Membrane bioreactor for treatment of high strength wastewater

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MEMBRANE BIOREACTOR FOR TREATMENT OF HIGH STRENGTH WASTEWATER

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ABSTRACT

This dissertation focused on sustainability of biological system and membrane filtration behavior in long SRT (300 days) condition. A lab-scale MBR with SRT of 300 days was set up and operated for 880 days. The results indicated that 300-day SRT MBR provided stable and sustainable treatment efficiency. The organic removal efficiency in terms of COD and TOC were more than 99%. The resulting MLVSS/MLSS ratio indicated that no accumulation of inorganic compounds took place in the long SRT MBR system. Permeate water quality was higher than the expected microfiltration membrane. The observed sludge yield for 300-day SRT MBR was $0.02277 \text{ gVSS.gCOD}^{-1}$ which was 20 to 40 times less than the values reported in the case of conventional activated sludge.

The study on the fouling tendency of mixed liquor from MBR showed that mixed liquor from 10-day SRT MBR posed a less filterability characteristic compared to the mixed liquor from 300-day SRT MBR. Supernatant was identified as the crucial factor in determining the mixed liquor filterability and cake resistance. As the supernatant comprised of the colloids, solute and macromolecule (EPS), it understood that the soluble EPS, colloid and solutes concentration might play an important role in determination of specific cake resistance. Both MF and UF membranes revealed that increase of mixed liquor concentration incurred the increase of cake resistance, especially when the mixed liquor concentration is higher than 8,000 mg/L MLSS concentration.

Two-stage MF membrane fouling was observed under the super-critical flux, critical flux and sub-critical flux circumstances. The fouling was initiated with a slow fouling stage and followed by a rapid fouling stage. The slow fouling stage caused a significant influence to the critical flux and rejection performance. The experimental results suggested that the formation of biofouling layer was started by the attachment of polysaccharide and formation the biogel layer on top of membrane surface. This process was namely adhesion of the substances onto the

other type of material. It further induced the attachment of protein, polysaccharide and bioparticles, and formation of cake layer.

To derive a better understanding on the fouling mechanisms of microfiltration in submerged MBR system with constant flux mode, the evolution of membrane filtration data was analyzed in terms of blocking laws and cake filtration models. The experimental data presented a slow transmembrane pressure (TMP) increase followed by dramatic TMP increase through the entire filtration operation of 10-day and 300-day SRT MBRs. Analyses of fouling data showed that slow rate of fouling stage involved a mixture of fouling mechanisms such as complete blocking of some of the pores (complete blocking), superimposed of particles on fouling layer (intermediate blocking) and increase of fouling layer (cake filtration). On the other hand, the sharp TMP increase was resulted by the partial pore plugging and superimposed of particles on the fouling layer, resulting in a reduction in pore diameter. A simple perception of membrane fouling steps in MBR has been established based on the experimental data from this study and previous researchers work.

The study on cake layer revealed the correlation between imposed flux and cake retarding effect. An equation was established to portray the phenomenon of cake retarding effect on the fouled membrane. The integration of cake retarding effect into intermittent permeation operation was able to reduce the TMP, thereby extending the usage life of membrane. The results suggested that cake retarding effect was an important parameter for selection of a proper intermittent permeation cycle, hence longer the membrane life span.

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LIST OF SYMBOLS

A	membrane area (m^2)
α	specific cake resistance (m/kg)
α_{block}	pore blockage efficiency
α_{pore}	pore constriction efficiency
BSA	bovine serum albumin
C_b	bulk concentration (mg/L)
C_w	the solute concentration adjacent to the membrane (mg/L)
CAS	conventional activated sludge
COD	chemical oxygen demand (mg/L)
D_B	Brownian diffusion coefficient (m^2/s)
d_p	particle radius (m)
DO	dissolved oxygen (mg/L)
ε	cake porosity
EPS	extracellular polymeric substances
F/M	food to microorganisms ratio ($\text{kg COD} / \text{kg MLVSS.d}$)
HRT	hydraulic retention time (h)
IC	inorganic carbon (m/L)
J	membrane flux ($\text{m}^3/\text{m}^2.\text{s}$ or $\text{L}/\text{m}^2.\text{hr}$)
J_0	initial membrane flux ($\text{m}^3/\text{m}^2.\text{s}$ or $\text{L}/\text{m}^2.\text{hr}$)
J_v	membrane flux during the filtration process ($\text{m}^3/\text{m}^2.\text{s}$ or $\text{L}/\text{m}^2.\text{hr}$)
K_s	half-saturation constant (mg/L)
K_d	endogenous coefficient ($1/\text{d}$)
m_{cake}	cake mass (kg)
MBR	membrane bioreactor
MF	microfiltration
MLSS	mixed liquor suspended solids (mg/L)
MLVSS	mixed liquor volatile suspended solids (mg/L)

N_p	number of open pores
N_{p0}	number of initial open pores
NOM	natural organic matter
ρ	particle density (kg/m ³)
ρ_o	fluid density (kg/m ³)
Q	flow rate (L/d)
Q_i	influent flow rate (L/d)
Q_e	effluent flow rate (L/d)
Q_w	discharge flow rate (L/d)
Δp /TMP	transmembrane pressure (N/m ² or kPa)
PLC	programmable logic controller
R	filtration resistance (1/m)
R_m	resistance of the membrane (1/m)
R_t	total filtration resistance (1/m)
R_c	cake resistance (1/m)
R_p	internal blocking resistance (1/m)
r_p	pore radius (m)
r_{p0}	pore radius (m)
r_s	rate of substrate degradation (g COD/m ³ .d)
r_x	rate of bacterial growth (g VSS/m ³ .d)
r_d	rate of decay (g VSS/m ³ .d)
S	substrate concentration (mg/L)
S_i	influent substrate concentration (mg/L)
S_e	effluent substrate concentration (mg/L)
S_w	discharged substrate concentration (mg/L)
δ_m	membrane thickness (m)
SEM	scanning electron microscope
SMP	soluble microbial product

SOUR	specific oxygen uptake rate
SRT	solids retention time (d)
τ	retardation time (h)
TC	total carbon (mg/L)
TOC	total organic carbon (mg/L)
μ	fluid viscosity (N.s/m ²)
μ_b	specific growth rate (1/d)
$\mu_{\max}$	maximum specific growth rate (1/d)
UF	ultrafiltration
V	reactor volume (L)
V_{LO}	inertial lift velocity without particle-particle interactions for dilute suspension (m/s)
VLR	volumetric loading rate (kg COD/m ³ .d)
X	biomass concentration (mg/L)
X_i	influent biomass concentration (mg/L)
X_r	reactor biomass concentration (mg/L)
X_e	effluent biomass concentration (mg/L)
X_w	discharged biomass concentration (mg/L)
Y	biomass yield (g VSS/g COD)
γ_o	nominal shear rate (1/s)

CHAPTER 1

INTRODUCTION

1.1 Background of study

Conventional activated sludge (CAS) process is the most commonly method for wastewater treatment. The process involves the transformation of dissolved and suspended organic contaminants to biomass, water and carbon dioxide. Therefore, the biologically treated wastewater is able to meet the environmental requirements for discharge. Due to the competitive operating cost compared with other processes such as chemical treatment process, CAS has been widely used for the treatment of sewage and industrial wastewater. However, the CAS treatment results in large amount of excess biosludge which has to be disposed. The additional treatments such as separation, dewatering, digestion, incineration and landfill are needed to eliminate the excess biosludge. Nevertheless, the disposal cost of the excess biosludge has been estimated to be up to 60% of the total plant operating cost (Horan, 1990; Defrance and Jaffrin, 1999).

Water shortage and raw water quality deterioration has prompted many municipalities to look for alternative water resources such as seawater and municipal wastewater (Lu and Leung, 2003; Asano and Cotruvo, 2004; Bixio *et al.*, 2006). The reuse of biologically treated wastewater from municipal sewage treatment plant is a promising new resource. The CAS treatment is unable to provide a stable and high quality treated wastewater. The stability of the CAS process depends mainly on the performance of gravitational secondary clarifier where the sludge settleability is not easily controlled in the practice of conventional biological treatment plants.

Since the first membrane bioreactor (MBR) work was reported by Yamamoto *et al.* (1989), it has advanced rapidly and provided the opportunity for the overcoming of CAS problems. MBR is a combination of membrane filtration and biological treatment using activated sludge where the membrane primarily serves to replace the clarifier of CAS process (Yamamoto *et al.*, 1989; Chiemchaisri *et al.*, 1993; Lee *et al.*, 2001b). Application of MBR has expanded over the last decade due to the opportunity for water reuse/recycling using membrane processes, potential of

reducing costs of membrane technology and the increasingly stringent legislation (Fane, 1996; Côte *et al.*, 2004; Al-Malack, 2007). In comparison with the CAS process, MBR has merits with respect to the complete removal of solids from an effluent, superior effluent quality, low sludge production and small footprint (Stephenson *et al.*, 2000; Visvanathan *et al.*, 2000). With the application of membrane filtration for solid and liquid separation, biomass can be completely retained to maintain a high biomass concentration in MBR. A higher biomass concentration would lead to a more stable reactor performance even at fluctuated organic loading conditions.

The higher retention of biomass in the bioreactor also make it possible to achieve a long solids retention time (SRT) and low food to microorganisms (F/M) ratio, which are believed to minimize the biosludge production in the bioreactor (Shim *et al.* 2002; Yoon *et al.*, 2004; Bhatta *et al.*, 2006). MBR typically produce less sludge than other comparable CAS processes due to the long sludge ages (Ghyoot and Verstraete, 1999; Visvanathan *et al.*, 2000). Reported sludge production rates in MBR system varied between 0 to 0.34 kg MLSS (mixed liquor suspended solids)/kg COD (chemical oxygen demand) removed (Winnen *et al.*, 1996; Stephenson *et al.*, 2000; Pollice *et al.*, 2004). Currently, MBR tends to be operated with SRT of 25 to 300 days to maintain high biomass concentrations, reduce solids production and minimize reactor volume. Excellent MBR performance in the long term operation with no sludge discharge or little sludge discharge had been reported by some researchers (Muller *et al.*, 1995; Rosenberger *et al.*, 2002; Pollice *et al.*, 2007).

Although the effectiveness of an MBR system and reducing excess sludge production was demonstrated to a clear extent, the application of complete sludge retention MBR in the industrial field is still in question. This is due to the lack of a better understanding of the microbial behaviour such as consistency of biological degradation, effect of soluble microbial product (SMP) and microbial activity, etc (Ross *et al.*, 1998; Han *et al.*, 2005; Liu *et al.*, 2005). More dead or inactivate microorganisms was discovered in MBR compared with CAS process. It had been noted that the total microorganisms and rate of specific nitrification, denitrification

and organic removal were lower than those in the CAS process (Zhang and Yamamoto, 1996; Han *et al.*, 2005). According to biological principle, a complete SRT is supposed to generate more dead or inactivate microorganisms in MBR. If so, this controversial issue of complete sludge retention in a MBR is the change in composition of the mixed liquor which may reduce the biological capability. This means that the microbial viability becomes more questionable in a MBR system with complete sludge retention, where dead or inactivate microorganisms have no chance to be discharged.

Clearly, the changes of biological operating conditions especially SRT will induce the revolution of microorganism species, alteration of physicochemical and biological properties of mixed liquor, and subsequently affect membrane performance (Le-Clech *et al.*, 2006). Filtration membrane used in MBR is facing membrane fouling phenomenon which is often referred to the gradual decline of permeate flow due to accumulation of various foulants within membrane pores and/or onto membrane surfaces. The membrane fouling significantly reduces the overall MBR performance, increases operating costs and reduces membrane life span (Belfort *et al.*, 1994). In MBR, membrane fouling is a result of the interaction between membrane material and components in the mixed liquor. As soon as the membrane surface comes into contact with a biological suspension, fouling would be occurred and followed by membrane flux decline. This fouling can be classified into (i) reversible fouling where it is referred to fouling that can be removed from the membrane with physical cleaning protocol, and (ii) irreversible fouling, which refer to the fouling that can only recoverable by chemical cleaning. Various factors affect membrane fouling in the MBR, and these can be classified in relation to the membrane (configuration, material, pore size), biomass characteristics (floc size, mixed liquor concentration, viscosity of mixed liquor, lysed cell, microbial product) and operating conditions (aeration, sludge age, flux)(Chang *et al.*, 2002; Le-Clech *et al.*, 2006).

In the long SRT MBR operation, it is important to understand the effect of high SRT operation to the mixed liquor characteristics, physiological state of

microorganisms, and the membrane fouling substances such as extracellular polymeric substances (EPS) and SMP. Nevertheless, the impact of the different foulants (EPS, MLSS, supernatant) on membrane fouling is discussed differently from one study to another. EPS was reported to provide a major influence to the filterability of mixed liquor (Rosenberger and Kraume, 2002). Although the EPS concentration tend to decrease with increasing SRT of biological reactor, contradicting results were reported on the effect of soluble and bound EPS toward membrane fouling (Mikkelsen and Keiding, 2002; Cho *et al.*, 2005a). Besides, long SRT MBR will tend to accumulate high MLSS concentration in the bioreactor and might be harmful for the membrane filtration performance. In addition, it was reported that the properties of mixed liquor, such as viscosity, concentration and composition of microbial product, and cell surface properties were changed at longer SRT (Chang and Lee, 1998; Shin and Kang, 2003). The existing resources revealed that the impact of high MLSS concentration to the fouling in submerged MBR system is not exactly clear. Rosenberger and Kraume (2002) showed that MLSS concentrations between 2000 to 24000 mg/L had little influence on filterability. Le-Clech *et al.* (2003b) indicated that there was little difference in critical flux for the concentration of MLSS ranging from 4000 to 8000 mg/L, whereas a significant increase in critical flux was observed when the MLSS concentration was increased to 12,000 mg/L. On the other hand, a different conclusion was reported by Meng *et al.* (2005) where MLSS concentration had some influence on the membrane permeability such as cake resistance and cake layer permeation factor. Meng *et al.* (2005) suggested that the MLSS concentration should below 10, 000 mg/L for to maintain an effective MBR operation. In addition, contradicting results were also reported on the effect of mixed liquor fraction (suspended solid, colloids and solutes) toward membrane fouling. Wisniewski and Grasmick (1998) reported that 50% of the total resistance could be due to the soluble compounds. Whereas, another study revealed that suspended solids cause the greatest amount of fouling among the sludge fractions (Defrance *et al.*, 2000). While, Bouhabila *et al.* (2001) reported the supernatant (colloid and solutes) contributed to 76% of the total fouling resistance.

In summary, although the desirable low sludge generation, the long SRT MBR is neither widely accepted nor applied mainly because the unclear stability of biological performance under long SRT condition and difficulty in establishing any generic knowledge pertaining membrane fouling in MBRs due to complexity of biological system. To explore the reliability of low sludge MBR, this research was devoted to derive a fundamental understanding on long SRT MBR by achieving the following objectives.

1.2 Research objectives and scope of work

The major objectives accomplished from this study were: (i) the investigation of the sustainability of biological performance in the long SRT MBR (300-day SRT) operation in terms of organic degradation, inorganic accumulation and sludge yield performance, (ii) the correlations between mixed liquor and filtration performance under the long SRT condition.

Specific objectives of this research consist of:

- examine biological performance in both short and long SRT MBR systems
- study the effect of mixed liquor on membrane fouling under long SRT condition
- investigate the formation dynamics of biofouling layer and its effect on the filtration performance
- explore the MF fouling mechanisms in the submerged microfiltration MBR

The scope of study was limited to the effects of 300-day SRT MBR operation toward biological stability and membrane filtration performance. A lab-scale automation MBR was fed with synthetic industrial wastewater, and used for this research study. In the first stage, the effect of 300-day SRT condition on biological

performance was examined in terms of organic removal, biomass growth, inorganic accumulation and sludge yield. The biological sustainability was assessed through the stability of the above parameters. Subsequently, the second stage of the study was dealt with the membrane performance in 300-day SRT condition. The membrane filtration performance was examined through the effect of 300-day SRT mixed liquor on the membrane resistance, effect of biofouling layer on critical flux and membrane rejection. Results obtained from MF membrane filtration in 300-day SRT MBR was analyzed by four blocking models, followed by an establishing of a MF fouling behaviour under 300-day SRT condition.

1.3 Organization of thesis

The report is divided into 10 chapters. Chapter 1 provides a brief introduction on the biological treatment methods and the setback faced in the MBR system. It also states the research objectives, overview and organization of this study. Chapter 2 is the literature review encompassing the membrane filtration process, membrane fouling mechanisms mathematical models on the fouling behavior and biological performance in long SRT environment. Chapter 3 presents the methodology, design, experimental procedure and analysis methods that use in this study. The sustainability of biological performance under 300-day SRT MBR was examined in Chapter 4. Chapter 5 presents the effect of foulants on membrane performance in 300-day SRT MBR. The relationship between MLSS, supernatant and cake resistance are examined through the measurement of specific cake resistance and filtration resistance tests. Chapter 6 discusses the development of biofouling layer and its effect to the filtration performance. Chapter 7 discusses the EPS distribution in biofouling layer and the contributions of biofouling layer to the enhancement of permeate quality. Chapter 8 presents the fouling behavior in submerged microfiltration MBR system. Four blocking models are applied to verify the fouling tendency and behavior during the filtration time. Chapter 9 presents the cake compressibility as a function of membrane flux and the usage of the cake layer.

Chapter 10 presents the conclusions based upon the results from this research study. The recommendations for future works are also proposed in this chapter.

CHAPTER 2

LITERATURE REVIEW

2.1 Membrane bioreactor

The MBR consists of bioreactor and membrane filtration unit, which replaces the step of the secondary clarification for biomass separation (Mallevalle *et al.*, 1996). The biological processes include the process of organics degradation and nutrient removal, both nitrogen and phosphorus removal using aerobic, anaerobic or anoxic conditions. While the membrane is used for filtration process to draw out the treated wastewater and retain the biomass in the biological reactor. MBR offer numerous advantages over the conventional activated sludge process including complete solid separation, superior quality effluent, reduced land requirements, high volumetric loading, small footprint, longer SRTs and less sludge production (Owen *et al.*, 1995; Stephenson *et al.*, 2000; Parameshwaran *et al.*, 2001; Wisniewski, 2007). The retention of all suspended matter and most soluble compounds leads to excellent effluent quality, capable of meeting more stringent, future discharge limits (Chiemchaisri *et al.*, 1992). Since no suspended solids are lost in the clarification step, the SRT is independent with the hydraulic residence time (HRT). Therefore, full control of SRT provides optimum control of the microbial population and flexibility in operation (Trouve *et al.*, 1994). The capability for operating the MBR at very high sludge ages without having the obstacle of settling, allows high biomass concentrations in the bioreactor and promote the slow growing organism (nitrifiers, bacteria) which capable of degrading complex compounds (Urbain *et al.*, 1996; Melin *et al.*, 2006). High molecular weight, soluble compounds, which are not readily biodegradable in conventional systems, are retained in the MBR. Thus, their residence time is prolonged and the possibility of oxidation is improved. Ultimately, the non-biodegradable compounds are discharged with the sludge rather than the treated water.

With respect to COD removal, MBR was reported for handling 1.2 to 3.2 kg COD/m³.day with corresponding >90% removal efficiencies. The MBR performance appears to be relatively insensitive to HRT with values of HRT ranging from 2 to 24 hours resulting in very high COD removal percentages (Stephenson *et al.*, 2000). The reported MLSS concentration in aerobic MBR range

from 2.5 to 20 g/L. The high biomass concentrations could to enhance the organic degradation performance, but it could also play a significant role in membrane fouling. A higher MLSS concentration correlates to a higher TMP or a lower permeate flux due to sludge cake formation on the membrane surface (Meng *et al.*, 2005). Typically, MBR are able to operate well at longer SRT, the sludge produced is often less than CAS processes. However, the change in characteristics of a microbial community with varying SRT in turn affects the filterability of the sludge (Cicek *et al.*, 2001; Liao *et al.*, 2001; Rosenberger and Kraume, 2002; Witzig *et al.*, 2002; Pollice *et al.*, 2007).

2.1.1 MBR configuration

Solid/liquid separation bioreactor employs microfiltration or ultrafiltration membrane modules for the separation of liquid and retention of biomass in the bioreactor. The membranes can be placed on the external circuit of the bioreactors or submerged directly into the bioreactor as shown in Figures 2.1 and 2.2. In the external MBR unit, the mixed liquor is transferred out from the bioreactor toward the external membrane unit. Under an operating pressure, the treated wastewater will filter through the membrane. The retained biomass is then returned to the bioreactor (Mallevalle *et al.*, 1996). While, in the submerged MBR unit, membrane module is submerged into the biological reactor, the permeate is withdrawn from the bioreactor by a pump (Yamamoto *et al.*, 1989; Wisniewski, 2007). Nevertheless, the energy consumption of the external MBR seems higher than the conventional activated sludge process (Le-Clech *et al.*, 2006). This is due to the high cost incurred by recirculation pump, which connects the main reactor with a membrane unit and generates high crossflow velocity on the membrane surface to maintain the permeate flux. In order to maintain adequate shear at the membrane surface, external MBR recirculation flows are often 20-30 times the product water flow. These high recirculation flows increase energy consumption, making external MBR uneconomical for large municipal wastewater treatment applications (Gander *et al.*, 2000). Thus the solution for this problem is to submerge the membrane into the reactor without recirculation. A submerged MBR is superior to an external MBR in

relation to the power consumption because suction pressure in submerged MBR is generally much lower than that in external MBR and also because power consumption of recirculation pumps is absent in submerged MBR (Yamamoto *et al.*, 1989). The submerged/immersed MBR therefore has the potential to be applied to small wastewater treatment plants that require low cost treatment systems. Côté *et al.* (1998) reported energy consumption rates of 2 – 10 kWhm⁻³ for external MBR unit and 0.2 – 0.4 kWhm⁻³ for submerged MBR unit.

