fouling characteristics of membrane bioreactor under different sludge characteristics

MBRs with different sludge characteristics, bulking sludge and normal sludge, were investigated in this study to evaluate their effects on membrane performance.

4.1.1 Performance of membrane bioreactor treatment under different sludge conditions

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 is clearly shown in Figure 4.1 (a) 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 (Jenkins *et al*., 1993). The theories of the overgrowth of filamentous bacteria are: (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 (Dalentoft & Thulin, 1997). 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. 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 (Tsai & Lee, 1998). Filamentous bacteria have lower half-saturation constant (Ks) and maximum growth rate (μ_{max}) than floc-forming bacteria, which therefore is the main theory of aerobic selector. In this way the sludge was successfully shifted from filamentous bacteria to flco-forming bacteria as seen in Figure 4.1 (c) 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. Figure 4.2

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 Figure 4.2 (a) and (b). The average TOC and NH_3-N in the MBR influent was 158±20.0 mg/L 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 regardless of the sludge characteristics (Figure 4.1). 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 (Figure 4.2 (b)). The result indicates that membrane bioreactor is a reliable wastewater treatment process. The excellent pollutant removal renders MBR a promising process for wastewater reuse.

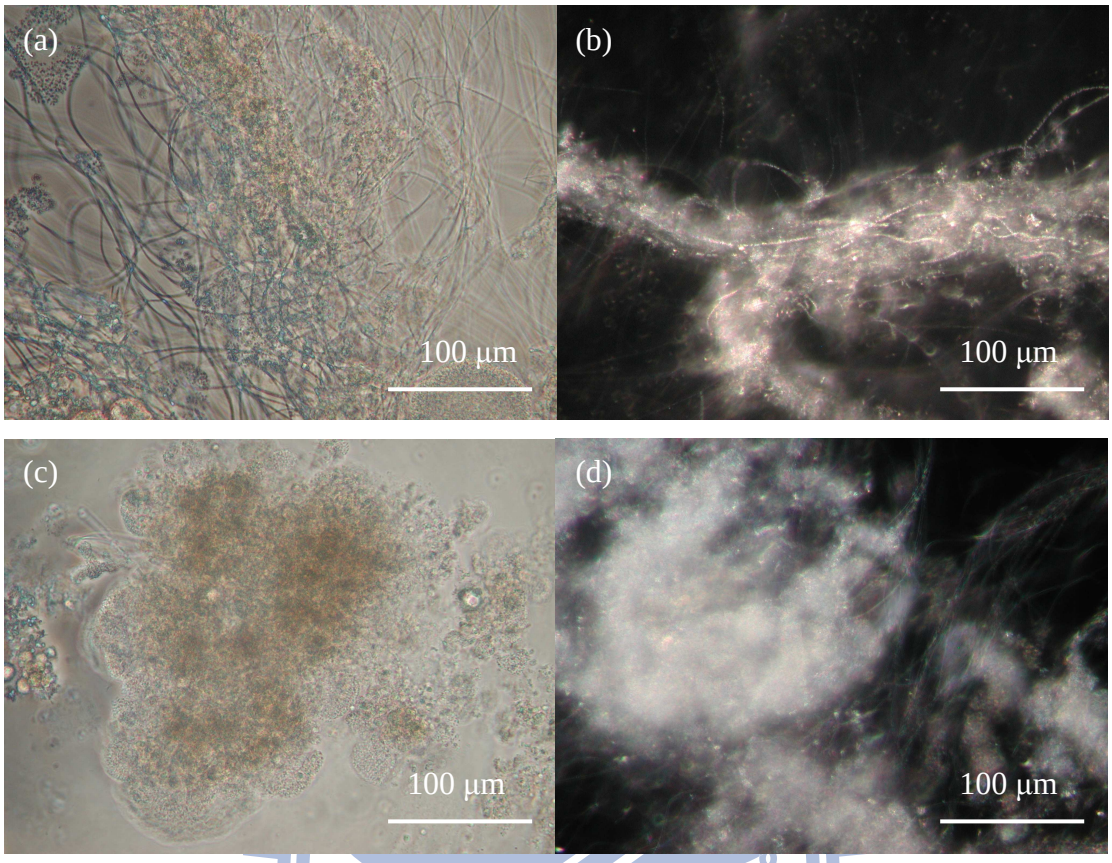


Figure 4.1. Microscopic images of sludge flocs: (a) and (b) overgrowth of filamentous bacteria without installation of the selector; (c), and (d) floc-forming bacteria after installation of the selector.

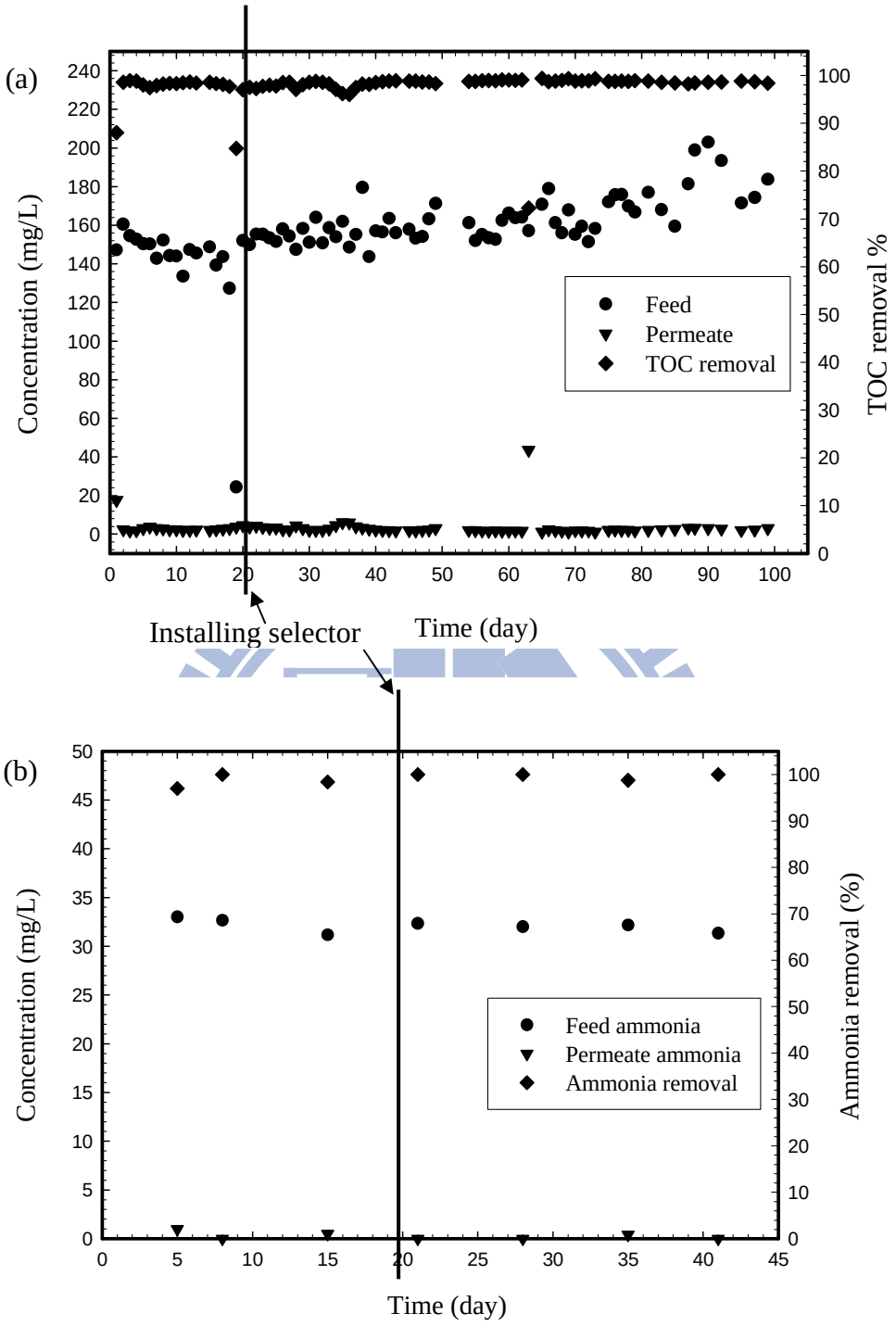


Figure 4.2. (a) TOC and (b) ammonia nitrogen removals by MBR treatment in bulking sludge and normal sludge.

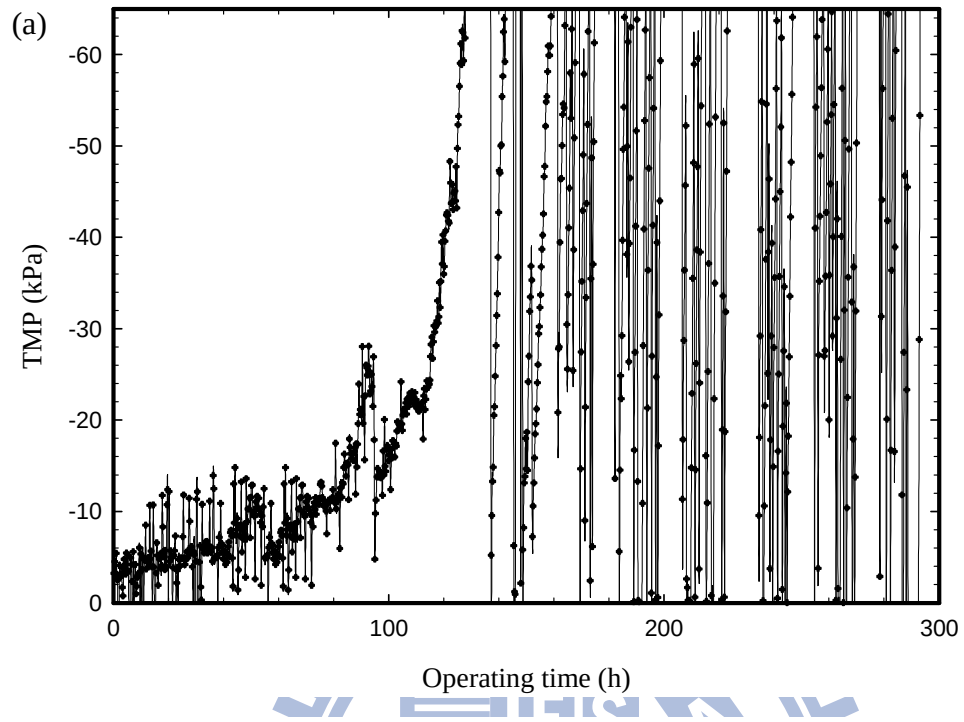
4.1.2 Impact of bulking sludge on membrane fouling

Bulking sludge, on the other hand, had significant impact on membrane fouling, as illustrated in Figure 4.3 (a). 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 hours. 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 Figure 4.3 (b). 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 fouling stage. After the floc-forming bacteria stabilized and became steadily dominant in the bioreactor, the fouling rate became steady and relatively slow. Meng *et al* (2006b) reported that the excess growth of filamentous bacteria formed a non-porous cake layer on the membrane surface which interfered with the membrane filtration. Meng *et al* (2006 a) and Meng & Yang (2007) 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* (1999) also reported that bulking sludge have higher fouling tendency than normal sludge and pinpoint sludge. However, Li *et al* (2008) had found an opposite result that filamentous bacteria had negligible effect on membrane fouling. The contradict results might be due to the different influent wastewater and processes discussed in 2.1.2.5.

Particle size distributions of normal sludge and bulking sludge are shown in Figure 4.4, in which the flocs of normal sludge are obviously larger than that of bulking sludge. The D (4,3) volume weighted mean of bulking sludge and normal sludge was 326 μm and 164 μm, respectively. The result is consistent with the findings of other studies (Meng *et al*., 2006a; Meng *et al*., 2006b; Li *et al*., 2008), 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 (Chang *et al*., 2002; Rosenberger & Kraume, 2002). According to Carmen-Kozeny equation, specific cake resistance is a function of particle diameter, porosity of cake layer, and particle density. The specific cake resistance is inversely proportional to the square of the particle diameter. Thus smaller particles size will result in greater cake resistance. However, the severe fouling in

bulking sludge cannot be explained by particle size alone. There are some other important factors resulting in the severe fouling.

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 4.1. The supernatant TOC, representing SMP in mixed liquor (Liang *et al*., 2007), was about 12 times higher than that of normal sludge. The soluble EPS of bulking sludge was about 6 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 bound EPS in normal sludge and bulking sludge were about the same. The detail will be discussed in 4.1.3. CST is commonly used to represent dewaterability of sludge. The CST of the bulking sludge was significantly larger than that of normal sludge, which echoes the findings by Wang *et al* (2006) and Wu *et al* (2007) that CST values were positively correlated to membrane fouling. Rosenberger and Kraume (2002) have also reported that soluble EPS affected the filterability of activated sludge most significantly, in agreement with our result. As a result, CST seems to be a good indicator of sludge filterability.



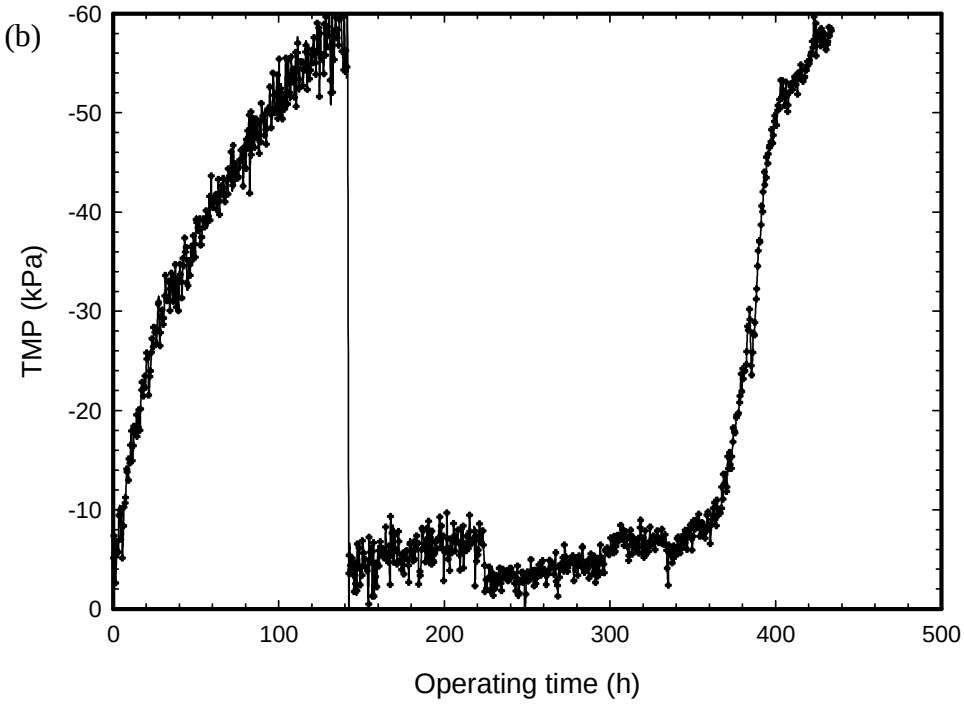


Figure 4.3. TMP profiles of different sludge properties: (a) filamentous bacteria and (b) floc-forming bacteria.

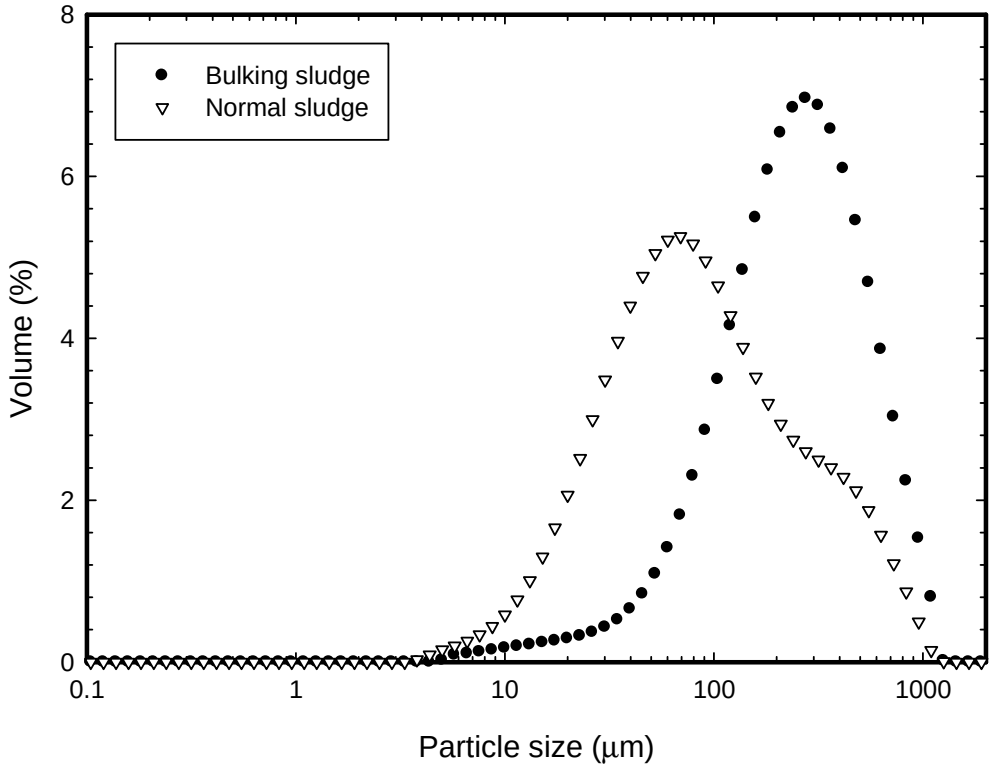


Figure 4.4. Particle size distributions of normal sludge and bulking sludge.

Table 4.1. Comparison of sludge characteristics between normal sludge and bulking sludge

	Supernatant TOC (mg/L)	CST (s)	Soluble EPS[a] (mg/L)	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.

4.1.3 Effect of sludge properties on EPS

Since EPS has been widely accepted as the major foulant in MBR (Nagaoka *et al*., 1996a; Cho & Fane, 2002; Kimura *et al*., 2005; Zhang *et al*., 2006a), 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 bound EPS. Figure 4.5 compares the concentration of soluble and cell-bound EPS in various sludge conditions. There was no significant difference in the production of 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 or soluble proteins in SMP influence the membrane performance in MBR (Mukai *et al*., 2000; Hernandez Rojas *et al*., 2005; Kimura *et al*., 2005; Rosenberger *et al*., 2005; Fan *et al*., 2006; Zhang *et al*., 2006b). However, Meng *et al* (2006a; 2006b; 2007) 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 bound EPS. The result differed from our observation, possibly because that they obtained the sludges from different MBR processes. Lately, Li *et al* (2008) also reported that bound EPS was the major contributor to membrane fouling. They pointed out that filamentous bacteria have no significant influence on membrane fouling. The contradictory 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 Figure 4.6 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 (Kimura *et al*., 2005; Jarusutthirak & Amy, 2006), 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 (Omoike & Chorover, 2004) 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 (Wu *et al*., 2007), which further confirms that severe fouling in bulking sludge caused by overgrowth of filamentous bacteria is due to the attachment of SMP on the membrane surface.

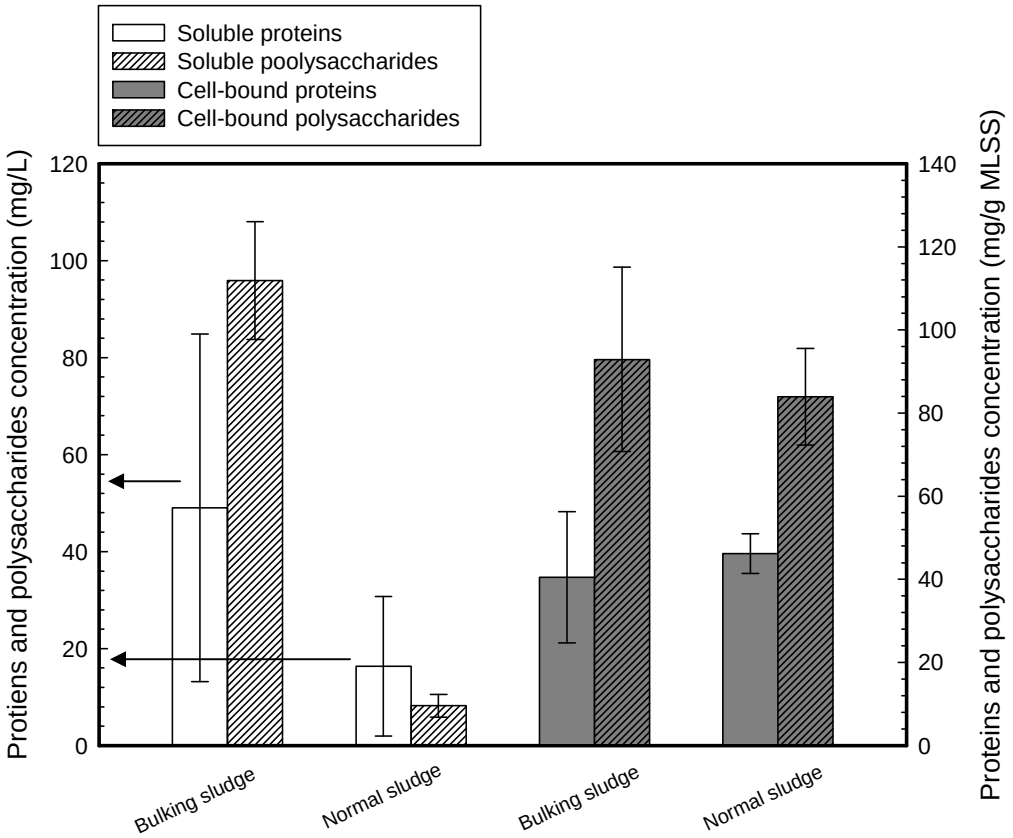


Figure 4.5. Comparison of EPS components in filamentous bacteria and floc-forming bacteria.

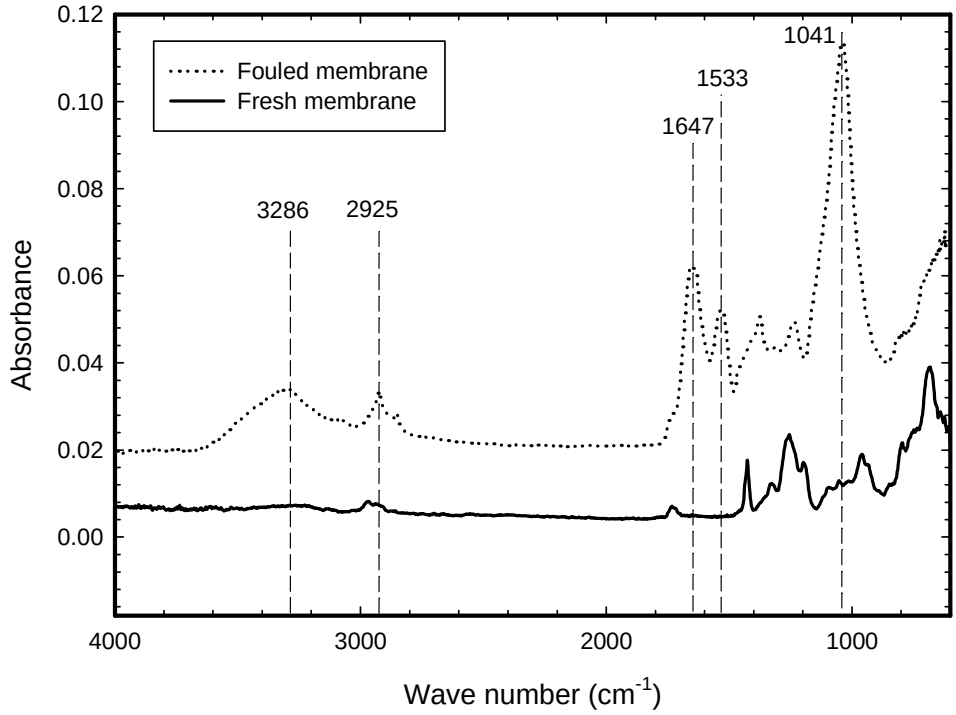


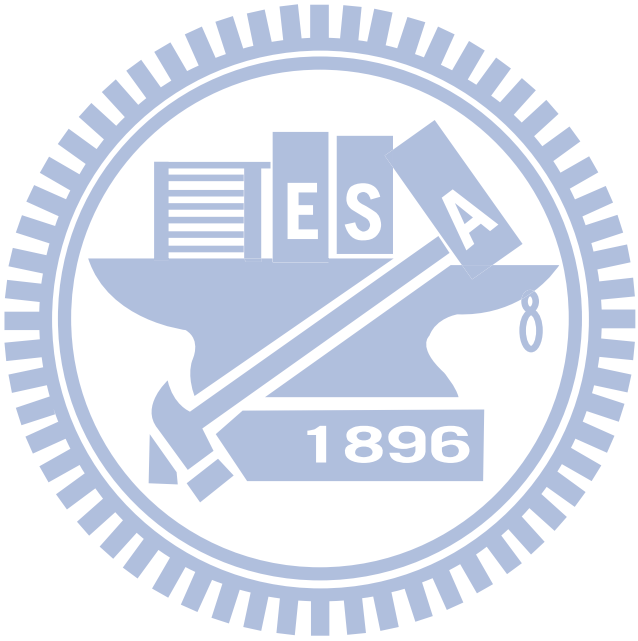
Figure 4.6. FTIR spectra of fresh and fouled membranes.