Figure 2.1 External/Side stream MBR system

Figure 2.2 Submerged MBR system

2.1.2 Current development of MBR in sludge minimization

Recent MBR tends to operate with long SRTs to maintain high biomass concentrations, reduce biomass production and minimize reactor volume. Low biomass production is an advantage of long SRT operation of MBR as it leads to lower costs and fewer problems in sludge management and disposal. Long SRT condition also enhances hydrolysis of biomass, such as self-digestion and decay process consequently reduce the biomass production. This generally occurs in the long SRT biological system where the available food supply in the surrounding wastewater is inadequate. In general, MBR typically produce less biomass than conventional wastewater treatment processes due to the long sludge ages (Ghyoot and Verstraete, 1999; Visvanathan *et al.*, 2000). Reported sludge production rates vary between 0 to 0.34 kg MLSS/ kg COD removed (Winnen *et al.*, 1996; Stephenson *et al.*, 2000; Pollice *et al.*, 2004; Al-Malack, 2007). However, the microbiological processes which are at the basis of the low sludge production in MBR and its interaction on the surface of membrane are not well understood yet.

2.1.3 Drawbacks of MBR

Although MBR offer many advantages over conventional processes, there are several aspects limiting wider use of the MBR process. One of the important limitations is the decrease in flux or increase in TMP caused by membrane fouling (Wisniewski and Grasmick, 1998; Defrance *et al.*, 2000; Bouhabila *et al.*, 2001; Chang *et al.*, 2001; Ozaki and Yamamoto, 2001; Wakeman and Williams, 2002). The membrane fouling disrupts continuous operation and requires frequent clean water or chemicals for membrane cleaning. In general, membrane fouling in MBR is likely to be caused by biological fouling (biofouling) which is related to the interaction between bioparticles and membrane. Biofouling is the undesirable deposition and accumulation of microorganisms, extracellular polymers, and cell debris on membrane surface and pore (Flemming *et al.*, 1996; Baker and Dudley, 1998; Le-Clech *et al.*, 2006; Yang *et al.*, 2006). It can be categorized into reversible and irreversible fouling. Deposition or adhesion of particulate matter is often reversible and is characterized as external fouling of the membrane surface by the

accumulation of aggregated cells, cell debris, and other rejected particles (Ma *et al.*, 2000; Wakeman and Williams, 2002). Irreversible fouling is characterized as internal fouling of the membrane pores by the deposition and adsorption of solute and colloid materials, which are similar in size to the pore diameter of the membrane (Ma *et al.*, 2000; Wakeman and Williams, 2002). Another disadvantage of MBR is the high capital investment, expensive membrane units and high energy costs due to the need for a pressure gradient and the aeration. In addition, long SRT operation may cause the accumulation of inorganic compounds in bioreactor which can be possibility harmful to the microbial population or membrane structure (Mallevialle *et al.*, 1996; Cicek *et al.*, 1999).

2.2 Biological processes

CAS process involves the transformation of dissolved and suspended organic contaminants to biomass, water and carbon dioxide, which are separated from the treated waters. It has been greatly applied for the treatment of sewage and industrial waste, due to the inexpensive operating cost compared to chemical treatment process. However, the disposal cost of the excess biomass produced by the CAS process may account for 60% of the total plant operating cost (Horan, 1990; Defrance and Jaffrin, 1999). In view of this, many research have been conducted to handle the excess biomass (Englande and Reimers, 2001; Stolarek and Ledakowicz, 2001; Tay *et al.*, 2001) and to reduce the amount of excess biomass generated by CAS (Ghyoot and Verstraete, 1999; Visvanathan *et al.*, 2000; Liu, 2003). Alternatively, minimization of excess sludge production can be achieved by the practice of long SRT operating condition. MBR easily satisfies a long SRT condition due to its ability to completely separate the HRT and SRT. Due to the long SRT condition, the sludge production in MBR is much lower comparing to CAS process (Gander *et al.*, 2000).

2.2.1 Microbial growth

The microbial growth curve can be divided into several distinct phases called the lag phase, exponential phase, stationary phase and death/ endogenous phase. When a microbial population is inoculated into a fresh medium, growth usually does not begin immediately but only after a period of time called the lag phase. After adapting to the new environment, microbial begin to grow during the exponential phase. Gradual decreases in substrate concentration and accumulation of metabolic products of inhibitory nature reduce the microbial growth rate. When the relative magnitude of maintenance metabolism increases and balances the rate of cell synthesis, microbial reach a stationary phase, where there is no net increase or decrease in cell number. Although no growth usually occurs in the stationary phase, many cell functions may continue, including energy metabolism and biosynthetic processes. In the final death/endogenous phase, microbial decay dominates due to depletion of available substrate (Orhon and Artan, 1994; Madigan *et al.*, 1997).

2.2.1.1 Kinetics of microbial growth

The growth of bacteria in an ideal medium can be quantitatively described by the Monod model:

$$\mu_b = \mu_{\max} \frac{S}{S + K_s} \quad (2.1)$$

Where μ_b is the specific growth rate (d^{-1}), $\mu_{\max}$ is the maximum specific growth rate (d^{-1}), S is substrate concentration (mg/L) and K_s is the half-saturation constant (mg/L). Thus, the rate of bacterial growth in term of mass per unit volume and time can be written as:

$$r_x = \frac{dX}{dt} = \mu_{\max} \frac{S}{S + K_s} X \quad (2.2)$$

where X is biomass concentration in the system (mg/L)

The growth yield coefficient, Y is the amount of biomass produced immediately upon consumption of the growth substrate or oxidation of the electron donor in the case of autotrophic bacteria (Metcalf and Eddy, 2003). Y is defined as

$$Y = \frac{dX/dt}{-dS/dt} \quad (2.3)$$

Combination of equations 2.2 and 2.3 gives the following expression for the rate of substrate degradation:

$$-r_s = -\frac{dS}{dt} = \frac{\mu_{\max}}{Y} \frac{S}{S + K_s} X \quad (2.4)$$

2.2.1.2 Microbial decay

According to the maintenance theory, a portion of biomass is degraded to supply maintenance energy through endogenous respiration. Endogenous metabolism of cells is usually defined as respiration of internal rather than exogenous carbon source resulting in a decrease in the microbial biomass. This mean that the cells oxidize themselves to meet maintenance energy. It is generally assumed that microbial decay occurs following a first order pattern with a constant coefficient (K_d). The decay rate is expressed by:

$$-r_d = K_d X \quad (2.5)$$

2.2.2 Solids retention time

The age of sludge is determined by the amount of time that biomass is retained within a bioreactor. When SRT is varied, the sludge characteristics are affected. These characteristics include changes in floc settling properties, EPS composition, flocculation capability and dewaterability (Liao *et al.*, 2001; Pollice *et al.*, 2007). In general, low SRTs are associated with a rapid rate of microbial growth and higher

rates of sludge production, while high SRTs are associated with slow growing microbes and low rates of sludge production. Recently, many studies have been conducted in SRT conditions to reduce the production of microbial/biomass with the endogenous respiration/metabolism (Droste, 1998; van Loosdrecht and Henze, 1999). During the death/endogenous phase, the metabolism of biomass is called endogenous metabolism, where the incoming substrate could be finally respired to carbon dioxide and water, while results in a lower biomass production (Gaudy and Gaudy, 1980; Martinage and Paul, 2000; Pollice *et al.*, 2004).

The long SRT or complete retention of biomass allows operation at much higher biomass concentrations. The higher the biomass concentration, the lower the F/M ratio becomes. All with the effect that the microorganisms utilize a growing portion of the carbon content of the feed for maintenance purposes (endogenous metabolism) and consequently less for growth (Rosenberger *et al.*, 2002). Long SRT condition can minimize excess sludge production. This can be applied to all process that achieved long SRT should give similar results. When the sludge load becomes low enough, no or almost no excess sludge is produced any more. Stephenson *et al.* (2000) presented literature data on sludge production and concluded that extremely low sludge production is possible for the operating condition at low F/M ratio and high SRT. In CAS process, the theory of endogenous respiration is associated with the biomass decay and the oxidation of the biomass decayed (carbon) to carbon dioxide and biomass debris. Although the debris is ultimately biodegradable, its rate of biodegradation is so low that for all practical purposes. It is inert to further biological attack in most biochemical operations, causing it to accumulate, reducing the fraction of active biomass in the suspended solids (Grady *et al.*, 1999).

A MBR system can maintain higher MLSS compared to a CAS process through membrane separation technology, which can accomplish perfect solid/liquid separation (Yamamoto *et al.*, 1989). Therefore, MBR system can easily achieve long SRT environment. The changes of SRT will affect to the biological process in term of biomass properties and removal capability. So far, literature indicate that

many MBR processes have operated with a longer SRT compared to CAS process and gave rise to higher treatment efficiency (Buisson *et al.*, 1998; Ueda and Hata, 1999; Han *et al.*, 2005). Besides this, low sludge production has been reported in MBR system with long SRT condition (Gander *et al.*, 2000; Innocenti *et al.*, 2002).

However, the biological treatment efficiency would not be linearly proportioned to biomass concentration because the specific bioactivity can be reduced at substrate deficient states (Han *et al.*, 2005). Furthermore, membrane fouling becomes an important issue as the acceleration of membrane fouling occurs in the higher biomass condition (Takeshi and Yasuhiko, 1991). As reported by Shin and Kang (2003) and Chang and Lee (1998), long SRT condition has changed the properties of mixed liquor, such as viscosity, amount and composition of microbial product and cell surface properties. These properties could also influence membrane fouling. Nevertheless, there have not much information on the effect of SRT on the membrane fouling mechanism. Chang and Lee (1998) observed that membrane fouling tendency was increased as SRT decreased. Whereas, Han *et al.* (2005) reported the membrane fouling rate increased as SRT increased. Since membrane fouling is one of the most important obstacles of MBR processes, it is needed to understand the influence of SRT on membrane fouling.

2.3 Membrane mass transport mechanism

Permeation through a membrane demands that some force be applied to drive matter across it (Stephenson *et al.*, 2000). Membranes have the capability to transport different components at different rates depending on the physical and/or chemical properties of components involved and of the membrane. The movement of the various components takes places as a result of one or the other kind of driving force acting on them as shown in Table 2.1.

Table 2.1 Driving force and membrane separation process

Driving Force	Separation Process
Potential	Electrodialysis
Pressure	Reverse osmosis, nanofiltration, ultrafiltration, microfiltration
Temperature	Membrane distillation
Concentration	Dialysis

(adapted from Cardew and Le, 1998)

Under the simplest operational conditions, the pressure driven permeate flux can be describe by Darcy’s law (Ho and Sirkar, 2001) as

$$J \equiv \frac{1}{A} \frac{dV}{dt} = \frac{\Delta p}{\mu R_m} \tag{2.6}$$

where J is the flux in $\text{m}^3/\text{m}^2.\text{s}$, Δp is the trans-membrane pressure in N/m^2 , μ the fluid viscosity in $\text{N.s}/\text{m}^2$ and R_m is the resistance of the membrane in units of m^{-1} . Mass transport in membrane processes can be expressed using resistance in series model, concentration polarization model and membrane blocking model.

2.3.1 Resistance in series model

Resistance in series model is the simplest model to describe the membrane filtration behavior (Field *et al.*, 1995; Lee *et al.*, 2001a; Chang *et al.*, 2002).

$$J = \frac{\Delta p}{\mu(R_m + R_c + R_p)} \tag{2.7}$$

where R_m is the intrinsic membrane resistance; R_c is the (reversible) cake resistance caused by the cake layer deposited over the membrane surface; R_p is the (irreversible) fouling resistance produced by adsorption of dissolved matter

and/or pore blockage within the membrane (Chang *et al.*, 2002). The resistances are conventionally measured through a series of filtration experiments comprising pure water filtration, sludge filtration and pure water filtration following filter cake removal.

2.3.2 Concentration polarization model

Concentration polarization describes the tendency of the solute to build up in the membrane solution interfacial region as shown in Figure 2.3. The extent to which this occurs depends on: (i) the propensity of the rejected species to diffuse which is related to its size, (ii) the notional thickness of the stagnant region, (iii) the rate at which solute is rejected. The latter two factors, on the other hand are determined mainly by the operating conditions themselves. The thickness of the stagnant region, normally denoted by δ , can be determined from the rheological properties of the liquid, the prevailing hydrodynamic conditions and the dimensions of the flow channel. The rate at which solute arrives in the stagnant film is simply determined by the flux and the rejection. Therefore, provided the system is well defined the degree of concentration polarization can be calculated and its effects on the operation of the membrane process assessed (Stephenson *et al.*, 2000).

Figure 2.3 Schematic representation of convective and diffusive solute transport within the concentration polarization boundary layer of thickness (δ) (Zeman and Zydney, 1996).

Colloidal materials transported to the membrane may form a cake that reduces permeate flux or obstructs the bulk flow over the membrane. Early efforts to describe colloidal transport to the membrane and the steady-state concentration profile near the membrane using mass transport expressions developed for solutes underpredicted permeate flux. Expressions for solute transport predict higher concentrations of colloids near the membrane, thus greater cake deposition and lower permeate fluxes than are actually observed in experiments and in practice. Numerous transport mechanisms for colloids species were proposed that might lead to reduced concentrations of colloids near the membrane and thereby resolve the so-called flux paradox. In fact, it appears that several of these proposed transport mechanisms are operative in determining the performance of membranes used to treat suspensions of colloid materials. In particular, inertial lift induced by wall effects has been shown to reduce the transport of larger colloids to the membrane surface, particularly at high crossflow velocities. In addition, shear induced diffusion effect tend to increase the backtransport of colloids from the membrane. Like Brownian diffusion, inertial lift and shear-induced diffusion are functions of particle size; Brownian diffusion decreases with increasing particle size, while inertial lift and shear-induced diffusion increase with particle size. Also, once

deposited as a cake, larger particles tend to produce less resistance to permeation for the same mass deposited. Thus, the performance of membrane facilities and the success of pretreatment are likely to depend on the characteristics of particle size distribution in the feedwater.

2.3.2.1 Film theory

Film theory can be applied to predict the steady state of microfiltration flux (Belfort *et al.*, 1994). The rejection of particles carried toward the membrane by the permeate flow gives rise to a thin fouling layer on the membrane surface, overlaid with a flowing concentration polarization layer in which particles diffuse away from the membrane surface as in Figure 2.3. Assuming a one dimensional system, near 100% rejection and a constant value δ for the boundary layer thickness, the concentration polarization under steady state conditions based on film theory can be defined as:

$$J = \frac{D_B}{\delta} \ln \left(\frac{C_w}{C_b} \right) \quad (2.8)$$

where D_B is the Brownian diffusion coefficient in m^2s^{-1} and C_w and C_b are the respective concentrations at the membrane surface and in the bulk solution: the ratio D/δ represents the mass transfer coefficient k in units of ms^{-1} . Note that this equation does not include pressure term, though the TMP is inferred by the flux value.

2.3.2.2 Brownian diffusion

Leveque solution for laminar flow and Brownian diffusive transport has been developed with integrated the Stokes Einstein equation into the film theory (Stephenson *et al.*, 2000). The length averaged flux is given by:

$$J = 0.807 \left(\frac{\gamma_0 D_B^2}{L} \right)^{1/3} \ln \left(\frac{C_w}{C_b} \right) \quad (2.9)$$

where J is permeate flux, m/s, D_B is Brownian diffusivity, m^2/s , L is length of channel, m, and γ_0 is nominal shear rate, $1/\text{s}$.

For the Brownian diffusion mechanism, an increase in shear rate results in an increase in permeate flux and an increase in particle size results in a decrease of permeate flux. However, models based on Brownian diffusion as promoted by concentration polarization are known to substantially underpredict the flux obtained during colloid filtration (Belfort *et al.*, 1994). To resolve this “flux paradox”, back transport models such as inertial migration, shear-induced diffusion and surface transport have been developed.

2.3.2.3 Shear-induced hydrodynamic diffusion

Shear-induced hydrodynamic diffusion, replacing Brownian diffusion for the larger sized particles ($> 1 \mu\text{m}$), is a result of particle-particle interactions and causes random displacements of the particles from their original streamlines. For dilute monodisperse suspensions ($\phi_b < 0.1$) with a maximum $\phi_m = 0.6$ (Davis and Sherwood, 1990):

$$J = 0.072 \gamma_0 \left(\frac{C_w d_p^4}{C_b L} \right)^{1/3} \quad (2.10)$$

As the permeate flux is predicted to increase with particle size and shear rate.

Where γ_0 is the maximum shear rate, $1/\text{s}$, d_p is the particle radius, m.

2.3.2.4 Inertial lift

Belfort and coworkers (Green and Belfort, 1980; Altena *et al.*, 1984; Drew *et al.*, 1991) have proposed that a possible resolution of the flux paradox is that the back diffusion of particles away from the membrane is supplemented by a lateral migration of particles due to inertial lift. In Poseuille flow, where the particles suspended in the fluid move along the streamlines, suspended particles migrate to an equilibrium position about 0.6 tube radii from the axis. Figure 2.4 shows the fluid velocity profile in Poseuille flow and migration velocities acting on a particle. This lift (from the point of the membrane) is inertial f origin (hence inertial lift) and is caused by the pressure difference (created by fluid velocity gradient perpendicular to the feed flow) on either side of the particle (Green and Belfort, 1980).

Figure 2.4 Schematic picture of fluid velocity profile in Poseuille flow and migration velocities acting on a particle

The inertial lift velocity without particle-particle interactions for dilute suspensions can be expressed as (Drew *et al.*, 1991):

$$V_{LO} = 0.577 \frac{\rho_0 d_p^3 \gamma_0^2}{16 \mu_0} \tag{2.11}$$

where ρ_0 is the fluid density; kg/m^3 μ_0 is the fluid viscosity, Pa.s

Thus the inertial lift velocity increases with the cube of the particle size and with

the square of the shear rate. Steady state flux for the inertial lift is reached when

$$J = V_{LO} = 0.036 \frac{\rho_0 a_p^3 \gamma_0^2}{\mu_0} \quad (2.12)$$

2.3.3 Membrane blocking model

Three separate mechanisms have been used to explain the flux decline associated with particle deposition during membrane filtration: pore blockage, pore constriction and cake filtration (Hermia, 1982). Pore constriction is only possible for membrane with relatively large pores that are easily accessible to the macrosolutes or particles. While pore blockage and cake formation will thus dominate when the pores are smaller than the particles. These three models are strictly only applicable to dead ends up on the membrane, however the models can all be adapted for crossflow operation if the proportion of un-deposited solute material can be calculated (Stephenson *et al.*, 2000).

2.3.3.1 Pore blockage model

In the pore blockage model, the rate of change in the number of open pores is assumed to be directly related to the rate of particle convection to membrane surface (Hermia, 1982; Bowen *et al.*, 1995):

$$\frac{dN}{dt} = -\alpha_{block} A J_v C_b \quad (2.13)$$

where α_{block} is pore blockage efficiency; A is area of the membrane, m², C_b is concentration of SS of the feedwater, kg/m³.

Cake formation is assumed to be negligible, i.e. R_c = 0. Substitution of Eq. 2.13 into Darcy's law and Hagen-Poiseuille equations yields upon integration

$$\frac{J_v}{J_0} = \exp\left(-\frac{\alpha_{block} A J_0 C_b}{N_{p0}} t\right) \quad (2.14)$$

where J_0 is the initial filtration flux through the clean membrane, N_{p0} is the initial pore number.

2.3.3.2 Pore constriction model

In the pore constriction model, the rate of change in the (cylindrical) pore volume is assumed to be proportional to the rate of particle convection to the membrane (Hermia, 1982):

$$\frac{d}{dt}(\pi \cdot r_p^2 \delta_m) = -\alpha_{pore} A J_v C_b \quad (2.15)$$

where δ_m is membrane thickness, m, r_p is pore radius, m.

yielding,

$$\frac{J_v}{J_0} = \left(1 + \frac{\alpha_{pore} A J_0 C_b}{\pi r_{p0}^2 \delta_m} t\right)^{-2} \quad (2.16)$$

2.3.3.3 Cake filtration model

In the cake filtration model, the hydraulic resistance provides by the particle cake is assumed to be proportional to the cake mass, m_{cake} , kg:

$$R_c = \left(\frac{\alpha_{cake}}{A}\right) m_{cake} \quad (2.17)$$

with rate of particle deposition directly related to the rate of particle convection:

$$\frac{dm_{cake}}{dt} = AJ_v C_b \quad (2.18)$$

substitution of Equations 2.17 and 2.18 into Darcy's law yields

$$\frac{J_v}{J_0} = \left(1 + \frac{2\alpha_{cake} J_0 C_b}{R_m} t \right)^{-1/2} \quad (2.19)$$

All three models predict a quasi-linear flux decline at initially short time, with the steepest decline seen for the cake filtration model. The reverse behavior is seen at extended long times, where the lowest flux is obtained with the pore blockage model (lower panel in Figure 2.5). At large times, the flux given by the pore blockage model decays exponentially with time. The pore constriction model shows a $(J_v/J_0) \sim t^{-2}$ dependence and the cake filtration model predicts $(J_v/J_0) \sim t^{-1/2}$. The difference in the fouling models becomes much more apparent in the plot of relative resistance, R/R_m versus time (upper panel in Figure 2.5). The pore blockage and constriction models both predict that R/R_m increase with increasing time with an increasing slope (concave up) while the cake filtration model predicts that the plot of R/R_m versus t is concave down. These differences can be used to distinguish between internal (pore blockage or pore constriction) and external (cake formation) fouling during filtration (Zeman and Zydney, 1996).