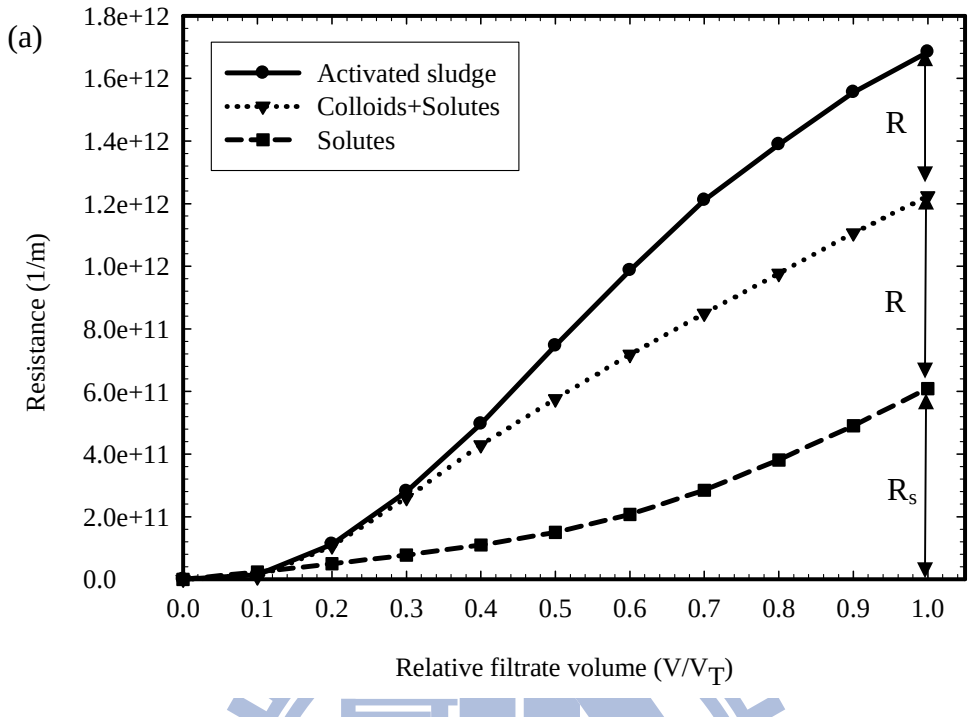
4.1.4 Effect of sludge fractions on membrane fouling

To provide more information concerning the contradictory results among other studies (Meng *et al*., 2006a; Meng *et al*., 2006b; Meng & Yang, 2007; Li *et al*., 2008) 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. Figure 4.7 illustrates the resistances of sludge fractions at different stirring rates. The difference between activated sludge and colloids + solutes represents the resistance of suspended solids. The difference between colloids + solutes and solutes represents the resistance of colloids. In order to compare the relative contribution of sludge fraction on membrane fouling in detail, the results obtained in Figure 4.7 was summarized in Table 4.2. 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 1,000 rpm, the resistance contributed by suspended solids disappeared completely while the majority of resistance came from the solutes. As shown in Table 4.2, 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 (Wisniewski & Grasmick, 1998; Defrance *et al*., 2000; Bouhabila *et al*., 2001; Lee *et al*., 2003; Bae and Tak, 2005a). Defrance *et al* (2000) and Bae and Tak (2005) concludes that suspended solids are the main contributor to membrane fouling because their systems were operated under relatively high flux and low cross flow. On the other hand, Wisniewski & Grasmich (1998) reported differently, that solutes were the main contributor to membrane fouling since their system was operated under high shear stress condition.

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 stress rate and is proportional to particles size (Belfort *et al*., 1994). 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 4.2 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 4.1.3 that SMP dominated the membrane fouling in MBR, and, therefore, membrane fouling will occur eventually even though the MBR is operated under subcritical condition.





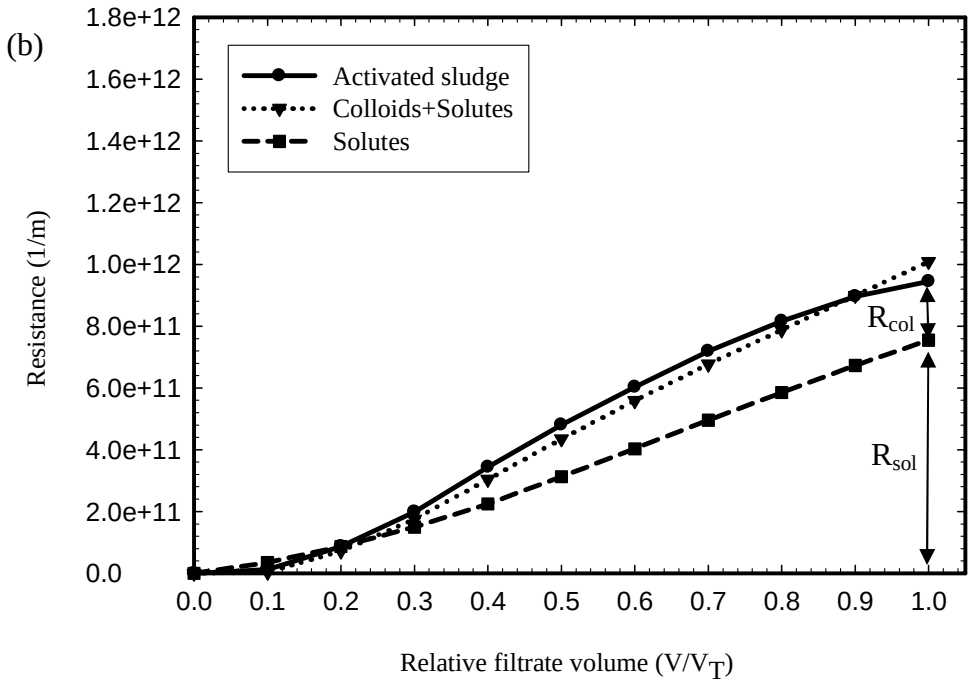


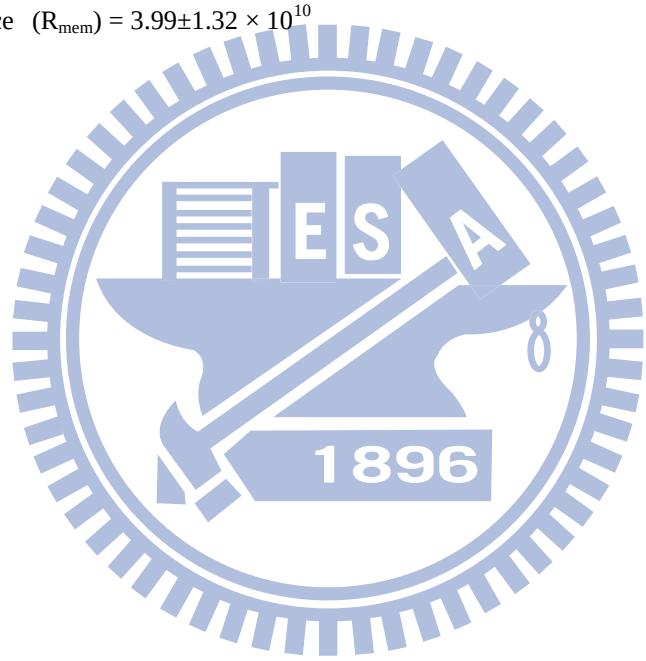
Figure 4.7. Resistances of sludge fractions at different stirring rates: (a) 400 rpm and (b) 1,000 rpm.

Table 4.2. Contribution of sludge fraction to resistance at different stirring rates

	Stirring rate			
	400 (rpm)		1,000 (rpm)	
	m^{-1}	% [a]	m^{-1}	% [a]
R_{ss} [b]	$4.60 \pm 0.04 \times 10^{11}$	27.33	0	0
R_{col} [b]	$6.15 \pm 0.02 \times 10^{11}$	36.52	$2.55 \pm 0.02 \times 10^{11}$	25.22
R_{sol} [b]	$6.09 \pm 0.14 \times 10^{11}$	36.15	$7.55 \pm 0.09 \times 10^{11}$	74.78

[a] Percentage in total resistance (%).

[b] Membrane resistance (R_{mem}) = $3.99 \pm 1.32 \times 10^{10}$



4.2 Effect of SRT on sludge characteristics and membrane fouling

4.2.1 Fouling rate at different SRTs

As we discussed in 2.1.3.1, SRT is one of the most important operating parameters affecting membrane fouling because SRT would directly alter the characteristics of biomass. In order to investigate the effect of SRT on membrane fouling, the membrane bioreactor was operated under three SRTs, 10, 30 and 60 days. The SRTs ranging from 10 to 60 days include most of the range of SRTs discussed in literature and are in the range of the optimum SRT (Meng *et al.*, 2009). Figure 4.8 illustrates the TMP profiles of the membrane bioreactors operated at SRT 10, 30 and 60 days. Figure 4.8 apparently shows that membrane fouling increased as SRT decreased. As the membrane bioreactor operated at SRT 10, the MBR suffered from the most serious membrane fouling. This result is in agreement with most published studies (Chang & Lee, 1998; Grelier *et al.*, 2006; Ng *et al.*, 2006; Zhang *et al.*, 2006b; Ahmed *et al.*, 2007; Holakoo *et al.*, 2007; Liang *et al.*, 2007; Al-Halbouni *et al.*, 2008; Dong & Jiang, 2009), though some studies showed the opposite result (Rosenberger & Kraume, 2002; Lee *et al.*, 2003). Figure 4.9 shows the membranes fouled at different SRTs. Comparing with the membranes fouled at SRT 30 and 60 days (Figure 4.9 (b) and (c)), the membrane fouled at SRT 10 days (Figure 4.9 (a)) clearly showed different fouling characteristics. Slime and transparent gel layer was observed on the membrane surface at SRT 10 days. However, sludge cakes apparently formed on the membrane surface at SRT 30 and 60 days. Thick cakes with deep red color were observed on the membrane of SRT 60. It is noted that all these pictures in Figure 4.9 were taken when TMP reached −60 kPa, which means that membrane had been seriously fouled. For subcritical operation, TMP jump is due to the cake layer formation as mentioned in 2.1.3.2. Therefore, cake layer should be observed on membranes when TMP jumps as membranes fouled at SRT 10 and 60 days. However, slime gel layer was observed at SRT 10 days instead of cake layer. These differences imply the different fouling mechanisms and foulants occurred at different SRTs.

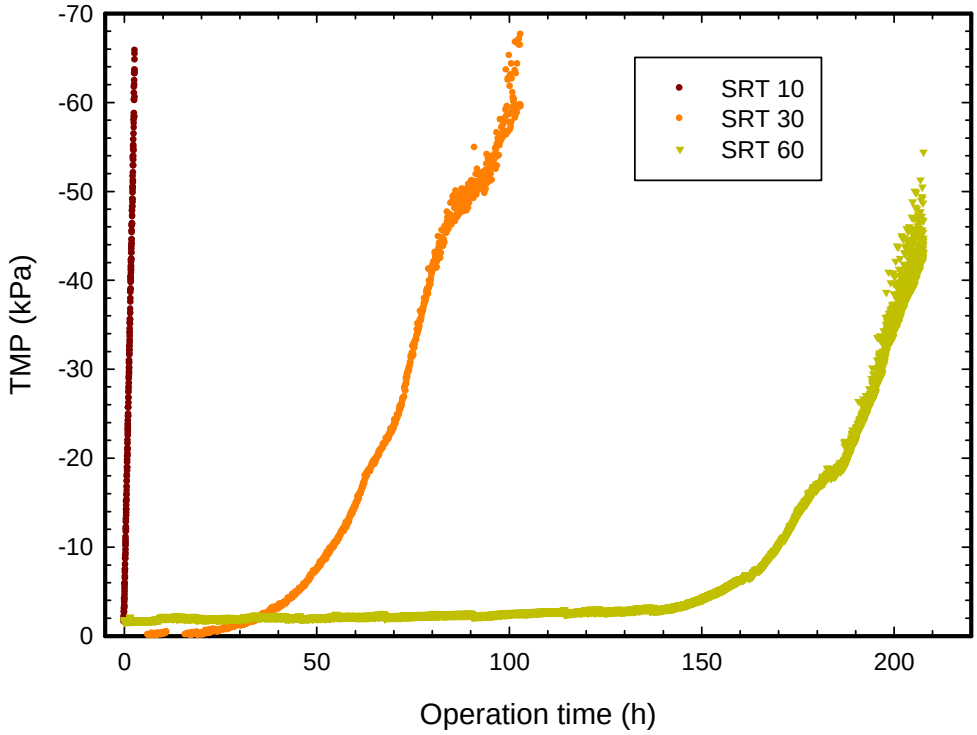


Figure 4.8. TMP profiles at different SRTs.

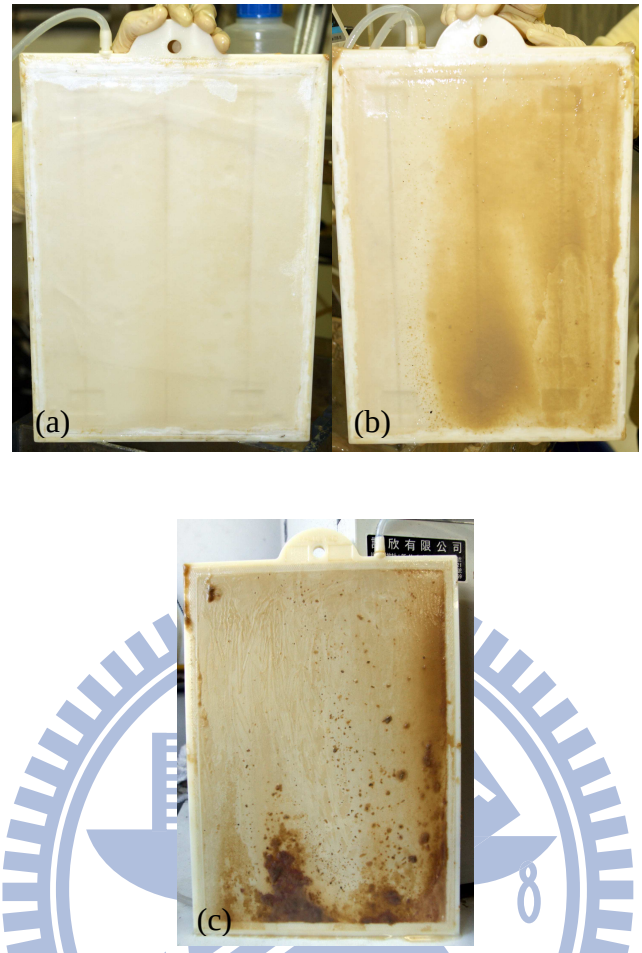


Figure 4.9. Pictures of the membranes fouled at different SRTs: (a) 10 days; (b) 30 days and (c) 60 days. All these pictures were taken when the TMP reached -60 kPa.

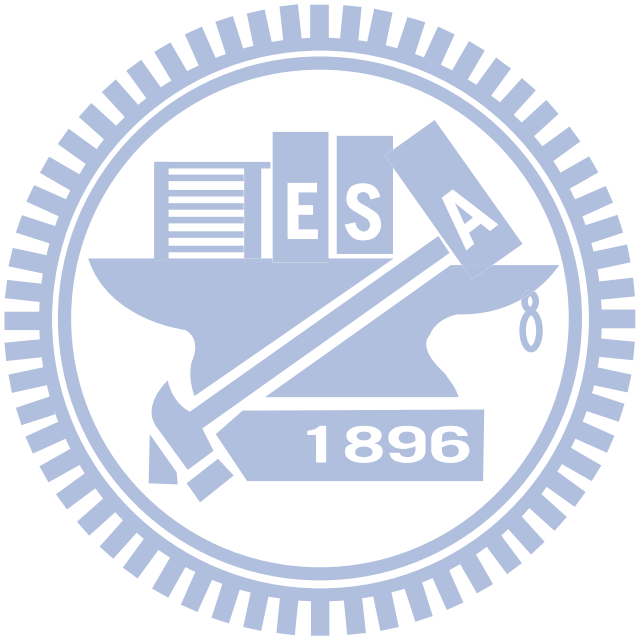
4.2.2 Sludge characteristics at different SRTs

To study the cause of difference in membrane fouling under different SRTs, sludge characteristics were investigated. Because SRT directly affects the sludge characteristics such as EPS production, particle size distribution and may subsequently result in the variation in membrane fouling. Figure 4.10 shows that the SMP (represented as TOC) in the mixed liquor decreased from around 17 mg/L to 4 mg/L when the SRT was switched from 10 days to 30 days, which was in agreement with previous studies that higher fouling potential found in shorter SRT was due to the increase of SMP or EPS in mixed liquor (Ng *et al*., 2006; Zhang *et al*., 2006b; Dong & Jiang, 2009). However, when the SRT was further increased to 60 days, the SMP in the mixed liquor still remained at around 4 mg/L, similar to those at SRT 30. The SMP of effluents remained between 2 to 3 mg/L regardless of the SRT. The severe fouling found in SRT 10 (Figure 4.8) can be explained by higher SMP concentration in the mixed liquor. The attachment of SMP may lead to the observation of slime gel layer which caused membrane fouling. Wang *et al* (2008) also reported that slime gel layer which was mainly composed of macromolecules, colloids and SMP, etc., was formed on the membrane. However, the concentration of SMP in the mixed liquor was similar in SRT 30 and 60 days, which cannot explain the difference in fouling rates of SRT 30 and 60 days.

Table 4.3 summarizes other properties of sludge at SRT 10, 30 and 60 days. Despite the lower concentration of MLSS, shorter SRT had higher fouling propensity. Thus MLSS would not be an important factor affecting membrane fouling in this study. In Table 4.3, it is noted that for SRT 30 and 60 days, SRT 30 days had higher bound EPS than SRT 60 days. This might result in the higher fouling propensity of SRT 30 days. After operating for a period of time, the local flux started to exceed the critical flux, resulting in initial deposition of sludge flocs on membrane surface. At this moment bound EPS had a critical effect on cake resistance. As shown in Table 4.3, higher bound EPS was found to have higher specific cake resistance. Cho *et al* (2005) also reported that bound EPS affected the specific cake resistance. Bound EPS and specific cake resistance had a sigmoid relationship between them. As a result, the MBR with SRT 30 days had higher fouling propensity than SRT 60 days due to higher cake resistance.

Figure 4.11 shows the particle size distribution of sludge flocs at different SRTs. It can be noted that there was no significant difference in particle size distribution among these three sludge samples. Only the MBR operated at SRT 10 showed relatively higher population of fine particles in sludge. This may cause a rapid flux decline at a shorter SRT because fine particles observed in this shorter SRT would gradually block the pores (Zhang *et al*., 2006a; Ahmed *et al*., 2007).

In summary, much rapid fouling rate observed at SRT 10 days is due to the SMP and fine particles attachment, resulting in a dense and slime gel layer on the membrane surface. For SRT 30 and 60 days, bound EPS greatly affects the fouling rate because higher bound EPS found in SRT 30 days results in higher cake resistance.



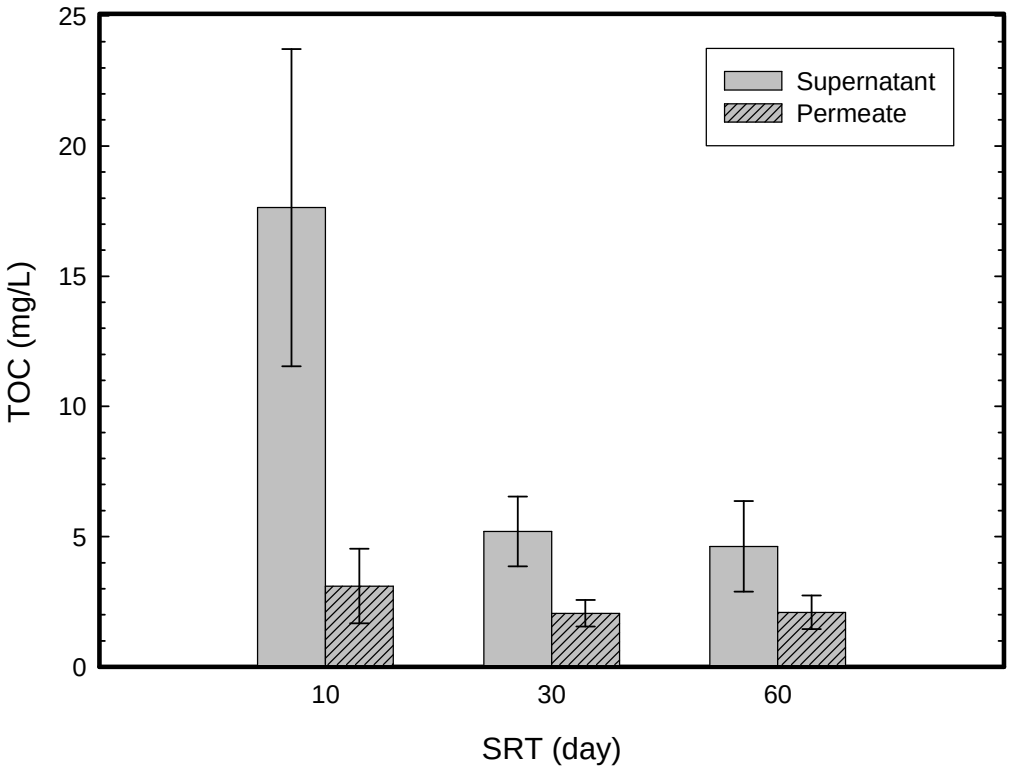


Figure 4.10. Concentration of SMP (represented as TOC) in mixed liquor and effluent at different SRTs.

Table 4.3. Sludge characteristics at different SRTs

	MLSS (mg/L)	Specific cake resistance (10^{13} m/kg)	SMP in mixed liquor		SMP in permeate		Bound EPS	
			Carbohydrates (glucose mg/L)	Proteins (BSA mg/L)	Carbohydrates (glucose mg/L)	Proteins (BSA mg/L)	Carbohydrates (glucose mg/g MLSS)	Proteins (BSA mg/ g MLSS)
SRT 10	3,014±615	12.00	9.72±1.81	2.05±0.99	3.38±1.58	0.52±0.48	20±3	46±29
SRT 30	9,728±868	7.19	7.53±1.40	0.43±0.26	6.66±3.92	0.09±0.21	30±8	26±3
SRT 60	12,051±1316	5.58	5.03±0.86	0.43±0.26	3.16±1.36	0.15±0.21	18±3	5±7

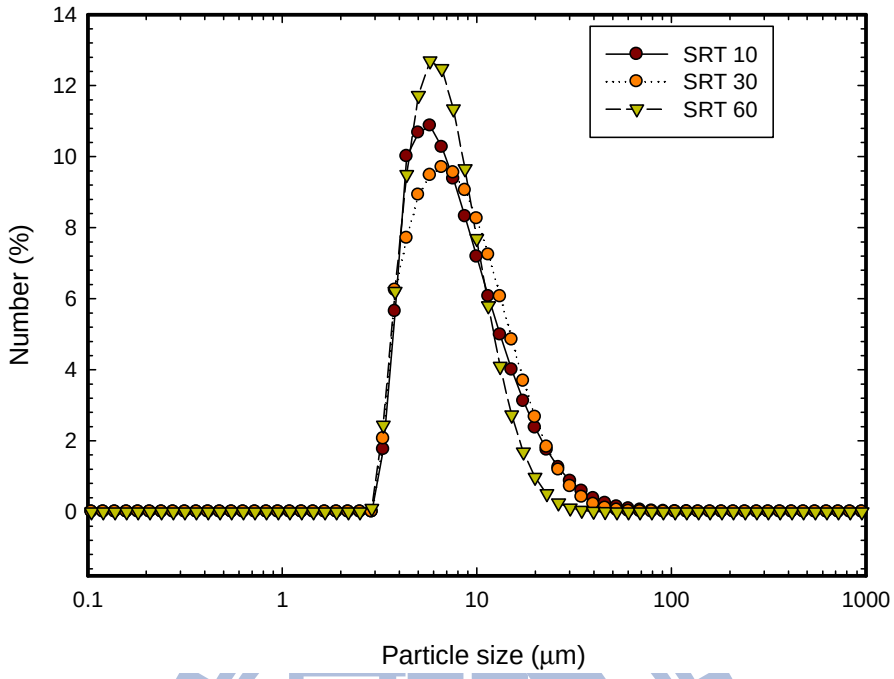


Figure 4.11. Particle size distribution of sludge at different SRTs.

4.2.3 SMP characteristics

As discussed in 4.1.3 and 4.2.2, SMP plays a vital role in membrane fouling. Furthermore, EPS or SMP are also frequently mentioned when regarding to MBR fouling, most studies correlate the quantity of EPS or SMP with fouling rate. Little information about the characteristics and components of SMP on MBR fouling is available. To evaluate the effect of characteristics and components of SMP on membrane fouling in MBRs, SMP was separated into parts of different MWCO by use of a series of ultrafiltration membranes. Moreover, SMP was also categorized into different parts according to its hydrophobicity by use of DAX-8 and XAD-4 resins. SMP in mixed liquor and effluent was analyzed and compared to elucidate its effect on membrane fouling.