Figure 2.5 Comparison of pore blockage, pore constriction and cake formation models. Upper panel show the normalized resistance, lower panel shows normalized flux (Zeman and Zydney, 1996)

2.4 Membrane fouling

Membrane contamination is usually called fouling which causes a higher energy use, a higher cleaning frequency and a shorter lifespan of the membrane. Membrane fouling phenomena present important limitations on the technology. The immediate effect of fouling is to cause a reduction in permeate flux; the long term effect may lead to irreversible fouling from microbial action on the membrane material and reduction of membrane lifetime. The drawback of membrane fouling has been

under investigation since the early MBRs, and remains one of the most challenging issues facing further MBR development (Le-Clech *et al.*, 2006; Yang *et al.*, 2006). Membrane fouling can be categorized into reversible and irreversible fouling. Reversible fouling referred to a fouling layer that can be readily removable from the membrane if an appropriate physical washing protocol is employed. Whereas, irreversible fouling deals with the internal fouling caused by adsorption of dissolved matter into membrane pores and pore blocking and is generally only removable by chemical cleaning (Chang *et al.*, 2002). It has been shown that irreversible fouling of a hydrophobic membrane (e.g. polysulfone, polypropylene, etc) is more significant due to chemical bonds with higher energy (Mallevialle *et al.*, 1996). Bowen *et al.* (1995) elucidated the consecutive steps of membrane blocking in flux decline during protein microfiltration; the smallest pores were blocked by all particles arriving at the membrane for the initial blocking process, then the inner surfaces of bigger pores were covered and afterwards, some particles covered other pre-existing particles while others directly blocked some of the pores, and finally, a cake layer started to build. Furthermore, colloid substances and protein also cause MF and UF membrane fouling by deposition or forming of a cake/gel layer (Ho and Zydney, 2000; Schafer *et al.*, 2000).

2.4.1 Classification of membrane fouling

Membrane fouling can be classified to physical, inorganic, organic or biological fouling. Physical fouling refers to the plugging of membrane pores by colloidal species, such that a certain proportion of the membrane surface is effectively blocked. Inorganic and organic fouling usually respectively refers to scalants and macromolecular species (Judd, 2004). Organic fouling in MBRs is also characterized as biofouling, it is a major problem, arising from biofilm formation in the pores or on the surface of the membrane (Ridgeway and Flemming, 1996).

2.4.1.1 Physical fouling

Particle membrane pollution can be defined as suspended and colloidal matter,

which absorbs to the membrane (Belfort *et al.*, 1994). Solids will plug the membrane, causing that the water that needs treatment is no longer able to pass through. When the membrane is plugged, more pressure is necessary to be able to perform the filtration or separation of solid-liquid. This causes energy costs to rise.

2.4.1.2 Inorganic fouling

Inorganic fouling also refers as scaling which means the deposition of particles on a membrane, causing it to plug (Cicek *et al.*, 1999). During the filtration process, membrane concentrate absorbs inorganic salts, such as calcium carbonate and barium sulphate, which are water-insoluble, can become over-saturated. This causes them to precipitate on membrane surface. Scaling causes the nominal flux to decrease (Judd, 2004). The consequences are, as has been noted before, a higher energy use, an increase of the cleaning frequency and a shorter life span of the membranes. Adding acids or anti-scalents to the system can prevent the precipitation of salts. Acids decrease the over-saturation of calcium carbonate, while anti-scalents decrease precipitation levels.

2.4.1.3 Organic fouling

Biofouling may be initiated with the deposition of individual bacteria cells on the membrane surface and the cells subsequently multiply and form a biofilm (William and Wakeman, 2000). This film can consist of organic matter from the feedwater such as natural organic matter (NOM) or microbial products, namely EPS. The EPS compound which comprise soluble and colloidal macromolecular species are largely responsible for organic fouling of membrane (Judd, 2004). The EPS has the ability to accumulate within pore structure as well as on the membrane surface leading to a decrease in filterability (Nagaoka *et al.*, 1996; Chang and Lee, 1998; Rosenberger and Kraume, 2002; Cho *et al.*, 2005a). The biofouling layer tends to be both reversible and irreversible. Deposition or adhesion of particulate matter is often reversible and is characterized as external fouling of the membrane surface by the accumulation of aggregated cells, cell debris and other rejected particles (Ma *et*

al., 2000; Wakeman and Williams, 2002). Irreversible fouling is characterized as internal fouling of the membrane pores by the deposition and adsorption of solute and colloid materials, which are similar in size to the pore diameter of the membrane (Ma *et al.*, 2000; Wakeman and Williams, 2002). Since particles deposition (sludge cake formation) creates an additional layer of resistance to permeate flow and pore blocking increases membrane resistance by decreasing the surface area of the membrane pores, these two phenomena can classify as mechanism of biofouling in MBR.

2.5 Factors affecting membrane fouling

The nature and extent of fouling are greatly related by three factors: mixed liquor characteristics, operating conditions and membrane characteristics (Chang *et al.*, 2002);

2.5.1 Membrane properties

Membrane properties such as hydrophilicity, pore size, charge, etc. have a direct impact on its fouling. Studies demonstrated that hydrophilic membranes yield the higher fluxes because of the hydrophobic nature of the interaction between membrane and biomass (Futamura *et al.*, 1994; Chang *et al.*, 1999; Madaeni *et al.*, 1999). This has lead to the modification of naturally hydrophobic polymeric materials (polyethylene, polypropylene, etc.) with some hydrophilic functional group, where a 25% increase in hydrophilicity will incur a 49% decrease in (bovine serum albumin) biofouling (Pieracci *et al.*, 1999; Chang *et al.*, 2002). While, the effects of pore size on membrane fouling are depends on the feed solution characteristics especially particle size distribution (Le-Clech *et al.*, 2006). MF membrane has a larger pore size and a higher permeate flux than UF under the same operating condition. Nevertheless, the permeate flux for MF declines more quickly than UF. This was due to the greater internal fouling for larger membrane pore size

(Chang *et al.*, 1994; Hong *et al.*, 2002).

2.5.2 Mixed liquor characteristics

2.5.2.1 MLSS concentration

In the development of MBR technology, many researchers have given attention to the effects of MLSS concentration on the membrane fouling (Wu *et al.*, 2007). However, the effects of MLSS on membrane fouling are not in accordance. Yamamoto *et al.* (1989) reported that the flux decreased abruptly if the MLSS concentration exceeded 40,000 mg/L in a submerged membrane bioreactor. Hong *et al.* (2002) claimed MLSS concentration has little impact on membrane fouling. A more recent study by Le-Clech *et al.* (2003b) indicated that there was little difference in critical flux for the concentrations of MLSS ranging from 4 to 8 g/L, but there was a significant increase in critical flux when the MLSS concentration was increased to 12 g/L. Contradicting result was reported by Meng *et al.* (2005) where the author claimed that MLSS concentration influenced the membrane permeability such as cake resistance. Trussell *et al.* (2007) conducted study in UF MBR with MLSS ranged from 12 to 18 g/L and showed that membrane permeability decreased as MLSS concentrations increased.

2.5.2.2 Sludge fraction

Mixed liquor can be fractionated into three idealized components, i.e. suspended solids, colloids and solutes. This approach has often been applied to account for the relative contribution of each biomass fraction on MBR fouling. Defrance *et al.* (2000) reported that the relative contributions of suspended solids, colloids and solute to the total filtration resistance were 65, 30 and 5 %, respectively. On the other hands, Bouhabila *et al.* (2001) revealed the relative contribution on fouling to be 24, 50 and 26% for suspended solids, colloids and solute, respectively. While, Wisniewski and Grasmick (1998) reported that 52% of the total resistance was attributed by the soluble compounds. In terms of fouling mechanisms, solute and colloidal materials are assumed to be responsible for the pore blockage of the

membrane, while suspended solids account mainly for the cake layer resistance (Itonaga *et al.*, 2004).

2.5.2.3 Floc size

According to the Carmen-Kozeny equation, the smaller the floc size, the greater the cake resistance (Chang *et al.*, 2002). In general, the floc size in MBR include a wide distribution, which ranges significantly from one study to another. Zhang *et al.* (1997) reported that the floc size in submerged MBR was 20-40 μm , while Lee *et al.* (2003) revealed the mean floc size distributions was increased slightly from 5.2 to 6.6 μm for SRT increasing from 20 to 60 days.

2.5.2.4 Extracellular polymeric substance

EPS are products of active secretion, cell surface material shedding, cell lysis and sorption from the environment (Wingender *et al.*, 1999). EPS are composed of a variety of organic substances, including mainly carbohydrates, protein and humic substances (Frolund *et al.*, 1996). EPS play an important role in the flocculation, settling and dewatering of activated sludge (Liao *et al.*, 2001). Nevertheless, many MBR studies identified that EPS as the most significant biological factor responsible for membrane fouling. Nagaoka *et al.* (1996) operated 3 bench scale MBR on synthetic wastewater and found that the increased resistance to filtration could be largely attributed to EPS attached to the membrane surface. Chang and Lee (1998) also reported that total EPS concentration was directly proportional to filtration resistance. Mikkelsen and Keiding (2002) reported that the high EPS content on the sludge presented a lower shear sensitivity and lower degree of dispersion, therefore led to better filterability. According to the literature, the EPS tend to be produced when organic substrates, nutrients, or oxygen are lacking. When MBR are operated under longer sludge retention times and higher biomass concentrations than those normally adopted in conventional activated sludge these conditions of stress are more likely to occur (Pollice *et al.*, 2007). Briefly, EPS has been recognized as the major contributor to membrane fouling. However, the relationship between soluble EPS and bound EPS toward membrane fouling is still unclear.

2.5.3 Operation condition

2.5.3.1 Aeration

In submerged MBR, aeration is used to provide oxygen for the biomass and also used to create the crossflow velocity to scour the membrane surface (Le-Clech *et al.*, 2006). The high crossflow velocity generated at the membrane surface tends to shear off the deposited materials and thus reduce the hydraulic resistance of the fouling layer. Ueda *et al.* (1997) examined the effects of aeration on cake removal and TMP using a pilot scale submerged MBR and concluded that fouling was reduced at higher air flow rate condition and fouling suppression by aeration was mainly through agitation of the membrane fibre. Furthermore, an optimum value of air flow rate was identified beyond which further increases had no effect. The similar phenomena also verified by some researches (Bouhabila *et al.*, 1998; Chang and Judd, 2002; Fane *et al.*, 2002; Le-Clech *et al.*, 2003; Psoch and Schiewer, 2005). Liu *et al.* (2003) investigated the effect of hydrodynamic on submerged MBR membrane and concluded that the membrane filtration resistance sharply increased at an aeration intensity below the critical aeration intensity.

2.5.3.2 Permeate flux

Flux selection is an important factor in determining fouling rate. It is generally considered that membrane fouling increases with increasing imposed flux, while it has been reported that fouling is not observed when imposed flux is maintained below the critical flux (Chang *et al.*, 2002; Judd, 2004). The critical flux value is dependent on the membrane characteristics, mixed liquor composition and operating conditions, therefore the critical flux has to be determined experimentally in each case (Cheryan, 1998).

2.5.3.3 Solids retention time

SRT will influence the mixed liquor characteristics (MLSS concentration, particle size, EPS content, etc.), which can then be directly related to fouling rates (Chang *et al.*, 2002). Bouhabila *et al.* (1998) conducted the study on MF MBR system and reported that 30 days SRT condition provided less fouling rate compared with 10

and 20 days SRT. Similar results also reported by Trussell *et al.* (2006) who stated that fouling rate increased when SRT was lowered from 10 to 2 days. In brief, the fouling rate is slow at long SRT condition. Nevertheless, the increase in MLSS concentration related to long SRT could also result in higher fouling propensity. Han *et al.* (2005) conducted study on the influence of SRT on MF membrane fouling and revealed the increased of membrane fouling when the SRT increased from 30 to 100 days. This was likely due the high MLSS concentration when operated at long SRT condition.

2.6 Fouling control

A number of techniques have been explored in order to overcome the membrane fouling problem such as aeration, intermittent suction, backwashing and chemical usage (Ueda *et al.*, 1997; Decarolis *et al.*, 2001; Hong *et al.*, 2002; Chen *et al.*, 2003; Le-Clech *et al.*, 2003b). These control strategies can be classified as techniques to prevent membrane fouling and techniques to alleviate membrane fouling when already present. Methods to prevent fouling include backwashing, backpulsing, relaxation, proper flux selection, optimizing the hydrodynamics of the MBR system, and choosing or developing the most applicable membrane module design and membrane material (Fane *et al.*, 2000; Ma *et al.*, 2000; Bouhabila *et al.*, 2001; Wakeman and Williams, 2002). While the fouling alleviation techniques are referred to physical and chemical cleaning. Cleaning is the removal of foreign material from the surface and body of the membrane (Cheryan, 1998). The frequency of cleaning is a critical economic factor, since it has a profound effect on the operating life of a membrane.

2.6.1 Critical flux

Critical flux has been proposed as a method for measuring the maximum flux or TMP that can safely be applied and still keep the system running effectively, i.e.

with no or little fouling and with reduced frequency of chemical cleaning. Field *et al.* (1995) introduced the concept of critical flux, working on constant flux filtration of yeast cells with MF. They defined the critical flux as the flux below which an increase of TMP with time did not occur. Howell (1995) defined the critical flux as the below which there is no deposition of colloids on the membrane. Based on theoretical definitions of mass transport, the critical flux can be defined more generally as the flux at which the hydrodynamic force transporting the particle towards the membrane pore is exactly balanced by the opposing back transport forces (Bowen *et al.*, 1999). It should be recognized, however that diffusion is a statistical process and that not all particles in a population will follow the same path. As a result, conditions that are believed to prevent the average particle from depositing on membrane surface will not guarantee that all particles of a particular size and density will remain detached from a surface. This also leads to the inference that there is no such thing as a critical flux at which there will be zero fouling. Rather, critical flux should be considered to be the operating condition that separated slow fouling from rapid fouling.

There several methods to evaluate the critical flux of a filtration system. Flux-step method is the most common method where an incrementally increase the flux for a fixed duration for each increment, giving a stable TMP when the applied flux is below critical flux. If critical flux is exceeded, TMP is observed to increase with time while flux is held constant (Le Clech *et al.*, 2003a; Neal *et al.*, 2003). Chen *et al.* (1997) detected the critical flux using the hysteresis that occurred when the flux was successively increased and decreased. Li *et al.* (2000) used direct microscopic observation of deposited materials to evaluate the critical flux. Chan *et al.* (2002) and Huisman *et al.* (1999) determined the critical flux by examining deviations from linearity in the plot of TMP versus the permeate flux. Espinasse *et al.* (2002) used resistance to filtration to estimate the critical flux, by plotting the normalized resistance against the permeate flux. However, since flux (with constant TMP) or TMP (with constant flux) changes with time, definition of the critical flux using this method was inexact. According to Huisman *et al.* (1999), reproducibility for this method was about $\pm 15\%$. Kwon *et al.* (2000) studied the critical flux evaluated by

two methods, based on particle mass balance or based on the increase in TMP required to maintain a constant permeate flux. They found the critical flux evaluated by the former method was lower than by the latter one.

In general, the critical flux decreased with increasing concentration of particles. However, addition of larger particles resulted in higher critical flux (Defrance and Jaffrin, 1999; Huisman *et al.*, 1999; Kwon *et al.*, 2000; Li *et al.*, 2000; Gesan-Guiziou *et al.*, 2002). The critical flux decreased with increasing concentration of dissolved organic materials (Chen, 1998; Li *et al.*, 2000; Manttari and Nystrom, 2000; Metsamuuronen *et al.*, 2002). However Defrance and Jaffrin (1999) reported that the role of dissolved matter in determining critical flux was small since the difference in fouling resistance was only 5% for the DOC

2.6.2 Aeration

The role of aeration in submerged MBRs is not only to provide oxygen to the biomass but also to limit or even prevent particle deposition (Le-Clech *et al.*, 2003b). An increase in air flow rate at the membrane surface will limit the fouling process in submerged MBR system. During the aeration period, air bubbles form and cause a higher turbulence. Because of this turbulence the fouling is removed from the membrane surface. However, if the optimum aeration rate was achieved, the further increase of aeration rate will not effect on fouling suppression (Ueda *et al.*, 1997).

2.6.3 Intermittent suction

Some researchers have been reported that intermittent suction of treated water can curb the membrane fouling (Yammamoto *et al.*, 1989; Ueda *et al.*, 1997; Hong *et al.*, 2002). Alternating between periods of suction and stoppage of suction, it was assumed that the cake layer deposited on membrane might be depressurized and partially detached during a cessation of suction.

2.6.4 Backwashing and backpulsing

Backwashing is a common practice whereby the permeate is pumped back through the membrane at periodic intervals. It has been found that backwashing successfully remove most of the reversible fouling due to pore blocking, transport it back into the bioreactor, and partially dislodge loosely attached sludge cake from the membrane surface (Le-Clech *et al.*, 2006). The backwashing can be accomplished with gas or liquid and it is even possible under certain circumstances to add a cleaning agent to the backwash fluid. When backwashing is applied, the pores of a membrane are flushed inside out (Decarolis *et al.*, 2001). It is assumed that the backwashing will pushes particles out of clogged membrane pores and dislodges accumulated particles from the membrane surface. The pressure on the permeate side of the membrane is higher than the pressure within the membranes, causing the pores to be cleaned. Permeate is mostly used for a backwashing, because the permeate chamber is free of contagion. The backwash must be maintained long enough to fully flush the volume of a module at least once. Backwashing is effective at removing loosely adhered foulant from the membrane; however, it has proven to be ineffective when the sludge cake is adhered strongly to the membrane or if the pores are blocked with foulant (Bouhabila *et al.*, 2001; Wakeman and Williams, 2002). Backpulsing is similar to backwashing, but is shorter in duration (<0.1 seconds) and may be operated continuously or periodically (Silva *et al.*, 2000; Wakeman and Williams, 2002). Backpulsing has been particularly useful at minimizing the adherence of colloids (Wakeman and Williams, 2002).

2.6.5 Chemical cleaning

When the above-mentioned cleaning methods are not effective enough to reduce the flux to an acceptable level, it is necessary to chemically clean the membranes. Chemical cleaning is the use of chemical reactions to weaken the cohesion forces between the foulants and the adhesion forces between the foulants and the membrane surface (Chen *et al.*, 2003). During chemical cleaning process, membranes are soaked with a solution of chlorine bleach, hydrochloric acid or hydrogen peroxide. First, membrane is soaked into the cleaning solution for a

number of minutes and after that a forward flush or backward flush is applied, causing the contaminants to be rinsed out. Chemicals, such as hydrogen chloride (HCl) and nitric acid (HNO₃), are added to the permeate during backward flush. As soon as the entire module is filled up with permeate, the chemicals need to soak in. After the cleaning chemicals have fully soaked in, the module is flushed and finally put back into production. The chemicals that have been used for membrane washing include sodium hypochlorite, hydrogen chloride, sodium hydroxide and surfactant (Yamamoto *et al.*, 1994; Ueda *et al.*, 1996; Ueda and Hata, 1999; Judd and Jefferson, 2003). The use of 0.05% sodium hypochlorite probably aided in removal foulants deposited within the membrane surfaces (Sofia *et al.*, 2004).

Over time, membrane processes will also typically experience some degree of irreversible fouling which cannot be removed through chemical cleaning. These irreversible fouling occurs in all membrane systems, over a wide range of rates, and eventually necessitates membrane replacement.

2.7 Summary

Long SRT operating condition has been identified as an effective way for reducing the biomass production in MBR. Some of the researchers have reported the zero sludge produced in the long SRT condition (Muller *et al.*, 1995; Witzig *et al.*, 2002; Rosenberger *et al.*, 2002). However, the application of MBR with long SRT in industrial field is still in doubt; mainly due to the insufficient knowledge and experiment on microorganisms activity and system stability in the long SRT condition. Furthermore, the changed biological properties in the reactor will affect the cake layer deposited on the membrane surface and pores; subsequently causes the fouling on membrane surface. Hence, it is a need to understand the effect of long SRT's mixed liquor toward the membrane fouling. As discussed in the above chapters, membrane fouling is the consequence of interaction between membrane and mixed liquor which leads to frequent cleaning or replacement of membranes,

hence increases the operating costs. Additionally, the nature and extent of fouling are related to the mixed liquor characteristics, membrane characteristics and operating condition. There is not much information available regarding the effect of long SRT condition onto membrane filtration performance especially on the aspect of optimum imposes flux and rejection performance. Therefore, more comprehensive study is needed to provide a better understanding on the impose membrane flux, membrane rejection and fouling behavior under the long SRT condition.

CHAPTER 3

MATERIALS AND METHODOLOGY

3.1 Research approaches

There were two-phase studies in this research program, Phase I study focused on the understanding of biological stability of long SRT MBR. The performance of biological process was assessed in term of organic removal efficiency, sludge yield, inorganic accumulation and system stability, including the effect of SRT on biological performance of MBR. Phase II study focused on the performance of membrane filtration in the long SRT MBR. The effect of foulants (MLSS, EPS, supernatant) on membrane fouling was studied. Phase II study also investigated the development of biofouling layer and its effect on the filtration performance. A conception of MF fouling behavior in MBR system was also being established based on the analytical results. In addition, the effect of cake compressibility on membrane fouling was also studied. The research approaches are outlined in the following sections.

3.1.1 Biological performance and stability of long SRT MBR

Sustainability is achieved by biological systems if they successfully create and reproduce the environmental conditions which they require for robust existence. Stability through sustainability is an essential factor for a biological process to be implemented effectively. In this study, the biological performance and stability of a long SRT (300-day) MBR were assessed through the COD and TOC removal efficiency, biomass growth, MLVSS (mixed liquor volatile suspended solids) /MLSS ratio, sludge yield and microbial respiration. Furthermore, the sludge growth, biodegradation ability and microbial behavior in three different SRT conditions (5-day SRT, 10-day SRT and 300-day SRT) were also compared

3.1.2 Effect of foulants on membrane performance in long SRT MBR

Membrane fouling results from interaction between the membrane material and the components in the biological system. The mixed liquor composition of a biological process varies both with feed water composition and MBR operating conditions

employed. Thus, the significance of foulants effect toward membrane fouling is changed in different operating conditions. It is therefore important to study the effect of foulants on membrane performance in 300-day SRT MBR condition. This study was designed to evaluate the impacts of 300-day SRT mixed liquor such as MLSS concentration and supernatant on the specific cake resistance and membrane resistance.

3.1.3 Development of biofouling layer and its effect on filtration performance

Membrane fouling is an inevitable consequence of interactions between membranes and the mixed liquor, however, impedes widespread of MBR technology. The comprehensive understanding of biofouling formation and its effect to the filtration performance is needed to optimize and improve the usage of membrane. This research work was aimed to study the development of biofouling layer on the MF ceramic membrane. Furthermore, the changes of critical flux, permeate quality, TMP and membrane rejection versus the biofouling layer were also performed.

3.1.4 Fouling behavior in long SRT MF MBR

This study also designed to establish a conception of MF fouling behavior in long SRT MBR, which provides an overview of MF fouling steps in the long SRT condition. Four kinds of fouling mechanism models are applied to verify the fouling tendency and behavior during the filtration time.

3.1.5 Effect of intermittent permeation and cake compressibility on membrane fouling

As the cake layer is the main fouling layer in the MBR system, the cake compressibility should be taken into the consideration when assessing the membrane fouling. This study was designed to explore the cake compressibility as a function of membrane flux and the usage of cake compressibility in intermittent permeation operation mode.

3.2 MBR system, raw wastewater and operation conditions

Figure 3.1 shows the laboratory scale setup of a submerged MBR system. Detailed schematic is shown in Figure 3.2. This system consisted of an activated sludge bioreactor having submerged microfiltration membrane module. The bioreactor was separated into 3 sections by baffles. The 3 sections were named the chemical oxygen demand (COD) removal tank (COD-tank), nitrogen removal (N-tank) and the membrane filtration tank (MBR-tank), and had working volumes of 6 L, 4 L and 10 L respectively. Aerations were provided in the COD-tank and MBR-tank to establish aerobic conditions. The aeration in the COD-tank and MBR-tank also provided mixing, while the aeration intensity was higher in the MBR-tank to generate higher crossflow and provide additional scouring of membrane surfaces to reduce fouling. Intermittent low intensity aeration was provided for the N-tank to simulate anoxic conditions. As aeration in the N-tank was intermittent, an overhead mixer was used to provide the mixing. All aerations were supplied by compressed air from an air blower to the diffusers located at the bottom of each section. Air flowrates to the diffusers in the individual tank were measured using digital air flowmeters. An ultrasonic level sensor was used to control the water level in the MBR-tank and thus maintained a constant total volume in the reactor. Upon detection of a lower level, the sensor will signal via the programmable logic controller (PLC) unit for the influent pump to start and wastewater will be fed into the system.

From the schematic diagram, the wastewater was fed through the COD-tank before overflowing into the N-tank and then finally overflowing into the MBR-tank. Sludge from the MBR-tank was recirculated back to the COD using a recirculation pump. The hydraulic retention time of each compartment was making up the total HRT. Dissolved oxygen (DO) and pH were measured using online DO and pH probes. A suction pump was used to obtain the membrane filtered permeate. The HRT of the system was controlled by the permeate flux. The flowrates were measured using digital flowmeters with signal feedback to the PLC. Transmembrane pressure was measured using a digital pressure switch also with

signal feedback. Four units of ceramic membranes used in the laboratory scale experiments were of MF type and have an effective pore size of $0.9\text{ }\mu\text{m}$. Surface area of each ceramic membrane is 0.024 m^2 . The membrane modules were placed in the centre of the reactor to ensure maximum contact with the coarse air bubbles to alleviate the fouling phenomenon commonly encountered in MBR.

Inoculation sludge was taken from Singapore Jurong Wastewater Reclamation Plant and assimilated for four weeks to the synthetic industrial wastewater before the submerged MBR operation. The characteristics of the synthetic industrial wastewater used for this study are listed in Table 3.1. DO in the COD-tank was kept above 4.5 mg/L while DO in the MBR-tank can only be kept above 3.5 mg/L . DO in the N/P-tank is generally below 0.5 mg/L . This is made possible by intermittent aeration. The coarse bubble aeration system was applied in membrane compartment where coarse diffuser was used to generate the coarse bubble. The aeration intensity of COD-tank, N-tank and MBR-tank was 36 , 30 and $36\text{ m}^3/\text{m}^2\cdot\text{hr}$ (where the aeration intensity was the airflow rate divided by the cross sectional area of the riser), respectively. PLC system is employed for the fully automation control to the MBR system. Detailed operating conditions of the experimental runs are summarized in Table 3.2.

Figure 3.1 Laboratory scale submerged MBR system

Figure 3.2 Schematic diagram for laboratory scale submerged MBR

Table 3.1 Characteristics of the synthetic industrial wastewater

Component	Concentration
COD (mg/L)	1000±5
Soluble COD (mg/L)	543±5
particulate COD (mg/L)	456±5
TOC (mg/L)	334±0.2
Soluble TOC (mg/L)	209±0.2
TN (mg/L)	30±5
TP (mg/L)	1.35±0.5
pH	7.0-7.5
SS (mg/L)	200±10

Table 3.2 Operating conditions of the laboratory scale submerged MBR

Parameters	value
Working volume (L)	20
HRT (hr)	8
SRT(d)	200
Flux ($\text{L}/\text{m}^2\cdot\text{hr}$)	26
VLR ($\text{kgCOD}/\text{m}^3\cdot\text{day}$)	3
Temperature ($^{\circ}\text{C}$)	25
pH	6.5 - 8.0

Constant flux: the flux was kept constant by increasing the transmembrane pressure (TMP). Automatical flowmeter was used to monitor the permeate flux and to adjust the TMP accordingly to maintain a constant flux. The TMP was recorded over time.

Determination of membrane fouling tendency: A pressure indicator was connected in parallel to the permeate pipeline to obtain the transmembrane pressure (TMP). As the experiment was operating with constant membrane flux, the TMP served as monitoring tool for the membrane performance.

Membrane characteristics

MF ceramic membrane with effective pore size of $0.9\ \mu\text{m}$ was used to investigate the membrane performance in high MLSS system. The membrane is in tubular form and it is constructed by diatomaceous earth material with permeability of $2600\ \text{L}/\text{m}^2\cdot\text{hr}\cdot\text{bar}$. The membrane surface for one unit of MF ceramic membrane is $0.02402\ \text{m}^2$.

3.3 Membrane resistances determination

Membrane resistances were determined to assess reversible and irreversible membrane fouling. Before the microfiltration test was carried out, the pure water flux, J_0 was measured for each membrane to get the intrinsic membrane resistance (R_m). Before the test for the intrinsic membrane resistance (R_m), the membrane was immersed in 1000 ml of deionized water and the water was varied three times for an hour, at least. The rinsed membrane was kept in the deionized water in the refrigerator overnight. A 20-minute filtration with pure water was performed before the filtration experiment in order to compact the new membrane surface (i.e., compaction between membrane surface and supporting layer) and stabilize the permeate flux and pressure. In each individual testing, a new membrane was employed. The membrane was operated for 3 minutes just before the test started to stabilize the flux and pressure with constant permeate flux. The experiments were carried out under constant flux conditions where the increase of TMP value could be recorded. The total resistance at the end of filtration test (R_t) was then calculated with the permeate flux and TMP at the end of each permeate test. The resistance at the end of filtration test (R_t) included the resistance by concentration polarization, by cake layer and by adsorbed layer. And then, membrane surface was flushed with water and cleaned with sponge to remove cake layer. After that the pure water flux was measured again to get the resistance of $R_m + R_p$.

3.4 Specific cake resistance determination

Specific cake resistance is the cake resistance normalized to the mass of materials deposited per unit of membrane surface area and it is a unique property of particles consistent with their size and conformation (Howell *et al.*, 1993). To determine the specific cake resistance of each fraction obtained from the mixed liquor, the compression-permeability experiments were carried out in an unstirred filtration mode (Chudacek and Fane, 1984). Specific cake resistance can be determined experimentally from the elapsed time (t) and flux (J) obtained.

$$\frac{1}{J^2} = \left(\frac{\mu R_m}{\Delta P} \right)^2 + \frac{2\mu\alpha C_b}{\Delta P} t \quad (3.1)$$

where α is the specific cake resistance (m/kg) and C_b is the particle density (kgm⁻³).

3.5 Critical flux determination

The effective critical flux of the feed was determined by increasing the flux in a step-wise fashion (every 15 minutes) while monitoring the corresponding TMP.

The effective critical flux of the feed was determined by increasing the flux in a step-wise fashion (every 15 minutes) while monitoring the corresponding TMP. When a great TMP increased perceptibly over 15 minutes, the imposed flux was regarded as the critical flux. For each flux-step, two TMP values are reported: the initial TMP (TMP_i), defined as the TMP obtained after the initial sudden increase in filtration resistance following the step increase in flux, and the final TMP (TMP_f), defined as the TMP at the end of the step. From these two TMP values, parameter pertaining to fouling rate can then be defined as;

$$\frac{dTMP}{dt} = \frac{(TMP_f - TMP_i)}{(t_f - t_i)} \quad (3.2)$$

where t_i is the initial time new step flux begin, t_f is the end time of the step.

3.6 Particle size distribution

The sludge particle was examined using Malvern Master Sizer Model Hydro 2000S. The Master Sizer measures particle in the size range of 0.02-2000 μm based on the principle of laser diffraction. This instrument operates by passing a laser beam, which is diffracted by the particles in the suspended sample. The background reading given by the distilled water alone was measured first, then the measurement

of the sample in suspension. The particles-in-liquid suspension of suitable concentration was prepared by adding small portion of the sample to distilled water achieving an obscuration of 0.1-0.2. The concentration was derived using the Beer-Lambert Law. The Malvern uses an iterative technique to generate the results from the light energy data. Since repeated measurement of the same sludge sample exhibited different results, three replicate determinations were done. Results are given as mean particle size and standard deviation.

3.7 Extracellular polymeric substances extraction

3.7.1 EPS extraction from MBR's mixed liquor

The EPS extraction method followed that reported by Liu and Fang (2002) and Zhang *et al.* (1999). 10 ml of sample was centrifuged at 4000 rpm for 10 minutes; subsequently the supernatant was shifted to another tube. While the microbial pellet was recovered and resuspended in ultra pure water with total volume at 10 ml. For the microbial pellet, 0.012 ml formaldehyde (37%) was added and kept for 1 hour at 4°C, it followed with adding 0.8 ml NaOH (1N) and kept for 4 hours at 4°C. After that, the supernatant of the sample and microbial pellet were centrifuged (13,200 rpm, 20 minutes, 4°C) before chemical component analysis.

3.7.2 EPS extraction from biogel layer and cake layer

The fouled membrane was flushed with water, where (i) the washed away loose structure layer was collected as the cake layer, while (ii) the remained layer on the membrane was namely as the biogel layer. Subsequently, cake sample with 10 ml was filled into a vessel, while the biogel on the membrane was cutted into 4 cm² (4 cm x 1 cm) surface area, subsequently place into vessel and filled with 10 ml of ultra pure water. Both samples ware added with 0.012 ml formaldehyde (37%) and kept for 1 hour at 4°C; subsequently it followed with adding 0.8 ml NaOH (1N) and kept for 4 hours at 4°C. After that, the samples were centrifuged (13,200 rpm, 20 minutes, 4°C) before chemical component analysis.

3.8 Scanning electron microscope analysis

Membrane Morphology: Membrane surface was examined with a SEM, Stereoscan 420, Leica Cambridge Instruments. The samples were soaked in 2% glutaraldehyde for 2 hours, subsequently, washed in 0.1 M sodium cacodylate buffer for 3 times (20 minutes each time). The fixed membrane surfaces were dehydrated by successive passages through 40, 60, 80 and 100% ethanol. Then they were dried by Critical Point Dryer (model E3000) and finally observed by SEM.

3.9 Membrane cleaning

Two modes of off-site cleaning were applied: (i) mechanical and (ii) chemical cleaning. During the cleaning phase, the membranes were first taken out of service. In term of mechanical cleaning, the membrane was washed with soft sponge before placing in an ultrasonic bath for 30 minutes to remove the internal fouling. The surface of the membrane was then run over a tap for few minutes before placing back in service. Chemical cleaning of the membranes was carried out by soaking the membrane in 0.5% sodium hypochlorite (NaOCl) for one hour, consequently rinsing with distilled water 3 times before placing back in service.

3.10 Analytical methods

The following list encompassed the analytical methods that were used in this study:

- COD based on Method 5220D (AWWA, 1998) closed reflux, colorimetric method
- MLSS based on Method 2540D (AWWA, 1998)
- MLVSS based on Method 2540E (AWWA, 1998)
- SOUR based on Method 2710B (AWWA, 1998)

- TOC was analysed by a TOC analyzer (Shimadzu TOC-5000) based on a combustion-dispersive infrared gas analysis method. The TOC concentrations were not measured directly but through the subtraction of inorganic carbon (IC) from total carbon (TC) measurements. About 5 ml of sample filtered through 0.45 μ m filter paper was used for each TOC analysis.
- Carbohydrate based on the phenol-sulfuric acid (Dubois *et al.*, 1956) method with glucose as the standard.
- Protein based on the modification of the Bradford (1976) method (Sigma-Aldrich), with Bovine Serum Albumin (BSA) as the standard

CHAPTER 4

SUSTAINABILITY OF BIOLOGICAL PERFORMANCE IN LONG SRT MBR

4.1 Introduction

Recently, MBR is tends to operate in complete retention of biomass and long SRT conditions to minimize the biomass generation. The complete retention of sludge and long SRT allow MBR operate at high biomass concentration and low F/M ratio, with the effect that the microorganisms utilise a growing portion of the carbon content of the feed for maintenance purposes and consequently less for growth (Low and Chase, 1999). Theoretically, MBR runs at a very low F/M ratio or long SRT is supposed to achieve an extremely low sludge production (Yamamoto *et al.*, 1989; Muller *et al.*, 1995; Low and Chase, 1999; Stephenson *et al.*, 2000).

However, the application of the MBR with long SRT condition in industrial application is still in doubt; mainly due to the insufficient knowledge on microorganisms behaviour and system stability in the long SRT condition. According to microbial growth curve, the bioreactor with long SRT condition will incur the low F/M ratio, subsequently the microbial will enter the phase of endogenous where shortage of available substrate (Orthon and Artan, 1994; Madigan *et al.*, 1997). Some studies discovered more dead or inactivate microorganisms in MBR compared with CAS. The rate of specific nitrification, denitrification and organic removal were also reported lower than those in the CAS process (Zhang and Yamamoto, 1996; Han *et al.*, 2005). Those studied indicated that long SRT operation of MBR incurred in changing microorganisms composition of the mixed liquor which may reduce the biological capability. Huang *et al.* (2001) and Han *et al.* (2005) conducted the study on SRT effect (5 to 100 days) on MBR system, and suggested that decrease of microbial activity in long SRT condition could be due to the accumulation of inert biomass, which was a metabolic product of the endogenous respiration in MBR. If this is true, in a MBR with longer SRT, the accumulation is

supposed to be more distinct and their negative impact on MBR performance should be more significantly.

To date, understanding on long SRT MBR remains limited and there is scarce information on the microbial viability in long SRT condition. Hence, this chapter focused on the study of biological performance and stability of long SRT (300 days) MBR. It described the efficiency and sustainability of biological system, based on organic degradation, biomass growth, inorganic accumulation, sludge yield and microbial respiration performance. The effects of SRT on organic degradation, biomass growth, and microbial respiration were also discussed by comparing three different SRT conditions (5, 10 and 300 days). Based on the experimental results, a better understanding on sustainability of biological performance of long SRT MBR was obtained.

4.2 Design of Experiments

A ceramic MF MBR with 20 L of working volume was set up and operated with SRT of 300 days and HRT of 8 hours. The detailed description of the MBR setup and the operating condition was presented in Chapter 3. Table 4.1 presents the operating condition for MBR with SRT of 5 days, 10 days and 300 days. For the SRT control, sludge drawn out from the MBR was centrifuged with 3000 rpm, subsequently the separated supernatant was placed back into MBR, while the separated compact sludge was discharged. The volume of sludge drawn from MBR was 4 L/day, 2 L/day and 0.066 L/day for SRT with 5, 10 and 300 day, respectively. The following parameters were monitored through the entire experiment: COD removal, F/M ratio, MLSS, MLVSS, sludge yield and SOUR.

Table 4.1 Operating conditions of the submerged MBR

Parameters	5-day SRT	10-day SRT	300-day SRT
HRT (hr)	24	24	8
Flux (L/m ² .hr)	26	26	26
VLR (kgCOD/m ³ .day)	1	1	3

4.3 Results and Discussion

4.3.1 Biological performance of 300-day SRT MBR

The organic degradation, inorganic accumulation, permeate quality and biomass growth performances were used to assess the sustainability of biological performance of 300-day SRT MBR. The results were demonstrated as below,

4.3.1.1 Organic degradation

The performance of COD in submerged MBR treating the high strength synthetic industrial wastewater is exhibited in Figure 4.1. It can be found that the permeate COD had been reduced to 15 ± 5 mg/L from 1000 ± 10 mg/L of influent wastewater during the stable state in MBR. From the start, the COD removal of MBR has achieved 96%. As time went on, the efficiency was increased and remained at 98 - 99% and the effluent COD concentration maintained below 25 mg/L. The high COD removal of 99% derived from this submerged MBR system was attributed to the performance of both biological activities and membrane filtration. As shown in Figure 4.1, the MBR supernatant represented the performance of biological activities in MBR system. While the MBR permeate was used to represent the overall MBR performance. The performance of membrane filtration was obtained from the differences between MBR supernatant and permeate. The experimental results revealed that MBR supernatant fluctuated within 30 ± 15 mg/L of COD, while the MBR permeate altered within 10 ± 5 mg/L COD. In general, the biological process contributed to the 96% to 98% of COD removal, whereas membrane filtration contributed to 1% to 3% of COD removal.

The experimental data demonstrated that 300-day SRT submerged MBR was capable of treating the high strength synthetic industrial wastewater with 3 kg COD/m³.day. The high organic degradation achieved (98-99%) by 300-day SRT MBR was regularly higher than by conventional treatment plants (75-85% degradation efficiency) as reported by Rosenberger *et al.* (2002). This may be due to the complete retention of all particulate and microbial metabolic matter in the bioreactor by the membrane separation, establishing the microorganism that able to remove inert organic and hence improve the treatment efficiency. The result in Figure 4.1 shows the coupling of membrane filtration process had enhanced the treatment efficiency. In another word, submerged membrane filtration unit could

provide an additional defense frontier in wastewater treatment resulting in effluents with better quality.

Figure 4.1 COD performance of MBR with SRT of 300 days, HRT of 8 hours and organic loading of 3 kg COD/m³.day

4.3.1.2 Permeate water quality

One of the major advantages of the submerged MBR is the complete removal of SS due to the membrane filtration. SS in the permeate is non detectable while SS in influent wastewater was 200 mg/L. However, these results were due to the limitation of the method rather than reflecting the true value. Therefore, the turbidity and colour tests of the permeate water quality were investigated. Figure 4.2 shows the turbidity values of the permeate water varied from 0.136 to 0.123 NTU during the operation period. These values were half of the local tapwater (0.280 NTU) turbidity value. Colour₂₅₄ absorbance readings were taken from random permeate samples throughout the experimental run. The colour₂₅₄ absorbance reading for the permeate water varied from 0.0962 to 0.0912 a.u./cm as shown in Figure 4.2 which was better than the microfiltration effluent (0.15-0.3) as

indicated in Table 4.2 Those results clearly indicate the microfiltration membrane used for the 300-day SRT MBR system was capable for producing the clean treated water. In-depth study on the correlation of permeate quality and microfiltration membrane under the long SRT MBR will be discussed in Chapter 7.

Figure 4.2 Turbidity and Color₂₅₄ of permeate from MBR with SRT of 300 days, HRT of 8 hours and organic loading of 3 kg COD/m³.day

Table 4.2 Colour₂₅₄ of some wastewater types

Wastewater types	Absorbance at 254nm (absorbance unit/cm)
Primary	0.5 – 0.8
Secondary	0.3 – 0.5
Nitrified Secondary	0.25 – 0.45
Filtered Secondary	0.02 – 0.4
Microfiltration effluent	0.15 – 0.3
Reverse osmosis effluent	0.05 – 0.2

(adapted from Metcalf and Eddy, 2003)

4.3.1.3 MLSS development

The development of biomass concentration was monitored by determining MLSS and MLVSS concentration. The growth of MLSS is a very important parameter in indicating the stability of the submerged MBR system. Figure 4.3 indicates that the MLSS rose from an initial value of 4,500 mg/L which was attributed to the initial cultivated sludge inoculation and synthetic industrial wastewater. The MLSS concentration increased rapidly to 12,000 mg/L in the first 40 days, thereafter slowly increased to 17,500mg/L for the rest of experimental period. During day 40 to day 43, a disruption caused by a choke occurred in recirculation line. As display in Figure 4.3, this caused the accumulation of MLSS in the MBR tank which resulting in increase of MLSS concentration in MBR tank. The problem was rectified on day 43 and consequently the MLSS in the MBR tank resume to normal level.

Overall, MLSS concentration increased rapidly at the start up period, and increased slowly after 40 days of operation. At the initial stage, the bacteria could be subjected to unlimited supply of food and oxygen, which promoted bacteria to stay in the exponential growth phase. As the MLSS increased, the substrate became limited and the bacteria may enter the endogenous phase. The experiment results show no signs of deterioration of biomass growth through the entire experiment of 880 operation days. However the high MLSS concentration (17,500 mg/L) may incur more filtration resistance, hence increase the fouling propensity.

Figure 4.3 Development of biomass concentration in submerged MBR with SRT of 300 days, HRT of 8 hours and organic loading of 3 kg COD/m³.day

4.3.1.4 Accumulation of inorganic compounds

The MLVSS/MLSS ratio was rather stable over the whole experiment, with average values of 0.9 as shown in Figure 4.4. The MLVSS/MLSS ratio of this submerged membrane bioreactor was higher than CAS process which known to be 0.5-0.8 in most cases (Xing *et al.*, 2000). The relatively stable ratio of MLVSS to MLSS indicated that the amount of biomass and inorganic remainders constituted a dynamic balance. There was no obvious accumulation of inorganic compounds in the MBR system. The accumulation of inorganic compounds was calculated by considering the difference between MLSS and MLVSS in the MBR system. These results show that the incoming particulate material has not accumulated in the reactor, possibly due to hydrolysis or enzymatic solubilization producing compounds having molecular size compatible with permeation. The result is consistent with Rosenberger *et al.* (2002) who demonstrated that no decrease in the volatile fraction was observed with the MLVSS/MLSS ratio remaining constant at

approximately 0.70 continuously throughout two years operation with 18-20 g/L MLSS and 1.7 kg COD/m³.day of domestic wastewater.