Figure 4.12 shows the molecular weight distribution of the SMP in mixed liquor and effluent at SRT 10 and SRT 60 days. Regardless of SRT, both mixed liquor samples shows a bimodal pattern of SMP molecular weight distribution with the majority of SMP having a molecular weight >30 kDa and <5 kDa, which is in agreement with other studies (Liang *et al*., 2007; Huang *et al*., 2008). Molecular weight distribution of SMP was found to shift from larger molecular weight to smaller molecular weight when changing SRT 10 to 60 days. This phenomenon might be due to the decomposition of larger molecular-weight SMP by microorganisms (Huang *et al*., 2000; Shin & Kang, 2003). In contrast to the finding reported by Liang *et al* (2007), membrane sieving did work for SMP accumulation in MBRs. Around 20% of the SMP larger than 30 kDa was retained in the mixed liquor for both SRT 10 and 60 days, and around 4 % of the SMP between 30 and 10 kDa was retained for SRT 60 days. However, microfiltration membranes (0.4 μm) used in this study was much larger compared with the molecular weight of SMP, and, therefore, membrane sieving could not provide the explanation. The retention of larger SMP might be owing to the formation of self-forming dynamic membrane on membrane surface. As the membrane filtration reaches a steady state a dynamic membrane will have been formed on the membrane surface, which acts as a barrier to protect the membrane surface and pores from being fouled (Lee *et al*., 2001). The self-forming dynamic membrane implies that the rate of particle convection to the membrane surface is balanced by the rate of back transport. Figure 4.13 shows that TOC was greatly reduced to a lower value within 10 to 60 minutes of the filtration at both SRT 10 and 60 days. This means that the dynamic membranes have been stably formed on the membranes. The dynamic membranes can reject small components in the mixed liquor such as SMP. However, in the beginning of the filtration, an increase in TMP was not significantly observed, which means that the dynamic membrane would not result in apparent membrane fouling but improve membrane rejection instead.

Figure 4.14 shows that the hydrophilic fraction of SMP was the most abundant fraction in the MBR at SRT 10, which was not in agreement with the observation obtained by Liang *et al* (2007). This contradiction may be due to the difference in feed characteristic and operational condition. Figure 4.14 also shows that 54% of hydrophilic fraction was rejected in the mixed liquor and 36 % of hydrophobic fraction was rejected in the mixed liquor. The result implied that hydrophilic fraction had significant effects on SMP accumulation in the MBR. Hydrophobic interaction is generally considered important mechanism regarding to fouling (Madaeni *et al*., 1999). However, in this study only 36% of hydrophobic fraction was rejected in the mixed liquor, less than the 54% of hydrophilic fraction. Therefore, hydrophobic interaction seemed not to be the major fouling mechanisms of SMP in this study. SMP is mainly composed of carbohydrates and proteins. Proteins are more hydrophobic than carbohydrates (Shin & Kang, 2003). Figure 4.15 illustrates that carbohydrates represented hydrophilic characteristics and the hydrophilic fraction of carbohydrates accumulated in the mixed liquor. Therefore, the hydrophilic fraction of carbohydrates in SMP was most likely the main foulants in the MBR.

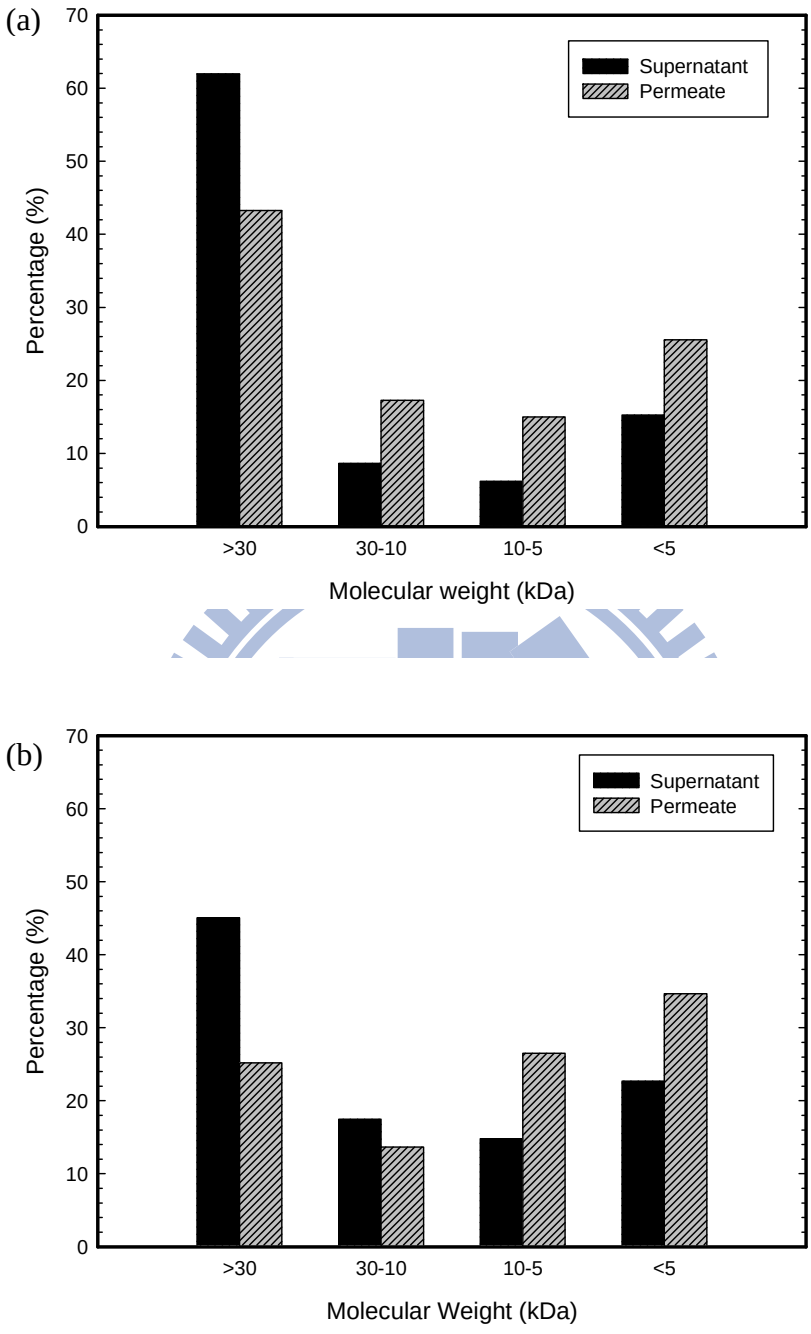


Figure 4.12. Molecular weight distribution of the SMP in mixed liquor and effluents: (a) SRT 10 days and (b) SRT 60 days.

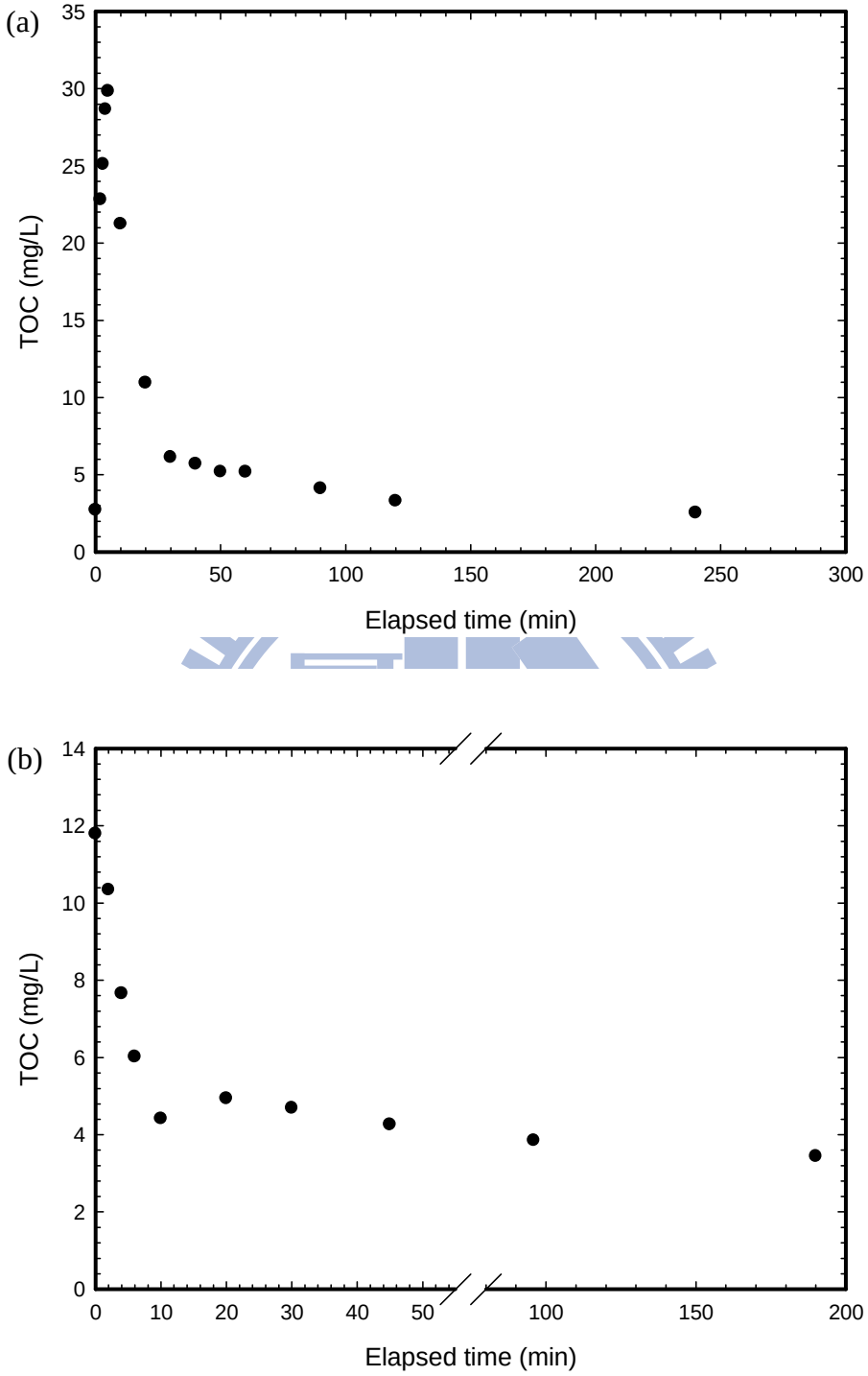


Figure 4.13. Changes of TOC with elapsed time: (a) SRT 10 days and (b) SRT 60 days.

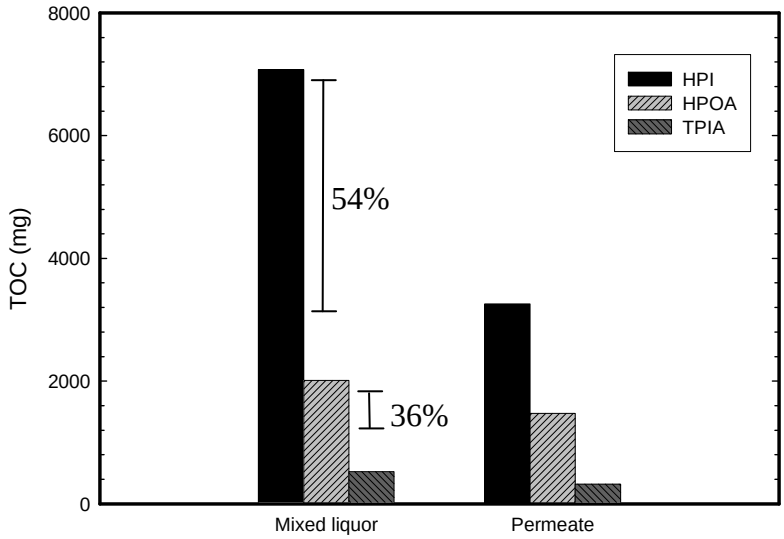


Figure 4.14. Hydrophilicity of SMP in the mixed liquor and effluent at SRT 10. (HPI: hydrophilic fraction; HPOA: hydrophobic acids; TPIA: transphilic acids)

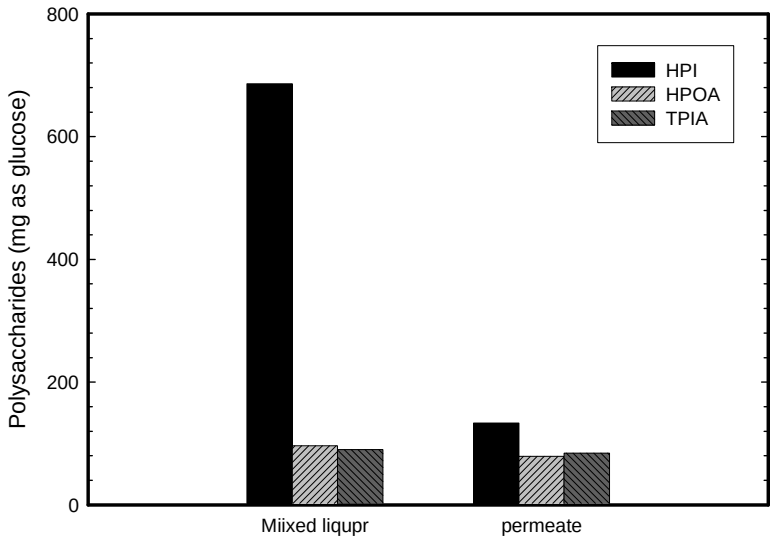


Figure 4.15. Hydrophobicity of polysaccharides in the mixed liquor and effluent at SRT 10.