Figure 4.4 MLVSS/MLSS ratio in submerged MBR with SRT of 300 days, HRT of 8 hours and organic loading of 3 kg COD/m³.day

4.3.1.5 F/M ratio

The F/M ratio decreased from 0.74 to 0.30 kg COD / kg MLVSS.day at the initial stage, it followed by a constant F/M ratio (0.20-0.26 kg COD / kg MLVSS.day) after 100 days of operation as shown in Figure 4.5. The trend of F/M ratio corresponded to the increment of MLSS concentration as demonstrated in Figure 4.1. The stable F/M ratio (0.20-0.26 kg COD / kg MLVSS.day) observed in the MBR with SRT of 300 days was slightly higher than the reported F/M ratio in submerged MBR system (Chiemchaisri *et al.*, 1993; Ueda and Hata, 1999; Rosenberger and Kraume, 2002). This might be due to the different feed compositions and operating conditions, which directly affected the growth of the microbial populations, hence delivering different F/M ratio. The observed F/M ratio in this study corresponds to the treatment of high strength synthetic industrial

wastewater; it clearly demonstrated that 300-day SRT MBR achieved a stable stage after day 100 where the F/M ratio was stable at 0.23 ± 0.03 kg COD/ kg MLVSS.day.

Figure 4.5 F/M ratio of submerged MBR with SRT of 300 days, HRT of 8 hours and organic loading of 3 kg COD/m³.day

4.3.1.6 Observed sludge yield

(i). Principle of observed sludge yield in MBR

The observed sludge yield for the MBR system was calculated based on the mass balance diagram of MBR with respect to organic matter and suspended solids as illustrated in Figure 4.6. This mass balance was developed from the kinetic of microbial growth and decay rate as review in Chapter 2.5.1. The major difference between the MBR and CAS mass balance is the complete biomass retention in MBR reactor.

Figure 4.6 Mass flow chart of MBR process

With the assumption that MBR is completely mixed and SS in influent and SS in effluent are negligible, the equation which describing the performance of MBR process in term of substrate and SS can be expressed as follows:

$$V \frac{dS}{dt} = Q_i S_i - Q_e S_e - Q_w S_w + r_s V \quad (4.1)$$

$$V \frac{dX}{dt} = r_x V - Q_w X_w \quad (4.2)$$

where V is the volume of bioreactor; S is organic concentration in terms of COD; Q is the flow rate and X is the sludge concentration.; r_x is sludge growth rate(VSS g/L.day) and r_s is the organic degradation rate (COD g/L.day). Subscripts i, e and w represent the system influent, effluent and discharged in the bioreactor, respectively.

At steady state,

$$\frac{dX}{dt} = 0; \quad \frac{dS}{dt} = 0 \quad (4.3)$$

Rearranging equations 4.1, 4.2 and 4.3 give:

$$-r_s = \left[\frac{Q_e(S_i - S_e)}{V} + \frac{Q_w(S_i - S_s)}{V} \right] \quad (4.4)$$

$$r_x = \left(\frac{Q_w X_w}{V} \right) \quad (4.5)$$

Subsequently, the observed sludge yield (Y_{obs}) could be obtained based on

$$Y_{obs} = r_x / -r_s \quad (4.6)$$

(ii). Observed sludge yield for 300-day SRT MBR

The sludge production from the metabolism of organic matter is usually represented by the observed sludge yield coefficient which can be calculated with Equation 4.6. A decreasing tendency of the observed sludge yield is shown in Figure 4.7. The initial observed sludge yield was approximately 0.24 g VSS/ g COD, subsequently it decreased to 0.02277 g VSS/ g COD after 400 days of operation time which was lower than CAS process with sludge yield at 0.4 – 0.8 g VSS/ g COD (Stephenson *et al.*, 2000; Metcalf and Eddy, 2003). This decreasing tendency of the sludge yield for increasing sludge concentration was also observed by Rosenberger *et al.* (2002) and Pollice *et al.* (2004). The results show that extremely low sludge production is possible for the submerged MBR system with the long SRT.

Figure 4.7 Observed sludge yield in submerged MBR with SRT of 300 days, HRT of 8 hours and organic loading of 3 kg COD/m³.day

4.3.1.7 Microbial activity

To verify the microbial activity (active and inactive microorganism) in 300-day SRT MBR system, microorganisms was taken out for specific oxygen uptake rates (SOUR) measurement. SOUR was considered to be equivalent to the overall metabolic activity of the sludge community and was used to elucidate the physiological state and metabolic activity of the bacteria present in the MBR system. The SOUR was recorded immediately after sampling to prevent the sludge community from physiological changes. Figure 4.8 displays the measured SOUR for the 300-day SRT MBR as the function of time. An increase of SOUR was observed at the initial experiment run where the SOUR was increase from 7.44 mg O₂/g vss.hr at day-1 to 16.92 mg O₂/g vss.hr at day 11. Subsequently, the SOUR was stable at 2.87±0.50 mg O₂/g vss.hr throughout the entire experiment run. It was believed that the increase of SOUR at the startup period was caused by the adaptation and growth of microorganism in the new environment. While the constant measured SOUR (2.87 mg O₂/g vss.hr) indicated the stable stage of the

300-day SRT MBR. The result showed that the microbial activity was stable at the 300-day SRT MBR and no deterioration trend was observed.

Figure 4.8 SOUR in 300-day SRT MBR as a function of time

4.3.1.8 Discussion on sustainability of biological performance in 300-day SRT MBR

Parameters in terms of organic degradation, inorganic accumulation, permeate water quality and biomass growth were used to assess the sustainability of biological performance in 300-day SRT MBR. Based on the results obtained from this study, the overall removal efficiency of COD for 300-day SRT MBR was more than 99%. Although the low respiration rate (SOUR) was observed in the 300-day SRT MBR, it did not affect to the organic degradation efficiency. Furthermore, the MBR system provided a stable permeate quality, microbial respiration, F/M ratio throughout the entire experimental run. MLVSS/MLSS ratio indicated that no accumulation of inorganic compounds was occurred in the 300-day SRT MBR system.

Additionally, the low observed sludge yield of 0.02277 g VSS/g COD in 300-day SRT MBR validated the capability of low sludge production in bioreactor under long SRT condition. The observed sludge yield in 300-day SRT MBR was 20 to 40 times lower than the reported sludge yield from CAS process. The low observed sludge yield under 300-day SRT condition could be deemed to the concept of 'maintenance energy' where under the endogenous phase of microbial ecology, most of the energy provided by the substrate consumed is used mainly for cell maintenance.

The high mixed liquor concentration (16,000 mg/L MLSS) was attained in the 300-day SRT MBR. The experimental results suggested that the high concentration of mixed liquor did not affect the biological performance of 300-day SRT MBR. On the other hand, this high mixed liquor concentration and 300-day SRT condition could promote the growth of slow growing microorganisms and enhance the organic degradation efficiency. Nevertheless, this high mixed liquor concentration might incur the changes of mixed liquor composition, hence affect to the membrane filtration.

The results suggested that the 300-day SRT MBR was able to provide a stable and sustainable biological treatment efficiency for the wastewater treatment, and no deterioration trend was observed throughout the 880 days of operation.

4.3.2 Effect of SRT on biological performance in MBR

4.3.2.1 Organic degradation

Figure 4.9 presents the biological and overall organic degradation performances of three different SRT condition MBRs. The biological removal efficiency of MBR was determined from the difference between influent wastewater COD concentration and MBR's supernatant COD concentration (collected after it was allowed to settle for approximately 30 minutes, and then filtered through 0.45 μm filter). This corresponds to the reduction in the conventional wastewater treatment plant. The overall removal efficiency was determined from the permeate of MBRs. The overall organic degradation efficiency (COD removal) was 97.46%, 98.02% and 98.94% for 5-day, 10-day and 300-day SRT MBRs, respectively. This overall organic degradation efficiency was attributed by the biological degradation and membrane filtration. The membrane filtration played a significant role in maintaining high and stable organic removal efficiency. It served as an additional purification process to retain the remaining inert organics and bacteria, hence improved the effluent quality.

The 5-day SRT MBR had the lowest biological removal efficiency as 77.64%, followed by MBR with 10-day SRT which was achieved 85.62% of biological degradation performance. The 300-day SRT MBR exhibited the highest biological degradation efficiency of 89.44%. The remaining organic in the MBRs comprised mostly of SMP which is a pool of organic compounds that result from organic degradation, inert organic, microbial decay and microbial product (Chudoba, 1985, Rittmann *et al.*, 1987; Sciener *et al.*, 1998; Shin and Kang, 2003). This study revealed that the 300-day SRT MBR posed a highest ability to degrade the SMP compared with 5-day and 10-day SRT MBRs. It also illustrated that SMP does not cause the inhibition and toxicity to the 300-day SRT MBR. Whereas, the 300-day

SRT system was help to improve the SMP degradation in biological treatment. This might be due to the longer bacteria retention time in the 300-day SRT MBR system, hence promoting the growth of low growth bacteria which was able to degrade the inert organic and SMP. With the assistance of membrane filtration, the overall organic removal was maintained above 97% in all MBRs.

Figure 4.9 COD removal for 5-day, 10-day and 300-day SRT MBRs

4.3.2.2 Biomass growth

The information on variation of biomass concentration with time was necessary for a better understanding of the performance in the bioreactor and its interaction with membrane surface. The development of biomass concentration was followed by determining MLSS and MLVSS concentration. Figure 4.10 shows the biomass growth for MBR with 5-day SRT, 10-day SRT and 300-day SRT conditions. It showed the rapid built up of biomass at beginning of the each experiment and then reached a steady state. In overall, the MLSS was stabilized at 690 ± 70 , 2450 ± 300 and 16130 ± 1000 mg/L for MBR with 5-day SRT, 10-day SRT and 300-day SRT

conditions, respectively. The high MLSS concentration for the 300-day SRT MBR was attributed to the longer bacteria retention time and higher organic loading (3 kg COD/m³.day) compared with 5-day and 10-day SRT MBR (1 kg COD/m³.day). The results demonstrated that the biomass in long SRT MBR was growing well and no deterioration took place.

Figure 4.10 Biomass growth curve for 5-day, 10-day and 300-day SRT MBRs

4.3.2.3 Inorganic accumulation

The accumulation of inorganic compounds was calculated by considering the difference between MLSS and MLVSS in the MBR system. MLVSS/MLSS ratio for MBR with SRT of 5 days, 10 days and 300 days was rather stable over the whole experiment, with average values of 0.880, 0.933 and 0.926, respectively as shown in Figure 4.11. The MLVSS/MLSS ratio of this submerged membrane bioreactor was higher than the conventional activated sludge process which known to be 0.5-0.8 in most cases (Xing *et al.*, 2000). The relatively stable ratio of MLVSS to MLSS implicated that the amount of biomass and inorganic remainders constituted a dynamic balance. There was no obvious accumulation of inorganic compounds in the MBRs with different SRT condition especially for the 300-day SRT condition. These results exhibited the incoming particulate material has not accumulated in the bioreactor. As discussed in Chapter 4.3.1.4, this phenomenon might possibly due to hydrolysis or enzymatic solubilization producing compounds having molecular size compatible with permeation.

Figure 4.11 MLVSS/MLSS ratio for 5-day, 10-day and 300-day SRT MBRs

4.3.2.4 Observed sludge yield

The sludge production from the metabolism of organic matter is usually represented by the observed sludge yield. The observed sludge yield for different SRT MBRs is shown in Figure 4.12. The average observed sludge yield for MBR with SRT of 5 days, 10 days and 300 days was approximately 0.1205, 0.2159 and 0.02277 g VSS/g COD, respectively. The MBR with SRT of 5 days presented a low observed sludge yield compared with MBR with SRT of 10 days as shown in Figure 4.13. This might be due to the washed out of microorganism at 5-day SRT condition where the microorganism was wasted from the system faster than it can reproduce. The results exhibited that the extremely low sludge yield can be achieved in the 300-day SRT condition. This may arise from the concept of maintenance energy where most of the incoming energy (oxygen and carbon sources) could be used for cell maintenance such as maintaining the internal osmotic condition, pH, mobility, etc. (Gaudy and Gaudy, 1980; Martinage and Paul, 2000). Beside that, cell lysis and cryptic growth may also contribute to the low sludge yield during the 300-day SRT condition (van Loosdrecht and Hence, 1999).

Figure 4.12 Observed sludge yield in 5-day, 10-day and 300-day SRT MBRs

4.3.2.5 Microbial activity

The measured SOUR values for MBR samples with SRT of 5 days, 10 days and 300 days is presented in Figure 4.13. MBR with SRT of 5 days presented the highest SOUR (19.05 mg O₂/g vss.hr). It followed by 10-day SRT MBR with SOUR at 4.88 mg O₂/g vss.hr. The lowest SOUR was 2.66 mg O₂/g vss.hr which was acquired from 300-day SRT MBR. The result showed that the SOUR was decreased as the SRT increases. Although the 300-day SRT MBR exhibited the low SOUR, this do not affected the performance of organic degradation as discussed in Chapter 4.3.2.1. The reduction of SOUR can be explained with microbial growth curve which divided into several distinct phases called lag phase, exponential phase, stationary phase and death/ endogenous phase. The 5-day SRT system was at the stage of exponential, where substrate is abundant for microorganisms and microbial begin to grow during the exponential phase. The decrease of SOUR at MBR with SRT of 10 days may due to the gradual decreases in substrate concentration and accumulation of metabolic products of inhibitory nature reduce the microbial growth rate. When

the relative magnitude of maintenance metabolism increases and balances the rate of cell synthesis, microbial reach a stationary phase, where there is no net increase or decrease in cell number. Although no growth usually occurs in the stationary phase, many cell functions may continue, including energy metabolism and biosynthetic processes. Lastly, the low SOUR for 300-day SRT MBR was at the endogenous phase where microbial decay dominates due to depletion of available substrate (Orthon and Artan, 1994; Madigan *et al.*, 1997). During the endogenous metabolism, most of the incoming energy (oxygen and carbon sources) could be used for cell maintenance rather than cell synthesis (Gaudy and Gaudy, 1980; Martinage and Paul, 2000).

The observation of the low SOUR in 300-day SRT MBR system also revealed the less consumption of oxygen during this endogenous stage. This is likely due to the less energy requirement for cell maintenance, thereby less oxygen was demanded. Maintenance energy refers to the energy that is utilized for maintaining the living functions of microorganisms such as turnover of cell materials, osmotic work to maintain the concentration gradients, motility and so on (Lawrence and McCarty, 1970; Liu and Tay, 2001). Therefore, this study presumed that smaller amount energy is required by the microorganisms during the long SRT MBR condition, where maintenance metabolism plays the dominant role. This can be explained why the low sludge production rate (Figure 4.13) and high COD removal efficiency (Figure 4.9) were achieved in this 300-day SRT MBR.

Figure 4.13 SOUR for 5-day, 10-day and 300-day SRT MBRs

4.3.2.6 F/M ratio

As the loading for MBR with SRT of 300 days was 3 kg COD/m³.day, which was 3 times higher than MBR with SRT of 5 days and 10 days. The evaluation of F/M ratio was used to study the biological condition for MBR with SRT of 5 days, 10 days and 300 days, respectively. The stabilized F/M ratio for MBR with SRT of 5 days, 10 days and 300 days is 1.65, 0.44 and 0.20 kg COD/kg MLVSS.day, respectively as presented in Figure 4.14. The result showed that the lowest stabilized F/M ratio was achieved in MBR with SRT of 300 days and organic loading of 3 kg COD/m³.day. Due to the low F/M ratio in MBR with SRT of 300 days, the microorganism in MBR with SRT of 300 days was likely at endogenous phase where microbial decay dominates due to depletion of available substrate. Therefore, low sludge yield was achieved compared to MBR with SRT of 5 days and 10 days as discussed in Chapters 4.3.2.4 and 4.3.2.5. Besides, high organic degradation efficiency was also presented by MBR with SRT of 300 days compared with MBR with SRT of 5 days and 10 days (Chapter 4.3.2.1). If the MBR with SRT

of 300 days is operated with same organic loading ($1 \text{ kg COD/m}^3\cdot\text{day}$) with MBR with SRT of 5 days and 10 days, lower F/M ratio, lower sludge yield and higher organic degradation will be achieved. On the other hand, high MLSS concentration was presented in MBR with SRT of 300 days and organic loading of $3 \text{ kg COD/m}^3\cdot\text{day}$, this high MLSS concentration might incur the high filtration resistance and cause the membrane fouling. The effect of mixed liquor toward membrane fouling propensity will be discussed in the following chapter.

Figure 4.14 F/M ratio for 5-day, 10-day and 300-day SRT MBRs

4.4 Summary

A 20 L MF MBR with SRT of 300 days was set up and operated for 880 days. The results demonstrated that 300-day SRT MBR was able to provide a stable and sustainable treatment efficiency for the synthetic industrial wastewater treatment in term of degradation, microbial activity and process stability. The following are the summary results of biological performance in 300-day SRT MBR:

- i. The overall removal efficiency of COD for 300-day SRT MBR was more than 99%. MLVSS/MLSS ratio indicated that no accumulation of inorganic compounds occurred in the 300-day SRT MBR.
- ii. Permeate water quality was higher than the expected microfiltration membrane. This probably due to the biofouling layer which played as a prefilter prior to the microfiltration membrane. Further study to elaborate the biofouling in associates with transmembrane pressure will be discussed in the following chapter.
- iii. The observed sludge yield was approximately 0.02277 g VSS / g COD after 880 days of operation time. It was almost 20 to 40 times lower than the CAS process which normally has the sludge yield at 0.4 – 0.8 g VSS/ g COD.
- iv. The comparison of 5-day, 10-day and 300-day SRT MBRs showed that the 300-day SRT MBR provided a better treatment performance which presented highest organic removal and lowest sludge yield compared with 5-day and 10-day SRT MBRs. No significant inorganic accumulation being observed in all the MBRs.
- v. Nevertheless, the 300-day SRT MBR presented the high MLSS concentration (16,000 mg/L). This high MLSS concentration might incur the high filtration resistance and cause the membrane fouling. The effect

of mixed liquor toward membrane fouling propensity will be discussed in the following chapter.

CHAPTER 5

INFLUENCE OF MEMBRANE BIOREACTOR (MBR) MIXED LIQUOR ON FILTRATION RESISTANCE

5.1 Introduction

The results obtained from the previous chapter have shown that the 300-day SRT MBR provided a high treatment efficiency and stability through the entire experimental run. The high concentration of mixed liquor (16,000 mg/L of MLSS) was observed in the 300-day SRT MBR, which may change the microorganisms composition in MBR. Hence, the high mixed liquor concentration might increase the filtration resistance, and cause the membrane fouling.

The existing resources presented the controversial results on the impact of high MLSS concentration on membrane fouling in submerged MBR system. Hong *et al* (2002) conducted the submerged MBR study for the effect of MLSS concentration onto the membrane fouling and concluded that membrane fouling was independent with MLSS concentration for the range between 3,600 to 8,400 mg/L. Similar result was obtained by Le-Clech *et al.* (2003) who found that there was insignificant relation between the MLSS concentration and membrane fouling for MLSS concentration ranged from 4,000 to 8,000 mg/L. However, a significant increase of permeate rate was detected when MLSS concentration being further increased to 12,000 mg/L (Le-Clech *et al.*, 2003). The authors presumed the changes may be correlated with activated sludge properties such as EPS, particle size, etc. The controversy phenomena was also reported by Meng *et al.* (2005) where MLSS concentration has some influence on the membrane permeability such as cake resistance and cake layer permeation factor. They suggested maintaining the MLSS concentration below 10,000 mg/L for a more effective MBR operation.

In addition, some of the MBR studies demonstrated that the membrane fouling was caused by several fractions of mixed liquor such as suspended solids, colloids and macromolecule (including EPS). In general, mixed liquor comprised of two main

fractions, namely microbial flocs and supernatant containing colloids and solutes. Contradicting results were reported on the effect of mixed liquor fractions toward membrane fouling. Defrance *et al* (2000) and Bae and Tak (2005) found that suspended solids was the main contributor to the membrane fouling in the biological system. Whereas, Wisniewski and Grasmick (1998) reported that 50% of the total resistance could be due to soluble compounds. While, Bouhabila *et al.* (2001) reported that the supernatant (colloid and solutes) was the main fraction that contribute to the total filtration resistance. Furthermore, the soluble EPS (part of supernatant) was reported to provide a major influence to the filterability of mixed liquor (Rosenberger and Kraume, 2002). Recent works has also demonstrated the importance of the organic colloidal mixed liquor fraction on long-term membrane fouling rates and the membrane critical flux (Fan *et al.*, 2006; Rosenberger *et al.*, 2006; Trussell *et al.*, 2006, Fan *et al.*, 2007).

EPS in biological system is generating from the natural secretions of bacteria, cell lysis and hydrolysis products which mainly composed of polysaccharides, protein, nucleic acid, lipids and other polymeric compounds (Flemming and Wingender, 2003; Laspidou and Rittman, 2002; Liu and Fang, 2002). Although EPS concentration tends to decrease with the increase of SRT for a biological reactor (Pollice *et al.*, 2005), inconsistent results were reported on the effect of soluble and bound EPS toward membrane fouling. The soluble EPS is referred to the EPS in the solution or supernatant, while bound EPS is referred to the EPS at the surrounding of bacterial cell wall and flocs. Mikkelsen and Keiding (2002) reported that sludge with higher bound EPS concentration provided better mixed liquor filterability based on investigation of a variety of different sewage mixed liquor. While Nagaoka *et al* (1996) reported a decrease of the filterability decreased with the bound EPS concentration increased. Cho *et al.* (2005b) explained that the higher amount of bound EPS in the sludge flocs, the higher the cake layer resistance. On

the other hand, Rosenberger and Kraume (2002) found that the bound EPS was insignificantly related with the filterability; whereas soluble EPS was the major factor affecting the filterability of mixed liquor.

These conflicts have given an impetus for the augmentation of the search for better understanding to membrane fouling problem in MBR. Therefore, the aim of this study was to investigate the fouling tendency by mixed liquor with SRT of 10 days and 300 days, and to identify the contribution of MLSS and supernatant on the MF and UF membrane fouling. The correlations between MLSS, supernatant, filtration resistance and specific cake resistance were also studied.

5.2 Design of Experiments

5.2.1 MBR mixed liquor

Two MBR were operated at the respectively SRT of 10 days and 300 days and they were fed with same synthetic industrial wastewater which consisted mainly of dairy wastes. Table 5.1 provides the information of the characteristics of mixed liquor with SRT of 10 days and 300 days, respectively.

Table 5.1 Characteristics of mixed liquor with SRT of 10 days and 300 days

Parameters	Mixed liquor	
	10-day SRT	300-day SRT
HRT (hour)	24	8
pH	7-7.5	6.5-7.5
COD removal (%)	98%	99%
MLSS (mg/L)	1,500-1,700	15,500-16,500
MLVSS (mg/L)	1,430-1,600	14,500-15,500
Particle size (μm)	130-200	63-90
Organic loading (kg/m^3)	1	3

5.2.2 Membrane

MF membrane (0.2 μm) and UF membrane (50 kDa), made of polyethersulfone was used in this study. The new membrane was first rinsed by letting it float (with shine-side facing downward) in ultrapure water for 90 minutes. The rinsing water was changed three times during the cleaning period.

5.2.3 Filtration apparatus

The schematic diagram of the filtration apparatus that used to investigate the filtration resistance and specific cake resistance is shown in Figure 5.1. The filtration experiments were performed in a stirred batch cell (110 mL capacity, membrane area $(1.28 \times 10^{-3} \text{ m}^2)$ with 200 rpm, which was connected to a nitrogen cylinder as pressure source. The permeate flux was continuously collected in a beaker placed on an electronic balance. Both pressure transducer and balance were connected to a computer for the data recording.

Figure 5.1 Schematic diagram for the filtration apparatus

5.2.4 Fouling analysis

5.2.4.1 Membrane resistance analysis

The resistance-in-series model was applied to evaluate the fouling characteristics of sludge suspension. According to this model, the permeate flux, J ($\text{L/m}^2 \cdot \text{hr}$) can be expressed as follows (Ho and Zydney, 2000; Kim *et al.*, 2001)

$$J = \frac{\Delta P}{\mu R_t} = \frac{\Delta P}{\mu (R_m + R_c + R_p)} \quad (5.1)$$

where ΔP is the transmembrane pressure (Nm^{-2}), μ is the viscosity of permeate (Nsm^{-2}), R_t is the total resistance (m^{-1}), R_m is the intrinsic membrane resistance, R_c is the cake resistance, and R_p is the fouling resistance due to irreversible adsorption and pore plugging.

The experiment procedure to reach each resistance value was as follows: (i) R_m was obtained through the water flux measurement with ultra-pure water. (ii) R_t was calculated from the final flux data of sludge filtration. (iii) And then, membrane surface was flushed with water and cleaned with sponge to remove cake layer. After that the pure water flux was measured again to get the resistance of $R_m + R_p$. The fouling resistance was obtained from procedures (i) and (iii) and cake resistance from procedures (ii) and (iii).

5.2.4.2 Specific cake resistance

The description on specific cake resistance testing is stated in Chapter 3.4.

5.3 Results and Discussion

5.3.1 *EPS distribution in mixed liquor and supernatant from 10-day and 300-day SRT MBRs*

As EPS is a major foulant in the MBR, it is necessary to characterize the EPS in the mixed liquor and supernatant for both 10-day and 300-day SRT conditions. In this study, EPS was divided into four sub-components, namely bound polysaccharide, soluble polysaccharide, bound protein and soluble protein. The bound EPS (polysaccharide and protein) referred to the EPS surrounding bacterial cell wall and flocs. While, the soluble EPS was referred to the EPS in solution. Figure 5.2 compares the EPS concentration measured for mixed liquor in MBRs operated with SRT of 10 days and 300 days condition. The EPS concentration in mixed liquor with SRT of 10 days was 97, 10, 93, 32 and 232 mg/g for bound polysaccharide, soluble polysaccharide, bound protein, soluble protein and total EPS, respectively. While the EPS concentration in mixed liquor with SRT of 300 days was 49, 2, 73, 15 and 139 mg/g for bound polysaccharide, soluble polysaccharide, bound protein, soluble protein and total EPS, respectively. The results indicated that mixed liquor with SRT of 10days associated with a higher EPS concentration for both soluble and bound EPS forms. As the soluble and bound EPS are identified to be the main factor that caused membrane fouling, the less EPS concentration will be more favorable for the membrane filtration process (Nagaoka *et al.*, 1996; Cho and Fane, 2002; Rosenberger and Kraume, 2002; Meng *et al.*, 2005). This implied that long SRT condition provided less EPS concentration compared to the short SRT condition in term of soluble and bound EPS

Figure 5.2 EPS distribution for the mixed liquor with SRT of 10 days and 300 days

5.3.2 Filtration resistance of UF membrane by mixed liquor from 10-day and 300-day SRT MBRs

5.3.2.1 UF filtration resistance by mixed liquor

The mixed liquor from 10-day and 300-day SRT MBR was fed into the stirred batch cell to investigate its fouling tendency. Figure 5.3 shows the flux patterns of UF membrane (50 kDa) under a constant pressure of 1 bar for the mixed liquor with SRT of 10 days and 300 days. Both mixed liquors displayed the similar initial membrane flux at 180 L/m².hr, after which the membrane flux in both cases declined remarkably in the initial filtration, where after the UF filtration flux reached the steady-state. The stable membrane flux was 40 L/m².hr for the mixed liquor from 10-day SRT MBR, but a lower flux of 15 L/m².hr was observed for mixed liquor from 300-day SRT MBR. The membrane flux results indicated that mixed liquor from 300-day SRT MBR (posed less EPS concentration) exhibited a greater filtration resistance compared to mixed liquor with SRT of 10 days (posed more EPS concentration). It implied that mixed liquor with SRT of 300 days

contained more foulant compared with the mixed liquor with SRT of 10 days. This result was contradictory to the literature review which reported that the higher the EPS concentration, the greater the membrane fouling (Nagaoka *et al.*, 1996; Cho and Fane, 2002; Rosenberger and Kraume, 2002; Meng *et al.*, 2005). This contradictory could be attributed to the higher MLSS concentration (16,000 mg/L) in 300-day SRT mixed liquor compared with the low MLSS concentration (1,680 mg/L) for 10-day SRT mixed liquor, hence incurring higher filtration resistance for 300-day SRT mixed liquor. Further investigate on the effect of MLSS concentration will be discussed in Chapter 5.3.2.3.

Figure 5.3 Filtration flux for the UF membrane (50kDa) with 1 bar pressure for mixed liquor from 10-day and 300-day SRT MBRs

5.3.2.2 UF filtration resistance by supernatant

Supernatant of the biological process is classified as one of the membrane foulant in MBR system. However, controversial findings on the contribution of supernatant in membrane fouling are found in the current literatures (Defrance *et al.*, 2000; Bouhabila *et al.*, 2001; Bae and Tak, 2005; Trussell *et al.*, 2006, Fan *et al.*, 2007). To explore the contribution of supernatant in the membrane fouling phenomenon, the supernatant from two different SRT conditions was investigated to examine its contribution in the filtration resistance, the results are shown in Figures 5.4 and 5.5. The supernatant used in this study was withdrawn from the centrifuged mixed liquor with 13000g.

For the MBR with SRT of 10 days and low MLSS concentration (1,600 mg/L), the resistance of supernatant was consistently 12-13% lower than the mixed liquor as shown in Figure 4. Under the steady-state condition, the supernatant with SRT of 10 days had a filtration resistance of $8.14 \times 10^{12} \text{ m}^{-1}$, which is 12.7% lower than the $9.32 \times 10^{12} \text{ m}^{-1}$ mixed liquor with SRT of 10 days. This data shows that the supernatant attributed to about 87.3% of the total resistance during the filtration of mixed liquor with SRT of 10 days. While, for the MBR with SRT of 300 days and high MLSS concentration (16,000 mg/L), the resistance pattern for mixed liquor and supernatant with SRT of 300 days was similar at the early filtration time. However, the resistance of supernatant rapidly reached the steady-state, whereas the mixed liquor increased gradually and spent a much longer time to reach the steady state as demonstrated in Figure 5.5. Under the steady state condition, the supernatant with SRT of 300 days had a filtration resistance of $1.23 \times 10^{13} \text{ m}^{-1}$, which just 50% lower than the $2.49 \times 10^{13} \text{ m}^{-1}$ mixed liquor with SRT of 300 days. It exhibits that the supernatant attributed to about 50% of the total resistance during the filtration of mixed liquor with SRT of 300 days. This implied that the contribution of supernatant to the total filtration resistance decreased as the SRT

increases. The finding is in agreement with the results reported by Lee *et al.*(2003) who carried out the study of supernatant on membrane fouling with three different SRT mixed liquor (20-day, 40-day and 60-day), and found that less effects of supernatant to the overall fouling resistance as SRT increased from 20 days to 60 days. Therefore, the results from our study can served as a further study on the effect of supernatant to the membrane fouling in a long SRT condition. The outcome from this study demonstrated that that the effect of supernatant on total filtration resistance was less significant in a 300-day SRT as compared to a 10-day SRT condition.

Figure 5.4 UF membrane (50 kDalton) resistances during the filtration with 1 bar pressure for mixed liquor and supernatant with SRT of 10 days

Figure 5.5 Filtration UF membrane (50 kDalton) resistances during the filtration with 1 bar pressure for mixed liquor and supernatant with SRT of 300 days

5.3.2.3 Effect of mixed liquor and supernatant on resistance characteristics

To further evaluate the characteristics of UF fouling, the resistance in series model was applied where the filtration resistance was classified to total resistance (R_t), membrane resistance (R_m), cake resistance (R_c) and internal fouling resistance (R_p). A series of resistance for mixed liquor and supernatant with SRT of 10 days and 300 days were tested and summarized in Figure 5.6. The cake resistance appeared as dominant factor affecting the overall filtration resistance. Whereas, the contribution of internal fouling (R_p) to the overall filtration resistance was relatively small compared to the cake resistance (R_c). The analysis of the filtration resistance revealed that mixed liquor and supernatant with SRT of 10 days and 300 days presented an adjacent R_m and R_p values, respectively and the only significant difference was the cake resistance (R_c). The experimental results demonstrated that cake resistance was greatly affected by mixed liquor and supernatant with SRT of

10 days and 300 days where mixed liquor with SRT of 300 days exhibited a higher cake resistance ($23.1 \times 10^{12} \text{ m}^{-1}$) compared to supernatant with SRT of 300 days ($10.6 \times 10^{12} \text{ m}^{-1}$), mixed liquor with SRT of 10 days ($7.56 \times 10^{12} \text{ m}^{-1}$) and supernatant with SRT of 10 days ($6.3 \times 10^{12} \text{ m}^{-1}$), respectively. It is presumed that the high cake resistance in the filtration of mixed liquor with SRT of 300 days is attributed to the high MLSS concentration (16,000 mg/L). The in-depth study on the effect of MLSS concentration is discussed in Chapter 5.3.2.4.

Figure 5.6 Filtration resistance for the mixed liquor and supernatant with SRT of 10 days and 300 days (where 10(m), 10(s), 300(m), 300(s) are referred to the mixed liquor with SRT of 10 days, supernatant with SRT of 10 days, mixed liquor with SRT of 300 days and supernatant with SRT of 10 days, respectively)

5.3.2.4 Effect of mixed liquor concentration on UF membrane fouling

As discussed in the above chapters, high MLSS concentration may be a critical factor in membrane fouling phenomenon. In order to investigate the effects of

MLSS on membrane fouling, the mixed liquor with different MLSS and similar particle size distribution (PSD) were prepared by dilution with deionize water. This provided the consistency of the mixed liquor properties, such as particles size distribution, EPS, SMP and etc. Hence, MLSS concentration was the only factor that could affect the membrane filtration.

Figures 5.7a and 5.7b show the impact of MLSS concentration on the total filtration resistance. Cake resistance was observed to make the highest contribution to the total resistance, where the higher MLSS concentration resulting to the greater cake resistance. Furthermore, under the high MLSS concentration ($> 8,000$ mg/L), the cake resistance exponentially increased with the increment of MLSS concentration as demonstrated in Figure 5.7b. On the other hand, the contribution of internal fouling was insignificant compared with the contribution of MLSS concentration for mixed liquor with SRT of 10 and 300 days. The details of the relative contribution by the cake resistance, internal fouling and membrane resistance are tabulated in Table 5.2. An average membrane resistance value of $8.84 \times 10^{11} \text{ m}^{-1}$ was measured for the 50 kDa UF membrane. While the resistance incurred by the internal fouling exhibited the constant value at $8.37 \times 10^{11} \text{ m}^{-1}$ and $7.47 \times 10^{11} \text{ m}^{-1}$ for mixed liquor with SRT of 10 and 300 days, respectively. This showed that the internal fouling was barely related with MLSS concentration. The relative contribution of cake resistance on total resistance increased from 18% to 81% when MLSS increased from 17 to 1,680 mg/L for mixed liquor with SRT of 10 days. For mixed liquor with SRT of 300 days, the relative contribution of cake resistance to total resistance increased from 4% to 93% when the MLSS increased from 16 to 16,000 mg/L. This revealed that as the MLSS concentration increases, the cake resistance will also increase and subsequently play the dominant fraction in the total filtration resistance.

Figure 5.7 UF filtration resistance as a function of MLSS concentration for mixed liquor with SRT of (a) 10 days and (b) 300 days

Table 5.2 The relative contribution of membrane resistance, cake resistance and pore blocking resistance to the overall filtration resistance

SRT	MLSS	R_t (1/m)		R_m (1/m)		R_c (1/m)		R_p (1/m)	
(day)	(mg/L)	($\times 10^{12}$)	%	($\times 10^{12}$)	%	($\times 10^{12}$)	%	($\times 10^{12}$)	%
10	17	2.00	100	0.86	43.2	0.366	18.3	0.77	38.5
	84	2.76	100	0.86	31.1	1.08	39.2	0.82	29.7
	126	3.04	100	0.82	27.0	1.33	43.7	0.89	29.3
	168	3.12	100	0.82	36.4	1.51	48.3	0.79	25.2
	840	5.46	100	0.89	16.3	3.66	67.0	0.91	16.7
	1680	9.32	100	0.91	9.8	7.56	81.2	0.85	9.1
300	16	1.26	100	0.83	65.8	0.05	4.3	0.38	29.9
	80	1.95	100	0.98	50.4	0.37	19.8	0.58	29.9
	800	3.48	100	0.85	24.4	1.81	52.0	0.82	23.6
	1600	4.48	100	0.97	21.6	2.64	58.8	0.88	19.5
	8000	7.49	100	0.80	10.7	5.63	75.2	1.06	14.2
	16000	24.9	100	0.99	4.0	23.1	92.9	0.77	3.1

5.3.2.5 Specific cake resistance (UF membrane) by mixed liquor and supernatant with SRT of 10 days and 300 days

(i). Contribution of mixed liquor and supernatant to specific cake resistance

The specific cake resistance was examined to explain the contributions of mixed liquor and supernatant from MBR system to filterability of suspension. The average specific cake resistances of the mixed liquor were 18.1×10^{14} , 9.32×10^{14} , 3.07×10^{14} and 2.21×10^{14} m/kg for 10-day SRT-mixed liquor, 10-day SRT-supernatant, 300-day SRT-mixed liquor and 300-day SRT-supernatant, respectively as shown in Figure 5.8. The results indicated that mixed liquor and supernatant with SRT of 300

days had a lower specific cake resistance value compared to the SRT of 10 days. As the specific cake resistance determines the filterability of suspension, Figure 5.8 reveals that the mixed liquor with long SRT had greater filterability compared to the short SRT condition. The measured particle size for mixed liquor with SRT of 10 days and 300 days was 167 and 76 μm , respectively. According to Le-Clech *et al.* (2006), floc particles are expected that cannot directly block the membrane pore entrance, nor would the floc deposit on the membrane surface due to drag forces resulting from the low/modest fluxes and the shear induced back transport phenomenon experienced by large particles. However, as the floc breakup and incur the expose of EPS present inside the floc structure into the bulk solution, membrane fouling will be severed (Chang *et al.*, 2002). This implied that the particle size of mixed liquor may not directly contribute to the filterability of bulk solution, whereas the EPS level in the bulk solution will be a key foulant contribute to the filterability of bulk solution.

The results also revealed that supernatant played an important role in the specific cake resistance where the relative contribution of supernatant to specific cake resistance was 50% and 72% for 10-day and 300-day SRT, respectively. Comparing the specific cake resistance and EPS from supernatant with SRT of 10 and 300 days, supernatant with SRT of 10 days showed a higher EPS concentration (41 mg EPS/g SS) and specific cake resistance (9.32×10^{14} m/kg) compared to supernatant with SRT of 300 days (17 mg EPS/g SS and 2.21×10^{14} m/kg membrane resistance). Therefore, it was suggested that the soluble EPS might be the key component contributing to specific cake resistance.

It is interesting to note that as the SRT increases, the specific cake resistance decreases. However, the cake resistance was found to be increased as discussed above. It suggests that the specific cake resistance and cake resistance may be

affected by different foulants such as MLSS and supernatant, respectively. As a brief summary, supernatant was the main contributor to the specific cake resistance, while MLSS concentration was significantly affected the cake resistance under the high MLSS concentration.

Figure 5.8 Specific cake resistance for the mixed liquor and supernatant with SRT of 10 and 300 days (where 10(m) is referred to the 10-day SRT mixed liquor and 10(s) is referred to the 10-day SRT supernatant)

(ii). Effect of mixed liquor concentration on the specific cake resistance of UF membrane

The measurement of specific cake resistance at different MLSS concentration for the mixed liquor with SRT of 10 days and 300 days is displayed in Figures 5.9a and 5.9b. The decreasing trend at the low MLSS concentration was due to the incomplete cake layer formation, therefore not taken into the analysis consideration (Chang and Kim, 2005). The results indicated that the increase extent of specific cake resistance fluctuated between 1.42×10^{15} and 2.07×10^{15} m/kg as the MLSS increased from 30 to 1600 mg/L for the mixed liquor with SRT of 10 days. On the other hand, the mixed liquor with SRT of 300 days showed a slight increase in specific cake resistance from 2.24×10^{14} to 3.07×10^{14} m/kg as the MLSS increase from 2000 to 16000 mg/L. This implied that the specific cake resistance was insignificantly related with MLSS concentration.

Figure 5.9 Specific cake resistance (UF membrane) as a function of MLSS concentration for mixed liquor with SRT of (a) 10 days and (b) 300 days

5.3.2.6 Correlation of MLSS, supernatant and UF membrane fouling

The literature revealed the contradicting conclusion on the effect of mixed liquor concentration to membrane fouling. Furthermore, the effect of mixed liquor fractions (microbial flocs and supernatant) are also discussed controversially. In order to explore the fouling mechanism in the biological reactor, there is a need to unearth the relationship between MLSS, supernatant and membrane fouling. Generally, the membrane fouling in the biological reactor is caused by the cake formation which can be measured by the cake resistance using resistance in series model. The cake resistance is related to cake mass (M), MLSS concentration (C_b), specific cake resistance (α) and membrane surface area (A_m) as expressed by Equation 5.3:

$$R_c = \frac{\alpha V C_b}{A_m} = \frac{\alpha M}{A_m} \quad (5.3)$$

The experimental results from this study revealed that UF filtration resistance also demonstrated the contribution of supernatant onto the cake resistance, where the fouling tendency of supernatant increased with the increase of SRT. In view of this, the supernatant parameter could be integrated into Equation 5.3, in the form of,

$$R_c = \frac{\alpha (M_{MLSS} + M_{supernatant})}{A_m} \quad (5.4)$$

Nevertheless, the relative contribution of supernatant to the total UF resistance decreased from 87% to 50% as the SRT increased from 10 days to 300 days. This phenomenon was due to a sharp increase in contribution of MLSS concentration to the total UF resistance during the filtration of mixed liquor with long SRT and high MLSS concentration. The experiment results showed that MLSS (microbial flocs)

concentration was an important parameter for the cake resistance, especially particularly under conditions of long SRT and high MLSS concentration. Hence, the parameter of MLSS concentration should be considered during the long SRT MBR operation where high MLSS concentration takes place. The higher MLSS concentration would bring a greater cake resistance, resulting in severe membrane fouling problems.

Furthermore, supernatant also played role in the specific cake resistance where the relative contribution of supernatant to specific cake resistance was 50% and 80% for 10-day and 300-day SRT, respectively. This may related with the soluble EPS, colloidal and solute concentration existed in the supernatant. As reported by Rosenberger *et al.* (2006), high polysaccharide concentration in the sludge supernatant corresponded to high fouling rates while low concentration corresponded to low fouling rates. Fan *et al.* (2006) reported that colloidal particles were a predominant factor controlling membrane flux, even though they make up a very small fraction of the total particles in MBRs. Therefore, the supernatant should also be considered into the specific cake resistance calculated as expressed by Equation 5.5.

$$R_c = \frac{(M_{MLSS} + M_{supernatant})(\alpha_{MLSS} + \alpha_{supernatant})}{A_m} \quad (5.5)$$

To conclude, cake resistance measured from the resistance in series model is recommended as an indicator to membrane fouling, while specific cake resistance acts as a parameter that assist on the cake resistance estimation. The MLSS and supernatant compounds may affect the density, porosity and filterability of cake layer; therefore they should be taken into consideration as shown in Equation 5.5.