Chapter 5

Fouling mitigation in MBRs by TiO_2-composite membrane

5.1 Characterization of TiO_2 and TiO_2 composite membranes

To characterize the synthesized TiO_2 particles and TiO_2 composite membranes, TEM, XRD, XPS, and contact angle goniometer were used.

5.1.1 Particle size and crystal structure of synthesized TiO_2

The structures of the TiO_2 particles synthesized in neutral and acidic colloidal sol were directly observed through TEM. As shown in Figure 5.1, the black spots displayed in these two pictures are the synthesized TiO_2 in neutral and acidic sol. It is noted that all TiO_2 particles were smaller than 10 nm regardless of the synthetic methods. Further use of the dynamic light scattering particle size distribution analyzer also confirmed that most TiO_2 particles synthesized in neutral sol were less than 10 nm (as shown in Figure 5.2).

TiO_2 exists in three crystalline phases, anatase, rutile, and brookite, among which rutile is thermodynamically stable, while the other two are metastable. The photocatalytic activity of TiO_2 depends on its phase structure, crystallite size, specific surface area and pore structure. Many researchers have claimed that TiO_2 in anatase form is an excellent photocatalytic material for air purification, water disinfection, hazardous waste remediation and water purification (Hoffmann *et al.*, 1995; Pekakis *et al.*, 2006). The XRD diffraction patterns of the two TiO_2 nanoparticles are shown in Figure 5.3, in which the 2θ of the eminent peaks are 25.24° for anatase and 27.46° for rutile. The TiO_2 nanoparticles synthesized in acidic suspension contain both anatase and rutile phases. The result was different from others' reports (Kwak *et al.*, 2001; Kim *et al.*, 2003; Luo *et al.*, 2005), in which the synthesized TiO_2 particles were composed entirely of anatase, suggesting that the acidic method may result in more than one mineral phase. On the other hand, the TiO_2 nanoparticles synthesized in neutral sol are composed entirely of anatase, which promises the highest photoreactivity and the best efficiency in anti-bio and anti-organic fouling when the UV light is introduced in future application.

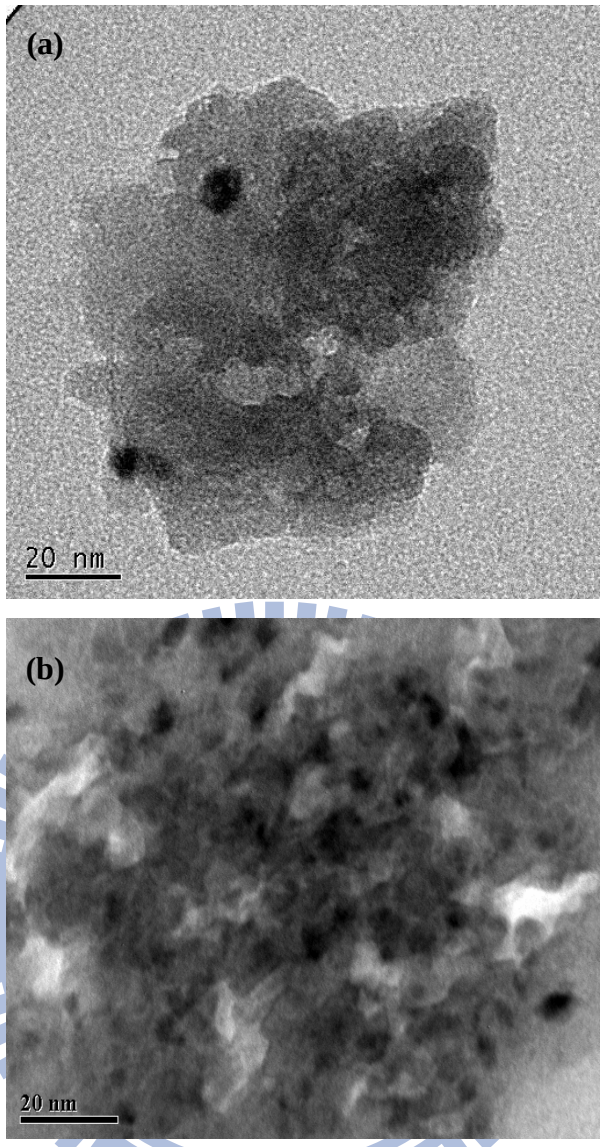


Figure 5.1. TEM micrographs of the TiO_2 particles: (a) TiO_2 nanoparticles in neutral sol and (b) TiO_2 nanoparticles in acidic sol.

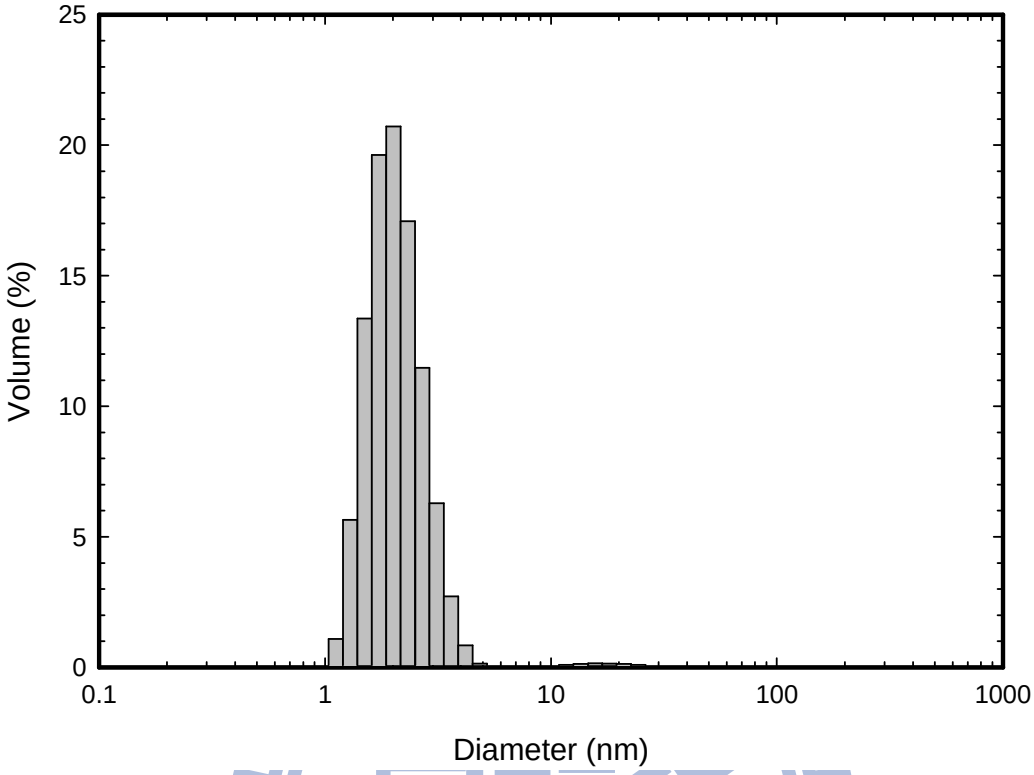


Figure 5.2. Particle size distribution of TiO_2 synthesized in neutral sol.

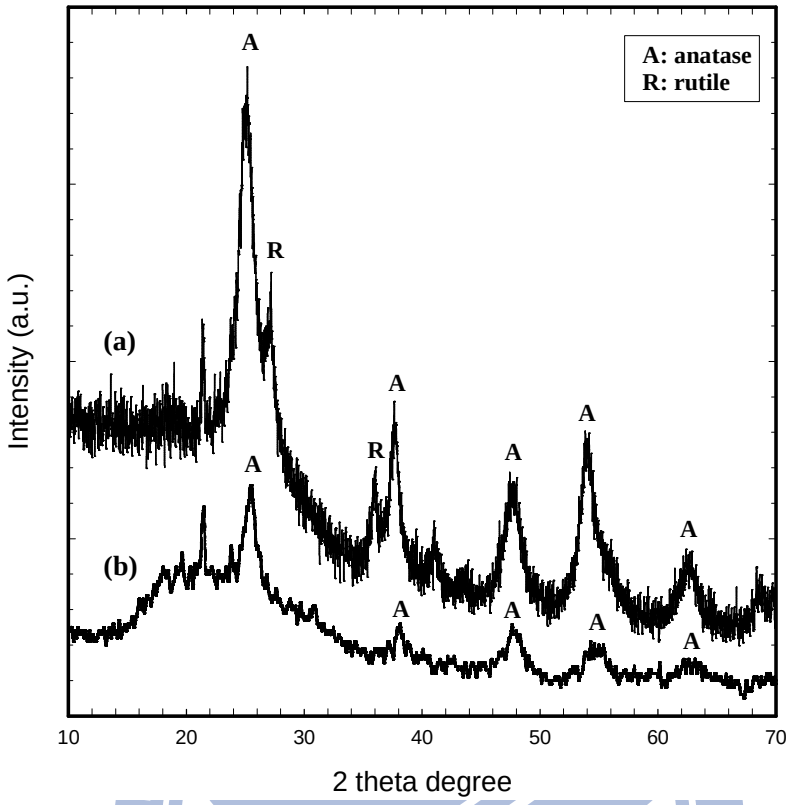


Figure 5.3. XRD patterns of the synthesized TiO_2: (a) TiO_2 nanoparticles in acidic sol and (b) TiO_2 nanoparticles in neutral sol.

5.1.2 Surface characterization of the TiO_2 composite membrane

XPS was conducted to confirm the coating of TiO_2 nanoparticles on the surface of the composite membrane. Figure 5.4 (a) is the full survey on the surface of the TiO_2 composite-CA membrane. The major constituents of the TiO_2 composite membranes are hydrogen, carbon, oxygen and titanium. Because XPS is insensitive to hydrogen, only the XPS analysis of C, O and Ti were shown. As shown in Figure 5.4 (b), the binding energies of Ti 2p core levels were 458.2 eV and 464.1 eV for Ti 2p3/2 and Ti 2p1/2, respectively, which suggested that the Ti was mostly as Ti^{4+}. The binding energy of O 1s core level shown in Figure 5.4 (c) was 530.1 eV, which suggested that the O was mostly as O^{2-}. The XPS spectra of the TiO_2 composite membrane confirmed that TiO_2 was indeed successfully coated on the membrane through the dip-coating method.

Contact angle was measured to evaluate the changes of hydrophilicity after coating TiO_2 on membranes. Contact angle of the virgin membrane and the TiO_2 composite membranes are summarized in Table 5.1. The contact angle of the virgin membrane is 89.13. After the membrane was coated one-time and three-time with TiO_2 particles, the contact angles of the TiO_2 composite membranes decreased to 80.72° and 21.18, respectively. The hydrophilicity of the membranes was increased by the immobilization of TiO_2 nanoparticles on the membrane surface. The reason of decreasing contact angle may be due to the aggregation of a great amount of TiO_2 nanoparticles on the membrane surface. This aggregation results in a large number of three-dimensional tiny voids between nanoparticles. Therefore, when a droplet is dropped on membrane surface, the droplet would spread instantly due to the capillary effects of the three-dimensional tiny voids and the hydrophilic effect of anatase TiO_2 nanoparticles in nature (Song *et al.*, 2008). As a result, the coating of TiO_2 may reduce membrane fouling by increased hydrophilicity (Luo *et al.*, 2005; Jung *et al.*, 2006).