5.3.3 *MF and UF fouling tendency in filtration of 300-day SRT mixed liquor*

5.3.3.1 *MF and UF filtration resistance for mixed liquor from 300-day SRT MBR*

The filtration resistance for MF (0.2 μm) and UF (50 kDa) membranes in filtering of 300-day SRT mixed liquor under constant pressure of 1 bar are shown in Figure 5.10. The result demonstrated that the MF filtration resistance increased to $15 \times 10^{12} \text{ m}^{-1}$ at the beginning of the filtration run, subsequently it stabilized at $23.5 \times 10^{12} \text{ m}^{-1}$. However, the UF resistance gradually increased to $25 \times 10^{12} \text{ m}^{-1}$ throughout the filtration run. In general, the total filtration resistance of MF was slightly lower than filtration resistance of UF during the filtration of 300-day SRT mixed liquor. As the total filtration resistance consisted of various resistances, it can be further segregated into membrane resistance, cake resistance and pore blocking resistance as shown in Figure 5.11. The analysis revealed that MF membrane provided a lower membrane resistance and cake resistance compared to UF membrane. The lower MF membrane resistance was due to the large MF membrane pore size as compare to UF membrane. The larger the pore size results in lesser the resistance for the filtration process. While the experimental results on cake resistance suggested that MF membrane provided a slightly low cake fouling compared to UF membrane in filtering of mixed liquor with 300-day SRT and 16,000 mg/L MLSS. Nevertheless, MF membrane presented a high pore blocking resistance compared to UF membrane. As presented in Figure 5.12, MF pore blocking resistance contributed to 9.0% of the total MF filtration resistance, while the UF pore blocking resistance only contributed to 3.1% of the total UF filtration resistance. This phenomenon could be due to the large pore size of MF membrane which allows more foulants to deposit into the membrane pore. Overall, MF membrane provided a slightly lower cake resistance compared to UF membrane, yet the high pore blocking in MF

membrane must also be taken into consideration when designing the filtration system.

Figure 5.10 Filtration resistance for mixed liquor with SRT of 300 days using MF and UF membranes

Figure 5.11 MF and UF filtration resistance in terms of membrane, cake and pore blocking resistances in filtering of mixed liquor with SRT of 300 days

Figure 5.12 The relative contribution of membrane, cake and pore blocking resistances to the overall filtration resistance in the filtering of mixed liquor with SRT of 300 days using MF and UF membranes.

5.3.3.2 MF and UF filtration resistance for supernatant from 300-day SRT MBR

Chapter 5.3.2.2 showed the high contribution of supernatant to the UF filtration resistance. This chapter was designed to examine the contribution of mixed liquor and supernatant onto MF and UF membrane. Figure 5.13 exhibits the MF and UF filtration resistance in filtering the mixed liquor and supernatant from 300-day SRT MBR. The MF filtration resistance for mixed liquor and supernatant from 300-day SRT MBR was $23.5 \times 10^{12} \text{ m}^{-1}$ and $19.9 \times 10^{12} \text{ m}^{-1}$, respectively. The MF filtration resistance for supernatant with SRT of 300 days was approximately 85% of the mixed liquor filtration resistance. On the other hand, the UF filtration resistance for mixed liquor and supernatant from 300-day SRT MBR was $24.9 \times 10^{12} \text{ m}^{-1}$ and $12.3 \times 10^{12} \text{ m}^{-1}$, respectively. The UF filtration resistance cause by the supernatant with SRT of 300 days was nearly 50% of the total UF filtration resistance of mixed

liquor with SRT of 300 days. The results illustrated that supernatant played an important role in the filtration process, especially in MF filtration.

Figure 5.13 Filtration resistances for mixed liquor and supernatant from 300-day SRT MBR using (a) MF membrane and (b) UF membrane under 1 bar pressure.

5.3.3.3 *Effect of mixed liquor concentration of 300-day SRT on MF and UF membrane fouling*

The effect of mixed liquor concentration (MLSS concentration) to MF (0.2 μm) and UF (50 kDa) membrane resistance was assessed and presented in Figure 5.14. Both MF and UF membranes demonstrated that the total filtration resistance increased as the mixed liquor concentration increased. The further analysis revealed that MF and UF membrane resistance was averagely measured at $5.70 \times 10^{11} \text{ m}^{-1}$ and $8.84 \times 10^{11} \text{ m}^{-1}$, respectively. While, the cake resistance of MF and UF membranes were positively related to the mixed liquor concentration. The correlation of cake resistance and mixed liquor concentration can be divided into two phases. The first phase referred to the mixed liquor concentration below 8,000mg/L of MLSS, while the second phase referred to the mixed liquor concentration above 8,000 mg/L of MLSS. During the first phase, the cake resistance increased slightly as the mixed liquor concentration increased from 16 to 800 mg/L of MLSS. Whereas, during the second phase, the MF and UF cake resistance sharply increased as the mixed liquor concentration increased from 8,000 to 16,000 mg/L. The pore blocking resistance was insignificantly related to the increase of MLSS concentration from 16 to 16000 mg/L. However, the MF membrane presented a higher pore blocking resistance compared to UF membrane as displayed in Table 5.3. This was likely due to the larger pore size of MF membrane where foulant can be easily deposited into the membrane pore; hence incurring the high pore blocking resistance.

Overall, the experimental results suggested that the increase of mixed liquor concentration will incur the increase of cake resistance of both MF and UF membranes, especially when the mixed liquor concentration is higher than 8,000 mg/L MLSS. This suggested that high mixed liquor concentration may not be encouraging for membrane filtration. Nevertheless, the operating techniques such as

operating the membrane flux below critical flux, backwash and more cleaning frequency may help to prevent and reduce the fouling problem.

Figure 5.14 The correlation of mixed liquor concentration and filtration resistance for (a) MF membrane and (b) UF membrane.

Table 5.3 The relative contribution of membrane resistance, cake resistance and pore blocking resistance to the overall filtration resistance for MF and UF membranes

Membrane	MLSS	R _t (1/m)		R _m (1/m)		R _c (1/m)		R _p (1/m)	
	(mg/L)	(x10 ¹²)	%	(x10 ¹²)	%	(x10 ¹²)	%	(x10 ¹²)	%
MF	160	6.01	100	0.55	9.2	4.41	73.3	1.05	17.5
	320	7.52	100	0.56	7.4	5.84	77.7	1.12	14.9
	1600	9.15	100	0.54	5.9	7.36	80.5	1.25	13.7
	4000	9.61	100	0.60	6.3	7.73	80.4	1.28	13.3
	8000	11.1	100	0.59	5.3	9.15	82.3	1.37	12.3
	16000	23.5	100	0.57	2.4	20.8	88.6	2.11	9.0
UF	16	1.26	100	0.83	65.8	0.05	4.3	0.38	29.9
	80	1.95	100	0.98	50.4	0.37	19.8	0.58	29.9
	800	3.48	100	0.85	24.4	1.81	52.0	0.82	23.6
	1600	4.48	100	0.97	21.6	2.64	58.8	0.88	19.5
	8000	7.49	100	0.80	10.7	5.63	75.2	1.06	14.2
	16000	24.9	100	0.99	4.0	23.1	92.9	0.77	3.1

5.3.3.4 *Filterability of mixed liquor with SRT of 300 days on MF and UF membranes*

The filterability of mixed liquor and supernatant with SRT of 300 days was also investigated using MF and UF membranes. The measured specific cake resistance was 4.17×10^{14} , 3.03×10^{14} , 3.07×10^{14} and 2.21×10^{14} m/kg, for mixed liquor using MF membrane, supernatant using MF membrane, mixed liquor using UF membrane and supernatant using UF membrane, respectively as shown in Figure 5.15. The relative supernatant specific cake resistance to total (mixed liquor)

specific cake resistance was 73% and 72% for MF and UF membranes, respectively. The experimental results illustrated that MF membrane caused a higher specific cake resistance for both mixed liquor and supernatant with SRT of 300 days compared to UF membrane. This portrayed the used of MF membrane incurred the low filterability for mixed liquor and supernatant compared to UF membrane. This could be due to the pore blocking taking place during the initial MF filtration process, hence incur the different specific cake resistance compared to UF membrane.

Figure 5.15 Specific cake resistance in MF(m) (for the mixed liquor using MF membrane), MF(s) (for the supernatant using MF membrane), UF(m) (for the mixed liquor using UF membrane), MF(s) (for the supernatant using UF membrane)

5.3.3.5 Correlation of MF and UF filtration resistance in 300-day SRT mixed liquor

Previous chapters show that the performance of MF and UF membranes were affected by the mixed liquor and supernatant concentration. The effect of mixed liquor and supernatant onto membrane fouling is related to the specimen characteristic, membrane properties and operating condition. In this study, the fix specimen (mixed liquor with SRT of 300 days) and operating condition were implemented, therefore the changes of filtration resistance was due to the membrane properties.

Due to the large pore size of MF membrane, the MF membrane resistance was lower than UF membrane. Nevertheless, the larger MF pore size also incurred the higher pore blocking resistance during the filtration run of 300-day SRT mixed liquor. Both MF and UF membranes demonstrated that the pore blocking resistance was insignificantly related to the increase of MLSS concentration from 16 to 16,000 mg/L. While cake resistance sharply increased as the mixed liquor concentration increased from 8,000 to 16,000 mg/L of MLSS. Additionally, the experimental results exhibited that supernatant was a key foulant for the MF fouling, where the measured MF filtration resistance for supernatant was approximately 85% of the total MF filtration resistance. While the UF filtration resistance caused by supernatant with SRT of 300 days was just 53% of the total UF filtration resistance caused by mixed liquor with SRT of 300 days. As the supernatant is consist of colloid and solute fractions, it is clear that colloid and solute were the foulants that cause the high pore blocking resistance and the high filtration resistance in the MF membrane.

5.4 Summary

The correlation among MLSS, supernatant, cake resistance and specific cake resistance in UF membrane had been carried out for the mixed liquor with SRT of 10 days and 300 days. Additionally, the fouling tendency of MF and UF membranes in dealing with mixed liquor from 300-day SRT MBR was also studied. Important results are summarized as follow:

1. Mixed liquor with SRT of 300 days had a higher fouling tendency over the mixed liquor with SRT of 10 days. Both mixed liquor with SRT of 10 days and 300 days SRT showed that internal fouling was insignificantly affected by the mixed liquor concentration. While, cake fouling was increased as the mixed liquor concentration increased.
2. Supernatant was found to be an important foulant that affected the UF membrane fouling where the supernatant attributed to about 87.3% and 50% of the total resistance for mixed liquor with SRT of 10 days and 300 days, respectively. While, under the long SRT condition and high mixed liquor concentration, the mixed liquor concentration was significantly related to the cake resistance.
3. Specific cake resistance test (UF membrane) revealed that mixed liquor from 10-day SRT MBR had a less filterability characteristic compared to the mixed liquor from 300-day SRT MBR. Supernatant was identified as the main contributor to the specific cake resistance, while MLSS concentration was insignificant to the specific cake resistance. The experimental data presented that the higher soluble EPS concentration (10-day SRT-supernatant) provided

the greater specific cake resistance. This suggested that the soluble EPS might be a crucial parameter to controlling the suspension filterability.

4. Supernatant was also a key foulant for the MF fouling, where the measured MF filtration resistance for supernatant was approximately 85% of the total MF filtration resistance. As the supernatant consists of colloid and solute fractions, it is believe that colloid and solutes were the foulants that cause the high pore blocking resistance and high filtration resistance in the MF membrane.
5. Both MF and UF membranes revealed that increase of mixed liquor concentration will incur the increase of cake resistance of MF and UF membranes, especially when the mixed liquor concentration is higher than 8,000 mg/L MLSS. It is suggested that operating techniques such as operate at sub-critical flux, backwash and more frequent cleaning can be applied to mitigate or reduce the membrane fouling.

CHAPTER 6

EFFECT OF BIOFOULING ON LONG SOLIDS RETENTION TIME MICROFILTRATION MBR

6.1 Introduction

The experimental results from the previous chapter revealed that cake fouling and pore blocking were major resistances for MF membrane fouling during the filtration of mixed liquor with SRT of 300 days. The literature review shows the membrane fouling in MBR is an inevitable consequence of interactions between membrane and the mixed liquor including as cells, cell debris, microbial products and feed composition. (Chang *et al.*, 2002; Judd, 2004; Judd, 2005; Le-Clech *et al.*, 2006; Yang *et al.*, 2006). To mitigate or reduce the fouling phenomenon, the understanding of the effect of biofouling layer on the membrane performance (optimum imposed flux and membrane rejection efficiency) is needed.

In order to prevent the membrane fouling and evaluate the optimum flux operation, critical flux concept has been introduced by Field *et al.* (1995) who reported that critical flux is point where decline of membrane flux with time does not occur if the imposed flux operated below the critical flux, and if the imposed flux is operated above the critical flux, fouling will occur. Flux-step method is the most common method where an incrementally increase of flux for a fixed duration for each increment, giving a stable TMP when the applied flux is below critical flux. If critical flux is exceeded, TMP is observed to increase with time while flux is held constant (Le-Clech *et al.*, 2003; Neal *et al.*, 2003). Critical flux has been proposed as a method for measuring the maximum flux or TMP that can be applied and still keep the system running effectively, i.e. with no or little fouling and hence reduced frequency of chemical cleaning. Therefore, the membrane flux that operates below the critical flux is named as sub critical flux operation which is one of the alternatives to minimize the fouling problem. The sub critical flux proposed that on start-up there exists a flux below which a decline of flux with time does not occur, whereas fouling takes place above this critical value (Field *et al.*, 1995; Howell,

1995).

Recent studies reported the accumulation of particles on the membrane surface, although operated below the critical flux. Cho and Fane (2002) operated flat sheet microfiltration anaerobic MBRs and reported a period of low TMP rise followed by a sudden and significant rise in TMP. They credited the low TMP rise was caused by deposition of extracellular polymeric substance (EPS) which may induce pore closure and surface fouling, hence incurred the slow membrane fouling stage. They believed that the sudden TMP jump was attributed by the rise of local flux in some regions of membrane. Ognier *et al.* (2002) studied aerobic MBR with an ultrafiltration ceramic membrane under SRT 3.5 days. They concluded that the occurrence of TMP jump in the long term experiment was caused by the progressive decrease of available membrane surface for permeate flow, hence occurred a local increase of the permeation flux value. Le-Clech *et al.* (2003) investigated the application of critical flux in submerged MBR. They reported that indefinite sustain operation does not exist in aerobic submerged MBR with 3 g/L of mixed liquor suspended solids and infinite SRT although operated at sub critical flux mode. These authors reported that flux step determination of the critical flux cannot be used to predict the long term TMP behavior, nevertheless it may provides a comparative data on fouling propensity. Wang *et al.* (2006) conducted study on the proper operational flux in MF MBR, they reported that the proper operational flux was 56% of critical flux.

Biological fouling is expected to be the major dominion towards to MBR fouling problem, which arise from biofilm formation in the pores or on the surface of the membrane (Ridgeway and Flemming, 1996; Judd, 2004; Judd, 2005). The understanding of linkage between critical flux, sub critical flux and fouling behavior is needed for unearth the flux behavior and the appropriate flux selection. The

enhancement of membrane rejection by biofouling layer was reported by some researchers who carried out the MF and UF filtration studies (Chang *et al.*, 2001; Sun *et al.*, 2006; Sun *et al.*, 2007). However, the relation between biofouling layer and rejection performance is yet to be fully understood, particularly in 300-day SRT MBR.

Therefore, the aim of this study was to investigate the role of biofouling toward the MF filtration and rejection performance in 300-day SRT MBR. Membrane surface morphology, permeate quality, TMP and membrane rejection were used to study the fouling behavior and its effect on critical flux value.

6.2 Design of Experiments

6.2.1 MBR system

The MBR system is described in Chapter 3, while the operating conditions and system performance for this study are summarized in Table 6.1. This study was started after steady MBR operation (after 310 operation days with a constant F/M ratio at 0.2727 kg COD/kg MLVSS) was established. In the experimental run, the HRT was fixed at 8 hours with SRT of 300 days operating condition. After the startup, parameters such as temperature, DO, pH, COD were used to monitor the overall performance of the MBR system.

Table 6.1 MBR system performance and operating condition

Parameter	Value
Organic loading Rate (kg COD/m ³ .day)	3
Influent COD (mg/L)	1000
MBR permeate COD (mg/L)	<20
Working volume (L)	20
HRT (hour)	8
SRT (day)	300
MLSS (mg/L)	12000
DO (mg/L)	>3
Temperature (°C)	23-25
pH	6.9-8.0
Airflow rate (L/min)	6
Membrane flux (L/m ² .hr)	15, 26, 55

6.2.2 Membrane

Tubular ceramic MF membrane made by diatomaceous earth material with 0.9 μm was used to investigate the biofouling in submerged MBR system. Polycarbonate track-etched membrane with different pore sizes (0.02, 0.10, 0.20, 0.45 and 2.0 μm) were used to measure the rejection performance of 0.02, 0.10, 0.20, 0.45 and 2.0 μm membranes, subsequently compare the rejection performance with the ceramic

MF membrane. The polycarbonate membranes are manufactured from high quality polycarbonate film and have sharply defined pore sizes, high flow rates and excellent chemical and thermal resistance.

6.3 Results and Discussion

6.3.1 Performance of MF filtration at various flux conditions

Flux step method has been carried out to determine the critical flux value, the fouling rate for the MF membrane as a function of flux is illustrated in Figure 6.1. The selection of the critical flux was based on the fouling rate which is lower than 10 Pa/min. Hence, it was concluded that the 27 L/m².hr was the critical flux for 0.9 µm MF ceramic membrane in 300-day SRT MBR with 12,000 mg/L MLSS. Subsequently, MF membrane was operated at 55, 26 and 15 L/m².hr membrane flux to study the MF filtration performance under super-critical flux, critical flux and sub-critical flux conditions as shown in Figure 6.2. It can be seen that the filtration of MF membrane with 55, 26 and 15 L/m².hr reached a serious fouling stage (40 kPa) at 2, 11 and 100 hours, respectively. It demonstrated that imposed flux at super-critical flux (55 L/m².hr) caused a rapid fouling, whereas operation under sub-critical flux (15 L/m².hr) provided a slow fouling rate. While, the imposed flux at critical flux (27 L/m².hr) also showed a fast fouling rate. This occurrence of fast fouling rate under 26 L/m².hr imposed flux illustrated the membrane fouling take place at the critical flux condition. The similar phenomena also reported by Cho and Fane (2002) where at the imposed flux (50 L/m².hr) close to their measure critical flux, the TMP jump occurred in less than 10 hours. The results concluded that biofouling on membrane surface was inevitable even though the imposed flux operated at critical flux or sub-critical conditions.

Figure 6.1 Fouling rate for clean membrane as a function of membrane flux in MBR with SRT of 300 days, membrane pore size of 0.9 μm and MLSS of 12,000 mg/L

Figure 6.2 Filtration performances at super-critical, critical flux and sub-critical flux in MBR with SRT of 300 days, membrane pore size of 0.9 μm and MLSS of 12,000 mg/L

6.3.2 Effect of biofouling on MF critical flux

To assess the effect of biofouling layer on the critical flux value, critical flux testing was conducted on the MF membranes at different extent of fouling where TMP value was used as the indicator for MF fouling status. The fouled membrane with 5 kPa was prepared by immersed a new MF ceramic membrane into the MBR, and operated with 26 L/m².hr, when the TMP reached 5 kPa, the critical flux test was conducted immediately for this fouled membrane. The same procedures were applied to obtain the critical flux value for fouled membranes with TMP of 10, 20, 30, 40 and 45 kPa, respectively. Figure 6.3 displays the results of critical flux assessment for five different degrees of fouled membranes (5, 10, 20 and 40 kPa). The critical flux selection was based on the fouling rate which was smaller than 10 Pa/min. The measured critical flux was 27, 18, 16, 12, 9, 8 and 5 L/m².hr for membranes with TMP of 5, 10, 20, 30, 40 and 45 kPa, respectively as exhibited in Figure 6.4. The decrease in critical flux with increasing TMP could be divided into two phases. During the first phase, a sharp decrease of critical flux from 27 L/m².hr to 14 L/m².hr as the TMP increased from 0 to 10 kPa. In the second period, the effective critical flux decreased slowly from 14 to 5 L/m².hr as a result of TMP increasing from 10 to 45 kPa. These changes of critical values may causes by the changes of filtration pore size which related to the formation of biofouling layer on the MF membrane. The correlation of biofouling layer and membrane performance is discussed in Chapter 6.3.6.

Figure 6.3 Fouling rate for different degree of fouled membrane in MBR with SRT of 300 days, membrane pore size of 0.9 μm and MLSS of 12,000 mg/L

Figure 6.4 Variation of critical flux as a function of TMP (degree of fouling) in MBR with SRT of 300 days, membrane pore size of 0.9 μm and MLSS of 12,000 mg/L

6.3.3 Effect of biofouling on membrane morphology

Critical flux value is dependent on the characteristics of the membrane, suspension particle, hydrodynamic and filtration conditions. Through the study, the properties of suspension particle, hydrodynamic and filtration conditions were constant; therefore the changeable parameters were the effective membrane properties such as available pore diameter and porosity. To illustrate the membrane morphology during fouling formation, SEM analysis of five sets of membrane with different fouling stages were compared. As shown in Figure 6.5a, the clean membrane exhibited a heterogeneous collection of the fossilized remains of diatom, which reflected the original texture of membrane surface as diatomaceous earth material. On the other hand, biofouling layer was observed on the membrane surface with TMP of 5, 10 and 40 kPa as illustrated in Figures 6.5b, 6.5c and 6.5d, respectively. The SEM images showed that biofouling layer had taken place during the initial filtration period, and the dominant foulant on membrane surface was presumably caused by the attachment of dissolved macromolecules, biomass, biomass product, soluble microbial product (SMP), lysed cell, and protein (Flemming *et al.*, 1997). It is interesting to note that ceramic membrane surface had been modified by the formed biofouling layer, where the effective membrane pore area was significantly decreased as shown in Figures 6.5a-d. This reduction of effective membrane pore size by the formed biofouling layer is suggested to be a factor that incur the increase of membrane resistance and pore blocking at the initial filtration period.