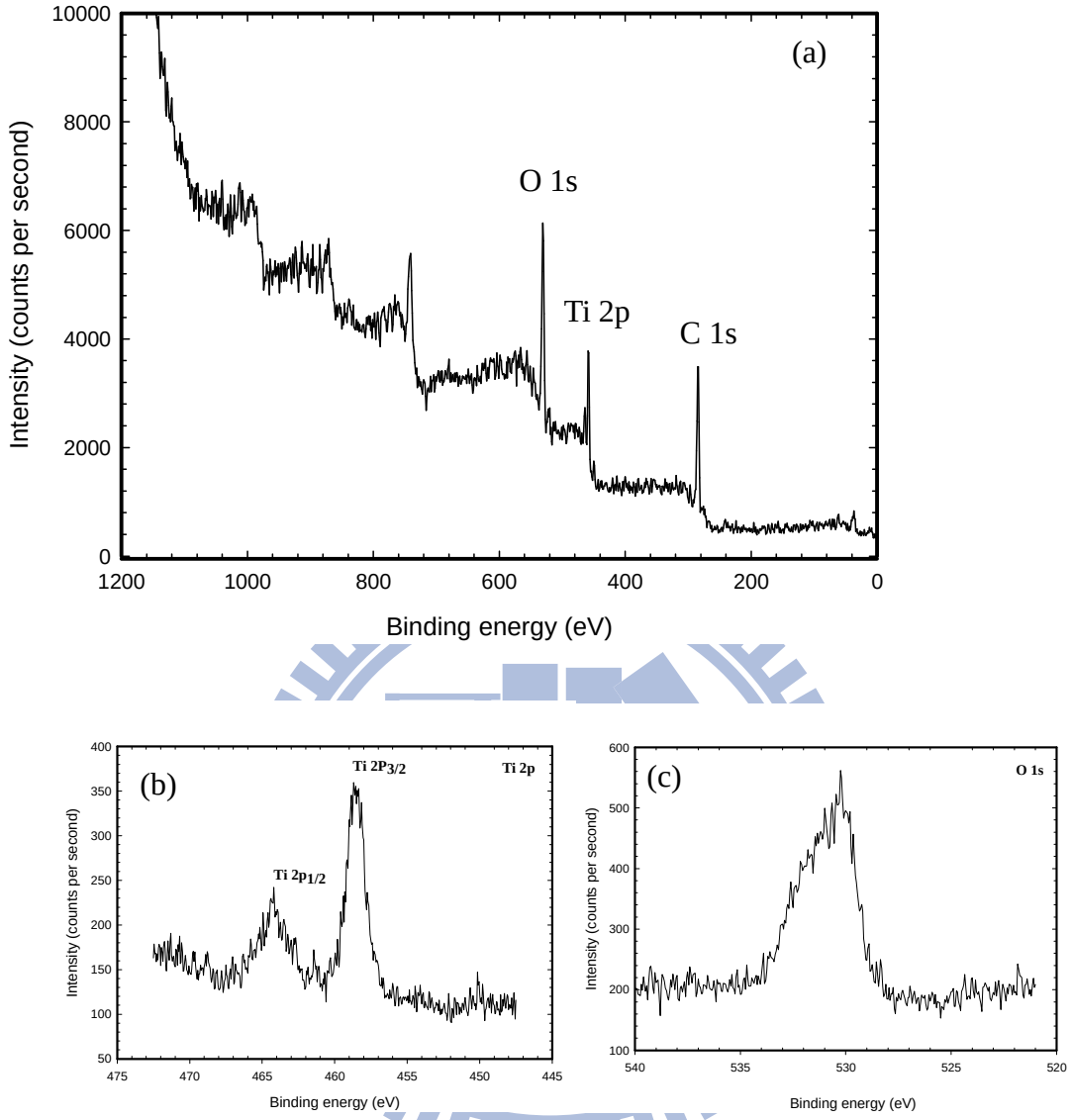


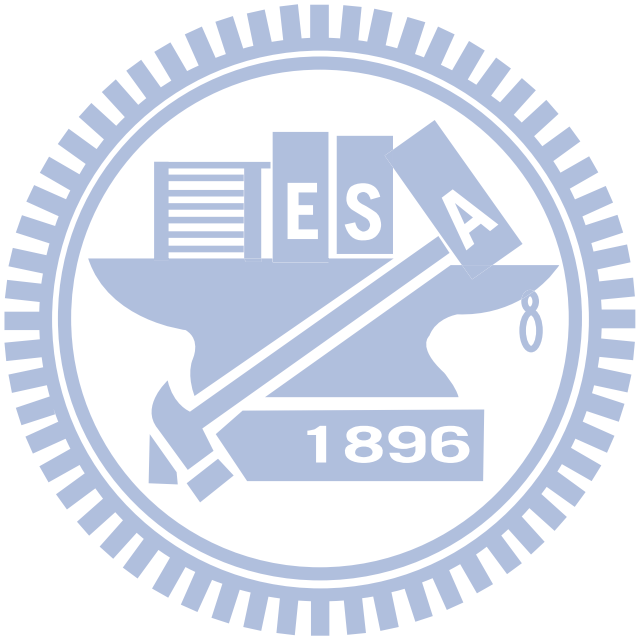
Figure 5.4. XPS reports of (a) full survey of TiO_2 composite-CA membrane; (b) TiO_2 2p and (c) O 1s core level of TiO_2 composite-CA membrane.

Table 5.1. Contact angle of the virgin membrane and the TiO_2 CA-composite membranes

	Contact angle (°)
Virgin membrane	89.13
Composite-1*	80.72
Composite-2**	21.18

*Composite membrane with one-time coating of neutral TiO_2 sol

**Composite membrane with three-time coating of neutral TiO_2 sol



5.2 Effect of TiO_2 composite membranes on membrane fouling

5.2.1 Fouling mitigation of the composite membranes

Two MF membranes (CA and MCE) were made into TiO_2 composite membranes by coating with neutral TiO_2 sol to evaluate the antifouling ability of membrane modification. The filtration resistance of the CA membrane and the TiO_2 composite-CA membrane are depicted in Figure 5.5 (a) and the filtration resistance of the MCE membrane and the TiO_2 composite-MCE membrane are shown in Figure 5.5 b. Both results indicate the improvement in fouling control by coating TiO_2 particles on membrane surface. Regardless of membrane materials membrane fouling can be reduced by coating TiO_2 on membrane surface. Hydrophilic surface can reduce hydrophobic adsorption between sludge and membrane because sludge cake formed on hydrophilic surface can be readily removed by shear stress (Parsmore *et al*., 2002; Maximous *et al*., 2009).

Flux declines of the virgin CA membrane and the TiO_2 composite-CA membranes dip-coated in acidic TiO_2 suspension are shown in Figure 5.6 for comparison. As shown in Figure 5.6, fouling reduction was also observed, which was consistent with others' results (Bae & Tak, 2005c; Luo *et al*., 2005; Bae *et al*., 2006; Choi *et al*., 2007). Results from Figure 5.5 and Figure 5.6 suggest that membrane modification can be a simple and effective way to reduce membrane fouling. To avoid the potential hazard of acidic TiO_2 suspension on membrane, TiO_2 composite membranes dip-coated in neutral sol would be more membrane-friendly, which could be applied for more pH-sensitive membranes.

The membrane was dip-coated in TiO_2 sol for various times to determine the optimal amount of TiO_2 particles on membrane surface for best fouling mitigation. The filtration resistance for different coating is illustrated in Figure 5.7. Although the 2-time coating further improved the filtration, the 3-time coating, on the other hand, reversed the effect. It is clear that increasing the amount of TiO_2 particles on membrane surface by increasing coating times ameliorated membrane fouling before a critical amount was reached. The SEM micrographs of the surface topography of the virgin membrane and the TiO_2 composite membranes, as shown in Figure 5.8, strongly suggest that the higher filtration resistance at 3-time coating is due to the blocking of the membrane surface. The surface of the TiO_2 composite CA membrane with 1-time coating by neutral TiO_2 sol is covered with TiO_2 of a nodular shape and the virgin CA membrane has a characteristic sponge-like structure. Figure 5.8 (c) shows that the surface pores of the TiO_2 composite CA membrane with 3-time coating by neutral TiO_2 sol were severely blocked. The loss of pores on the composite membranes contributed to the increased filtration resistance as reflected in the clean

water flux and the permeability of the virgin membrane and the TiO_2 composite membranes, as shown in Figure 5.9. Therefore, the amount of TiO_2 on membrane surface must be accurately controlled to obtain optimal antifouling effect.

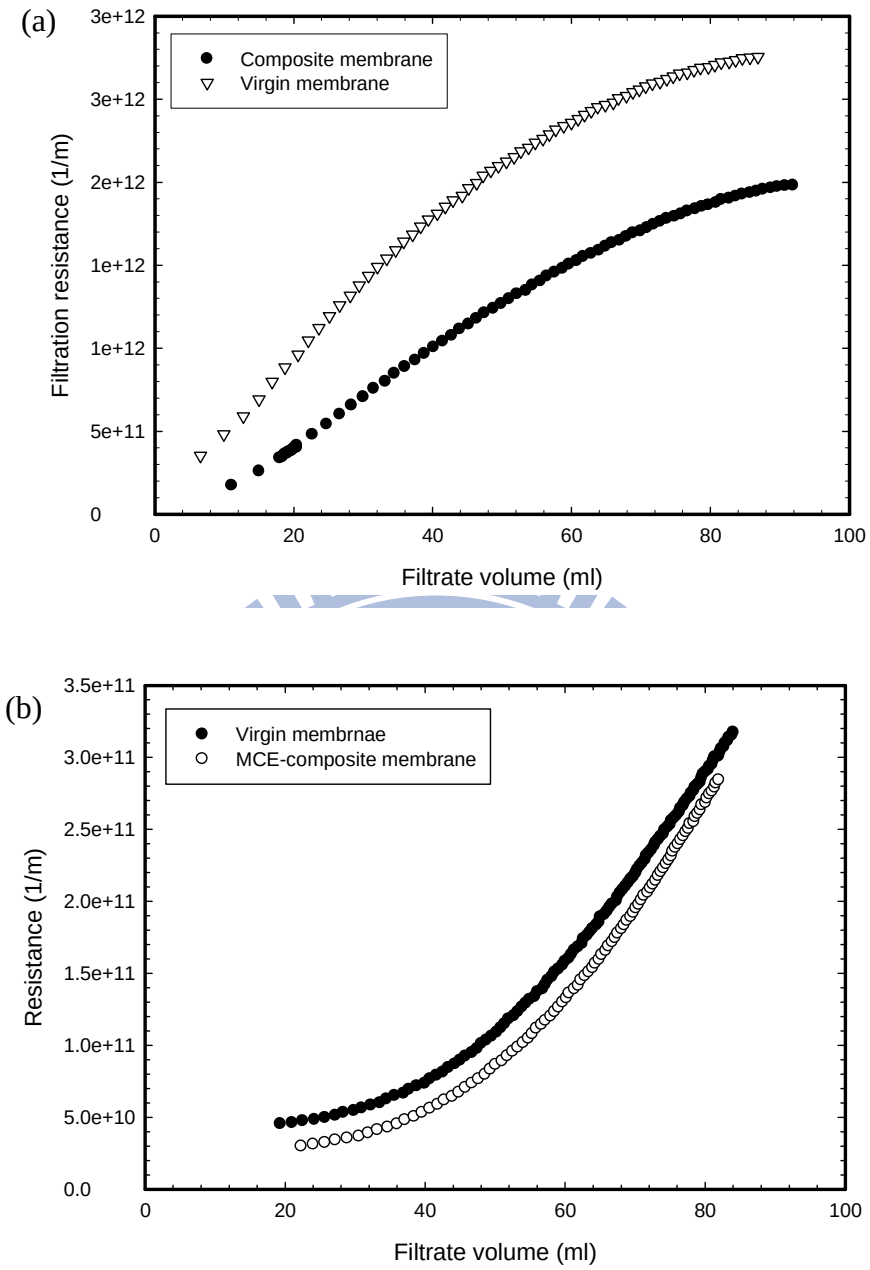


Figure 5.5. Fouling mitigation patterns of the virgin and the TiO_2 composite membrane: (a) composite-CA membrane (0.2μm) and (b) composite-MCE membrane (0.45μm). (coating with neutral TiO_2 sol)

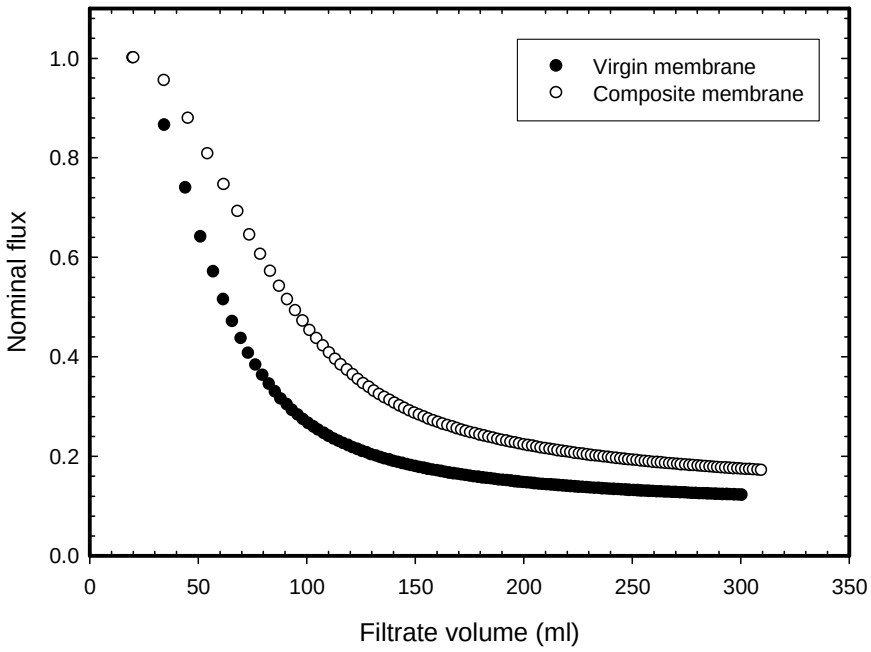


Figure 5.6. Flux decline of the virgin and the TiO_2 composite-CA membrane (0.2μm). (coating with acidic TiO_2 sol)

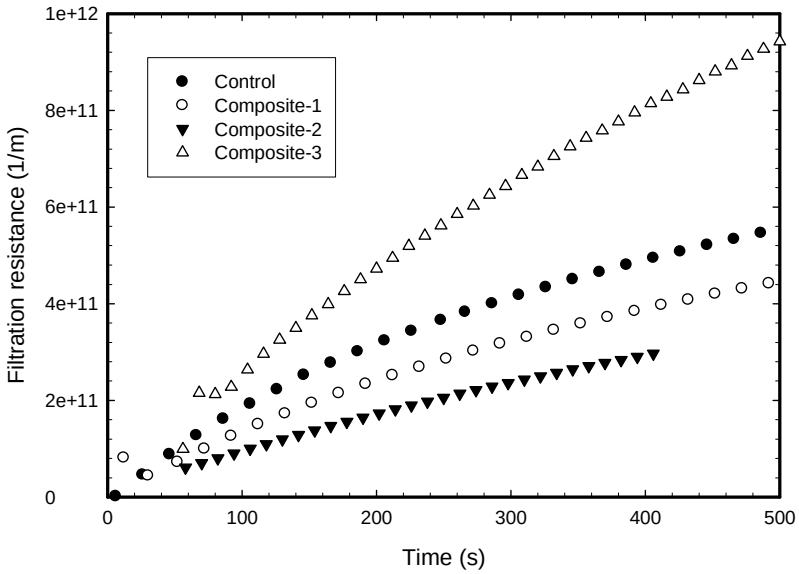


Figure 5.7. Antifouling ability of TiO_2 composite-CA membranes (0.45μm) with different dip-coating times in neutral TiO_2 sol.

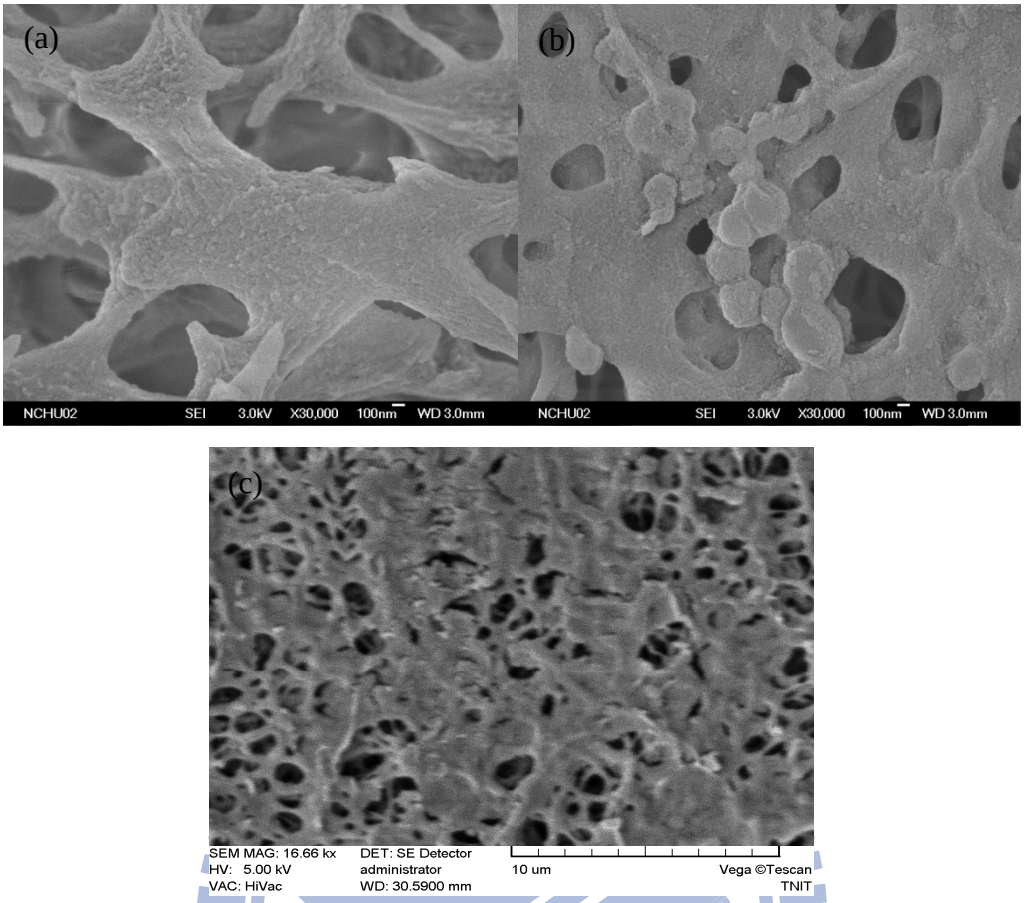


Figure 5.8. SEM micrographs of (a) virgin CA membrane, (b) composite-CA membrane coated with one-time coating of neutral TiO_2 sol, and (c) composite-CA membrane with three-time coating of neutral TiO_2 sol.

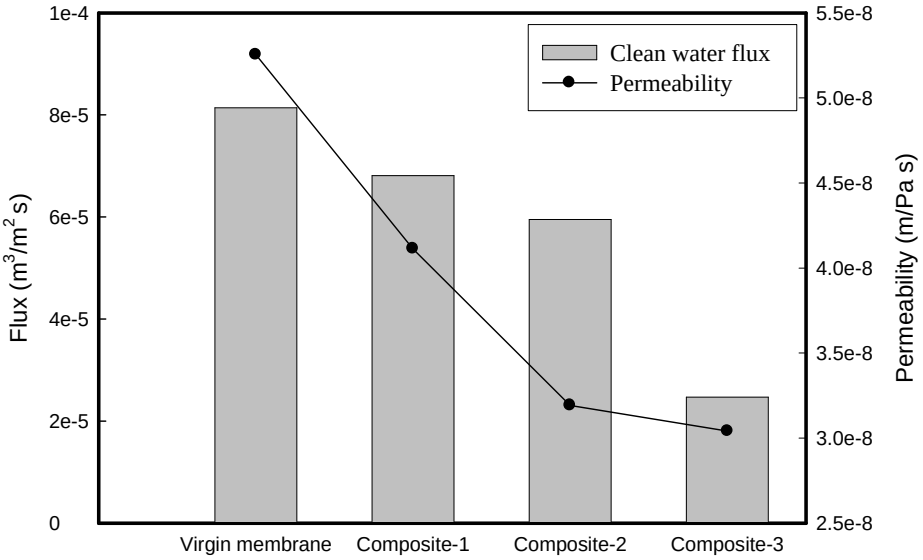


Figure 5.9. Clean water flux and permeability of the virgin membrane and the TiO_2 composite membranes.

5.2.2 Fixation of TiO_2 particles on composite membranes

In order to evaluate the reliability of the TiO_2 composite membranes for long time operation, these composite membranes were washed in an ultrasonic bath with a frequency of 40 kHz and a nominal power of 400 W. Table 5.2 summarizes the relative atomic concentrations of elements remaining on the membrane surface after various ultrasonic washing. It is noted that after ultrasonic washing for three minutes, the relative atomic concentration of titanium element decreased from 52.58 to 27.44 %. No significant reduction of Ti was observed at longer washing. The result indicates that the loosely attached TiO_2 particles were lost in the first couple minutes of ultrasonic washing. Most TiO_2 particles were tightly bound on the membrane even after vigorous membrane cleaning by ultrasonic washing. Therefore, the firm attachment of TiO_2 nanoparticles on membrane surface implies that the composite membranes are reliable for operation. The antifouling propensity would not significantly decrease when operating under high shear stress or performing physical or chemical cleaning.

Table 5.2. Relative atomic concentration of elements on the TiO_2 composite membrane surface under ultrasonic washing.

Sample[a]	Relative atomic concentration (%)		
	C	O	Ti
1	8.34	39.08	52.58
2	15.28	57.28	27.44
3	14.71	55.08	30.22
4	16.45	61.94	21.60

[a] Analysis were performed for the TiO_2 composite membrane: (1) freshly prepared, (2) after ultrasonic washing for 3 min, (3) after ultrasonic washing for 30 min and (4) after ultrasonic washing for 1 h.

Chapter 6

Conclusions and recommendations

6.1 Conclusions

The following conclusions have been made based on the results of this study:

(1) Even under severe sludge bulking, the MBR can still maintain excellent effluent. The removal rates of TOC and ammonia nitrogen were as high as 98% and 99%, respectively, regardless of the changes in sludge characteristics.

(2) Particle size distribution has no direct connection with the serious fouling by bulking sludge. The higher membrane fouling caused by bulking sludge can be contributed to the SMP released from filamentous bacteria.

(3) CST correlated well with SMP and can be a potential fouling indicator.

(4) Soluble polysaccharides and proteins, especially the former, rather than bound EPS are responsible for membrane fouling in MBR caused by filamentous bacteria.

(5) Membrane fouling in MBR under subcritical flux operation is caused by smaller particles such as colloids and solutes in the mixed liquor.

(6) In the range of SRT studied, SRT has significant impact on membrane fouling through the alteration of sludge characteristics particularly the concentration of SMP. The shorter the SRT, the severer the fouling.

(7) Longer SRT results in smaller molecular weight of SMP due to the decomposition by microorganisms. Longer SRT brings negligible fouling due to the rejection of small components by the rapidly formed dynamic membrane on the membrane surface.

(8) Hydrophilic fraction dominates in SMP, which is largely accumulated in the MLSS of the bioreactor. Hydrophilic carbohydrates are most likely the major foulant at SRT 10 days.

(9) TiO_2 coating on CA and MCE membrane can reduce membrane fouling by enhancing the hydrophilicity of the membrane surface. Both acidic TiO_2 suspension and neutral TiO_2 sol are effective in membrane modification for fouling reduction.

(10) Optimal amount of TiO_2 coating must be justified to avoid blocking membrane1

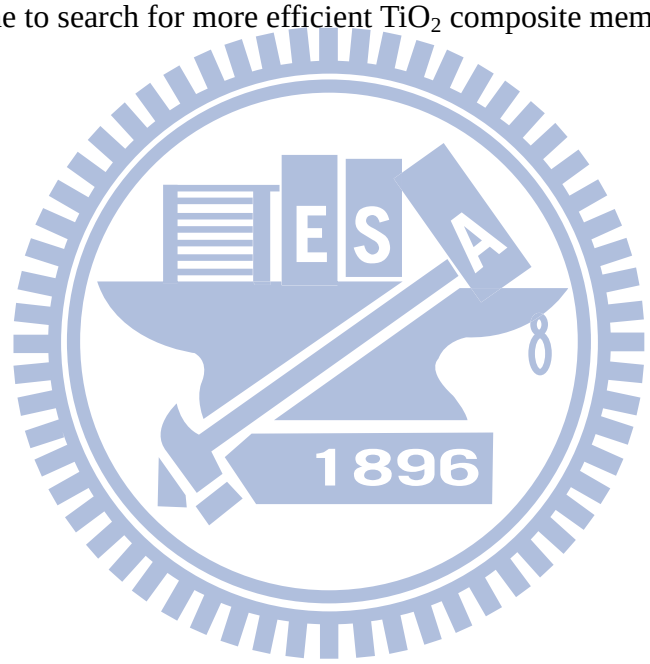
while reducing membrane fouling. Dip-coating of membrane can provide strong fixation of TiO_2 particles on membrane surface.

6.2 Recommendations

(1) Further investigation is needed to verify the findings in the real world situation.

(2) Temperature may have impact on sludge characteristics and therefore, the membrane fouling. It may be interesting to see if temperature affect any of the result.

(3) More studies on fouling mitigation by TiO_2 composite membranes can be done, such as applying UV on the membrane to further enhance its hydrophilicity and resistant to biofouling. More tests can also be performed to involve more types of membrane to search for more efficient TiO_2 composite membranes for fouling mitigation.



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