Figure 6.5 Membrane morphology at different filtration stages (a) clean membrane surface, (b) membrane surface during TMP of 5 kPa, (c) membrane surface during TMP of 10 kPa and (d) membrane surface during TMP of 40 kPa

6.3.4 Effect of biofouling on membrane rejection

The membrane rejection was determined by the difference between supernatant of bioreactor and MBR permeate. Figure 6.6 shows the membrane rejection performance for imposed flux at $26 \text{ L/m}^2\cdot\text{hr}$. Supernatant was collected from the centrifuged mixed liquor (3,000 rpm for 10 minutes), it reflects the performance of biological activities in MBR system. While, MBR permeate was referred to the permeate from submerged membrane. The supernatant of MBR exhibited a TOC concentration of $23 \pm 2 \text{ mg/L}$, it was constant throughout the filtration period. The

results demonstrated that membrane rejection increased from 72% to 88% throughout the filtration period. The greater rejection increment was increased from 72% to 85% during 0 to 10 kPa TMP condition. Subsequently, the rejection performance was maintained at 85% to 88% during 10 to 40 kPa TMP condition. The increment of rejection performance could be related to the membrane pore size and biofouling layer. As shown in Chapter 6.3.3, deposit or attachment of bioparticles took place under 5 kPa TMP condition and subsequently acted as a second filtration layer on top of membrane surface as indicated by SEM images. Therefore, it is suggested that the formation of biofouling layer at the initial period had substantially reduced the effective filtration pore size, resulting in enhanced membrane rejection performance.

Figure 6.6 Rejection performance versus membrane fouling degree for membrane flux of 26 L/m².hr

6.3.5 Correlation between rejection and filtration pore size

As most of the parameters were constant in this study, the enhancement of MBR permeate quality might likely related to the filter pore size (membrane pore and biofouling layer) and organic fraction in treated effluent. The treated effluent from biological system contains of various microbial and SMP which comes from the influent, biomass, lysed cell and soluble microbial product. Figure 6.7 displays the distribution of organic fraction for the treated effluent that used in this study. The distribution of organic fraction in treated effluent was 16.83%, 9.24%, 13.89%, 13.57% and 46.47% for organic size of 2.00-0.45, 0.45-0.20, 0.20-0.10, 0.10-0.02 and <0.02 μm , respectively. This showed that 50% of the supernatant organics was retained by the 0.02 μm membrane pore size. Furthermore, the results also demonstrated that more organic can be rejected as the filter pore size went smaller as exhibited in Figure 6.8. The simplified relationship between the effective filtration pore size and TOC in the study was as following,

$$pore_size = e^{\left[\frac{(TOC-6.4197)}{0.8379}\right]} \quad (6.1)$$

where TOC is expressed in mg/L and filtration pore size is μm . Equation 6.1 was valid in this study with the condition of feed water TOC of 23 ± 2 mg/L and pore size of 0.02 to 2 μm . It should be prudent in extrapolating this formula.

Using the equation 6.1, the effective filtration pore size versus the TMP values for this study is presented in Figure 6.9. The initial effective filtration pore size was 0.95 μm , it decline sharply to 0.20 μm at the TMP of 10 kPa. Consequently, the effective filtration pore size was fluctuated between 0.01 to 0.03 μm along the filtration time. The results indicated that the rapid decrease of effective filtration pore size occurred during the initial stage of filtration (0 to 10 kPa). It might be due to formation of biofouling on top of membrane surface, hence reduce the effective

filtration pore size as shown in SEM picture (Figure 6.5).

Figure 6.7 Organic fraction of treated biological effluent from MBR with SRT of 300 days, HRT of 8 hours and organic loading of 3 kg COD/m³.day

Figure 6.8 Correlation between filter pore size and permeate quality (TOC) with feed TOC of 23±2 mg/L

Figure 6.9 Effective filtration pore size versus TMP in 300-day SRT MBR with membrane flux of 26 L/m².hr

6.3.6 Correlation between biofouling process and membrane performance

Two distinct biofouling stages were observed through the entire filtration period, where a slow fouling stage followed by a fast fouling stage or TMP jump as shown in Figure 6.2. The scatter plot of the fouling rate versus fouling degree is presented in Figure 6.10. It appears that a relative low fouling rate was observed during 0 to 10 kPa, while a relatively high fouling rate was monitored when the TMP increase above 10 kPa. This data suggests that two different fouling mechanisms occurred before and after 10 kPa of fouling degree. The initial fouling stage (slow fouling rate) was likely related to the biofouling formation as display by SEM photos, and hence caused the reduction of effective filtration pore size during the TMP of 0 to 10 kPa. This biofouling layer took place in the separation process hence caused the enhancement of membrane rejection and also led to the increase in hydrodynamic resistance (the increase of TMP). Apparently, this slow fouling stage (0 to 10 kPa TMP) caused the significant influence to the critical flux and rejection performance.

On the other hand, the fast fouling stage might due to the rise of local flux or the compression of biofouling layer (Cho and Fane, 2002; Ognier *et al.*, 2002). The results revealed that fast fouling stage provided less impact to the critical flux and membrane rejection compared to the slow fouling stage.

Figure 6.10 Scatter plot of fouling rate versus fouling degree for imposed flux at (a) super-critical flux (55 L/m².hr), (b) critical flux and (26 L/m².hr), (c) sub-critical flux (15 L/m².hr) conditions.

6.4 Summary

This study illustrated the effect of biofouling layer onto MF ceramic membrane performance in terms of critical flux trend, membrane morphology and membrane rejection performance. MF ceramic membrane with 0.9 μm pore size was operated in 300-day SRT MBR with super-critical flux, critical flux and sub-critical flux. The results were summarized as following:

1. Formation of biofouling occurred when the imposed flux operated at critical flux and sub-critical flux conditions. This biofouling process can be divided into two stages where a slow fouling stage followed by a rapid fouling stage where slow fouling stage caused a signification influence to the critical flux and rejection performance
2. A great change of critical flux from 27 to 14 $\text{L}/\text{m}^2\cdot\text{hr}$ was observed as the TMP increased from 0 to 10 kPa. Subsequently, critical flux decreased slowly from 14 to 5 $\text{L}/\text{m}^2\cdot\text{hr}$ as a result of TMP increased from 10 to 45 kPa. The results revealed critical flux value was changing versus the filtration time and fouling degree. Therefore, biofouling effect onto the critical flux should be taken into consideration for the selection of operation flux.
3. The enhancement of rejection performance from 72% to 88% throughout the filtration period has been observed. The greater rejection increment was occurred during the slow fouling stage (0 to 10 kPa TMP). While rejection performance was maintained at 85% to 88% during fast fouling stage (10 to 40 kPa TMP).
4. A correlation between filtration pore size and rejection performance was

established to evaluate the changes of effective filtration pore size throughout the filtration process. The results showed that the greater reduction of effective filtration pore size occurred at the early filtration period (slow fouling stage) where the effective filtration pore size decrease rapidly from 0.95 μm to 0.20 μm . While, the fast fouling stage posed less effect to the reduction of effective filtration pore size.

CHAPTER 7

BIOFOULING DEVELOPMENT AND REJECTION ENHANCEMENT IN LONG SOLIDS RETENTION TIME MICROFILTRATION MBR

7.1 Introduction

Biofouling layer on filtration membrane appears as the Archellis heel of the submerged MBR which caused the membrane fouling and hence decreases the water production and increase of maintenance cost (Chang *et al.*, 2001; Judd, 2004). Many studies have been carried out to prevent and reduce the fouling problems, such as membrane modification (Tyszler *et al.*, 2005; Yu *et al.*, 2005), low flux operation, backwash (Schoeberl *et al.*, 2005; Le-Clech *et al.*, 2006), chemical cleaning (Sofia *et al.*, 2004), coarse bubbles aeration (Chang and Judd, 2002) and hydrodynamic conditions (Tardieu *et al.*, 1999). Nevertheless, biofouling on the membrane surface is inevitable which cause by the nature of biological system, where microorganism and bioparticles are the main component (Song, 1998; Judd, 2004).

Previous chapter revealed that the biofouling layer modified the membrane effective filtration pore size. The resulting effects of biofouling were the increased in filtration resistance and enhanced rejection performance. A superior filtration membrane must have an excellent rejection performance and high membrane flux. However, most of the studies only focused on the filtration membrane fouling prevention and fouling mechanism involved (Ognier *et al.*, 2002; Jiang *et al.*, 2003; Bae and Tak, 2005; Ye *et al.*, 2005; Fan and Zhou, 2007); few attentions have been involved in the study of rejection performance by the biofouling layer. The formation of biofouling layer on microfiltration membrane could significantly increase the filtration performance; hence increase the effluent quality (Choi *et al.*, 2005; Hay *et al.*, 2005). Choi *et al.* (2005) reported that fouled MF at cross-flow velocity of less than 1.0 m/s exhibited almost the same rejection efficiency as that of UF membrane. They concluded that biofouling layer was first responsible for dissolved organic carbon (DOC) rejection whereas DOC passing through the biofouling layer was further rejected by fouled membrane pores. Park and Lee

(2005) operated a jet loop type MBR with hollow fibre membrane (0.1 μ m), and observed the increase of soluble COD removal during the early stage of filtration run. They suggested that the additional soluble COD removal was due to the sieving and adsorption of soluble colloidal and organics by the matrix of biofouling layer and also the biodegradation by the active microbial communities in the biofouling layer.

While an effect on extent of solute rejection is expected as a result of membrane fouling, the contribution of biofouling layer to the solute rejection is yet to be fully understood. Literature revealed that the structure/matrix of biofouling layer was highly related to the EPS compound. Flemming and Wingender (2003) reported that EPS are considered as the key components that determine the structural and functional integrity of microbial aggregates. EPS form a three dimensional, gel like, highly hydrated and locally charged biofouling layer matrix, in which the microorganisms are more or less immobilized. In addition, EPS also being reported as the most significant foulant toward the membrane fouling problems (Nagaoka *et al.*, 1996). Cho and Fane (2002) suggested that EPS caused the initial and gradual TMP rise under the constant flux filtration.

Due to the complexity of biological component, it is difficult to obtain an unify or comprehensive understanding on biofouling structural and its effect to the solute rejection. More effort is needed to explore and optimize the use of biofouling layer on the MBR system, which in turn minimize the operation and membrane cost. This chapter aimed to investigate the biofouling development on MF membrane in MBR with SRT of 300 days, identify the EPS distribution on membrane surface and contribution of biofouling to the permeate quality.

7.2 Design of Experiments

7.2.1 MBR system

Detailed operating conditions of biological system were discussed in Chapter 6.2.1.

7.2.2 Membrane

Tubular ceramic MF membrane made by diatomaceous earth material with 0.9 μm was operated with 26 $\text{L}/\text{m}^2\cdot\text{hr}$ of membrane flux for study the biofouling development. While, polycarbonate track-etched membranes (0.015, 0.4 and 2.0 μm) were used to measure the rejection performance of 0.015, 0.4 and 2.0 μm , and subsequently compare the rejection performance with the MF membrane. The polycarbonate membranes are manufactured from high quality polycarbonate film and have sharply defined pore sizes, high flow rates and excellent chemical and thermal resistance.

7.2.3 Analytical methods and procedures

The procedures of EPS extraction and SEM analysis were stated in Chapter 3.7 and 3.8. The analytical methods for TOC, carbohydrate and protein were reported in Chapter 3.10.

7.3 Results and Discussion

7.3.1 Observation of biofouling layer development

The MF membrane (0.9 μm) was immersed into the MBR system and operated at a constant membrane flux of 26 $\text{L}/\text{m}^2\cdot\text{hr}$. Subsequently, the degree of membrane biofouling was represented by TMP values. The biofouling layer can be visually divided into two parts, (i) biogel layer where a gel-like layer attached on membrane

surface, (ii) cake layer which was identified as the multi biolayer. The biogel layer is a condensed layer and could hardly be washed out using the water flushing, while cake layer is a loose structure layer and can be washed away easily by water flushing. The pictures of clean membrane, biofouled membrane, biogel layer and cake layer were demonstrated in Figure 7.1. Flemming *et al.* (1997) reported that EPS presenting the gelling properties and play a strong role in forming sticky hydrogels on membrane surface. In addition, the gel-like layer form by the EPS was a three dimensional layer and highly hydrated in which the micro-organisms are embedded (Wingender *et al.* 1999; Flemming and Wingender, 2001). Therefore, it was believed that the biogel layer was comprised of EPS which strongly deposited on the membrane surface. The conceptual illustration of biofouling layer is shown in Figure 7.2. The biogel layer occurred at the early filtration period and attached on the membrane surface. As the filtration time prolonged, more bioparticles attached onto the gel like layer and hence formed the cake layer.

Figure 7.1 Picture of (a) clean membrane, (b) biofouled membrane, (c) clean membrane enlarge section, (d) biogel layer enlarge section and (e) cake layer enlarge section in MBR with SRT of 300 days, MLSS concentration of 12,000 mg/L and membrane flux of 26 L/m².hr

Figure 7.2 Conceptual illustration of biofouling layer

In order to understand the development of biofouling layer, SEM micrographs of the clean and fouled membrane specimens at different degrees of fouling have been taken to assess the biofouling layer as shown in Figures 7.3a-7.3e. The membranes were taken out from the MBR system for SEM analysis when the filtration TMP reached 5, 10, 20 and 40 kPa. The SEM image of the clean membrane surface (Figure 7.3a) shows the surface structure of a 0.9 μm ceramic membrane which was observed to be porous and free of particles with a heterogeneous collection of the fossilized remains of diatom, it reflected the original texture of membrane surface as diatomaceous earth material. However, SEM micrographs of the fouled membranes (Figures 7.3b-e) exhibited different surface morphologies compared with the clean membrane, it was non porous in appearance. While, there was visually no apparent difference in morphology between the fouled membranes, SEM images show that all the pores were covered with a biofouling layer, formed over the entire membrane surface. Obviously, biofouling layer had formed during the initial filtration stage (5 kPa), it had modified the ceramic membrane, and affected the filtration process. The effect of this biofouling layer on the filtration was studied and will be discussed in Chapter 7.3.3.

Figure 7.3 Membrane surface morphology at different filtration stages (a) clean membrane surface, (b) membrane surface during TMP of 5 kPa, (c) membrane surface during TMP of 10 kPa (d) membrane surface during TMP of 20 kPa, (e) membrane surface during TMP of 40 kPa. The filtration process was conducted in MBR with SRT of 300 days, MLSS concentration of 12,000 mg/L and membrane flux of 26 L/m².hr.

7.3.2 Chemical characteristics of EPS in biofouling layer

The microbial biofilm or floc consists of bacterial cells enveloped by a matrix of large polymeric molecules, namely EPS which composed of different classes of organic macromolecules such as polysaccharides, proteins, nucleic acids and humic substances (Nielsen *et al.*, 1997; Flemming and Wingender, 2001). It has been reported that the EPS play a significant role in the formation and behavior of microbial aggregation, including adhesion phenomena, matrix structure formation (Liu and Fang, 2003; Sponza, 2003). Therefore, it is important to gain more information on the EPS of biofouling layer which formed under SRT of 300 days. The EPS samples were taken from two distinct biofouling layers, namely biogel layer (Figure 7.1d) and cake layer (Figure 7.1e). Figures 7.4 and 7.5 indicate the EPS concentration distribution in the biogel layer and cake layer as a function of fouling (TMP), respectively. The measured EPS concentration was 0.15, 0.10, 0.20, 0.30 and 0.35 $\mu\text{g/L}\cdot\text{mm}^2$ at 5, 10, 18, 30 and 40 kPa, respectively as shown in Figure 7.4. Polysaccharide was the only substance that found in the biogel layer, little or no protein was detected. Additionally, the concentration of polysaccharides was linearly increasing with the degree of fouling (TMP) as shown in Figure 7.4. In general, polysaccharides is considered as the fundamental structural elements of EPS matrix, while protein is seen as the enzymes which is located in the EPS matrix (Flemming and Wingender, 2003). Therefore, the result from this study suggested that polysaccharides was the main binding agent, which attached onto the membrane surface (adhesive) and hence provided the connection for the further attachment of polysaccharides, protein and bioparticles.

The measured EPS concentration in the cake layer was in the range of 15 to 30 mg EPS/g SS, which consists of both protein and polysaccharide as shown in Figure 7.5. The concentration of protein was averagely higher than the concentration of polysaccharides. It is clear that cake layer on the membrane surface was likely due

to the attachment of biological flocs in MBR system which consist of high protein concentration compared with polysaccharides concentration (133 ± 10 mg EPS/g SS which comprised of 77 ± 10 mg protein/g SS and 56 ± 8 mg polysaccharides/g SS). As reported in previous studies (Urbain *et al.*, 1993; Frolund *et al.*, 1994; Bura *et al.*, 1998; Liao *et al.*, 2001), protein was the predominant polymer followed by polysaccharides measured as carbohydrate in all the samples studied. The predominance of proteins in the activated sludge EPS was possibility due to the presence of large quantities of exoenzymes from bacterial excretions such as lysates products and extracellular products in the floc, which depending on microorganism type and substrate properties as reported by Frolund *et al.* (1995).

The experimental results suggested that the formation of biofouling layer was started by the attachment of polysaccharide and formed the biogel layer on top of membrane surface. This process was namely adhesive, where the substances bind onto the other type of material. The formed biogel layer further induced the attachment of protein, polysaccharide and bioparticles, and formed the cake layer. Cohesive mechanism is expected to be the binding force during formation of cake layer (Flemming *et al.*, 1997; Mayer *et al.*, 1999). Meanwhile, the EPS matrix also plays a role in determining the pore size and porosity of the biolayer (Zhang and Bishop, 1994). As described by Flemming and Wingender (2001), the EPS polysaccharide was the main matrix that formed the biofilm and determines the biofilm structure.

Figure 7.4 EPS concentration distribution in biogel layer as a function of MF membrane fouling in MBR with SRT of 300 days, MLSS concentration of 12,000 mg/L and membrane flux of 26 L/m².hr.

Figure 7.5 EPS distribution in cake layer as a function of MF membrane fouling in MBR with SRT of 300 days, MLSS concentration of 12,000 mg/L and membrane flux of 26 L/m².hr.

7.3.3 *Effect of biofouling layer on MF performance*

7.3.3.1 *Organic removal performance*

Organic removal efficiency was defined as the difference between influent TOC and permeate TOC. While biological removal efficiency of MBR was determined by the difference between influent TOC and supernatant TOC (collected after the biological mixed liquor was centrifuged with 3,000 rpm for 10 minutes). Table 7.1 presents the organic removal performances by the biological and membrane processes. The results indicated that the organic removal efficiency could achieve 93.20% by means of biological treatment, whereas, with the assistance of membrane filtration, the TOC removal efficiency could further increase to 97.92%. Subsequently, when the membrane fouling occurred, the organic removal reached the highest degree at 99.07%. This suggested that the membrane filtration played a significant role in maintaining high and stable organic removal efficiency. It served as an addition purification process to retain the remaining inert organics and bacteria, hence improved the effluent quality. Whereas, the biofouling layer which formed on top of membrane surface, was also taking place during the filtration or rejection performance.

Table 7.1 TOC removal efficiency by biological process, membrane filtration and biofouling layer in MBR system

Type	TOC _{in} (mg/L)	TOC _{out} (mg/L)	TOC removal (%)
Bioreactor	340.20	23.14	93.20
Bioreactor + membrane	340.20	7.06	97.92
Bioreactor + membrane + fouling (40 kPa)	340.20	3.17	99.07

7.3.3.2 *Enhancement of permeate quality*

The result in Table 7.1 indicates that filtration performance not only depended on the membrane pore size, whereas biofouling layer (which formed on the membrane surface) also take place in filtration process. To further investigate the effect of biofouling layer on permeate quality, the permeate quality was measured as a function of membrane fouling; the result is shown in Figure 7.6. The wastewater that treated by the biological treatment in MBR exhibited an effluent TOC of 23.14 ± 1 mg/L for TOC, the membrane filtration was further reduced to 7.06 ± 0.10 mg/L TOC in the initial filtration period. Consequently, the permeate TOC concentration sharply decreased 4.10 mg/L when the TMP reached 5 kPa. After this, the permeate TOC was slightly reduced to 3.49 mg/L and fluctuated in the range of 2.56 and 3.49 mg/L. A significant improvement of permeate quality has been observed during the initial filtration period as indicated in Figure 7.6.

The tendency of improved permeate TOC might be attributed to the accumulation of organic compounds in the retentate and/or the foulant layer of cake/gel formation, which acting as a secondary membrane. The retained SMP was able to block membrane pores and form a cake/gel layer on the membrane surface as displayed in Figures 7.3a-7.3c. This cake/gel layer was found to be an effective secondary filtration layer to remove organic compounds which allowed smaller molecules passing through. As a result, a higher percentage of organics removal was achieved.

Figure 7.6 Permeate TOC as a function of MF membrane fouling in MBR with SRT of 300 days, MLSS concentration of 12,000 mg/L and membrane flux of 26 L/m².hr.

7.3.3.3 Rejection performance

In this Chapter, the rejection performance of biofouled membrane was studied and compared with the rejection performance by membranes (47 mm diameter) with different pore size (0.02, 0.45 and 2.0 μm). The rejection of biofouled membrane was determined from the difference between MBR’s supernatant (collected from the centrifugation of mixed liquor from MBR at 3000 rpm for 10 minutes) and MBR’s permeate (filtrate from the submerged MF membrane in MBR). While the rejection performance by membranes with different pore size was determined from the difference between MBR’s supernatant and filtrate (collected after the filtration of MBR’s supernatant with membrane with different pore size). The comparison of rejection performance by biofouled membrane, 2.0 μm membrane, 0.45 μm membrane, and 0.02 μm membrane are shown in Figure 7.7. The experimental

results revealed that the rejection of biofouled membrane increased sharply during the initial filtration period. The rejection performance of the biofouled membrane at 3 kPa was higher than the rejection performance of 0.45 μm membrane. During the 3 to 18 kPa TMP period, the rejection efficiency increased gradually to the UF quality (0.02 μm).

These experimental results implied that the membrane properties were significantly modified during the filtration period, as a result, the permeate quality was improved correspondingly. The increase of permeate quality was associated with the biofouling layer formed on membrane surface during the filtration process. This was consistent with the finding in previous studies, in which a better permeate quality was produced by the fouled MF membrane (Hay *et al.*, 2005; Sun *et al.*, 2006). Schafer *et al.* (2000) reported that the increased membrane rejection owned to the impacts of fouling occurrence on the membrane surface, such as pore blocking and cake formation. Such fouling development would result in a smaller membrane pore size, which subsequently improve the filtration performance. The major mechanism of organic matter rejection by MF membrane was size (steric) exclusion associated with the membrane pore size and molecular weight of organic matter in the filtration sample (Belfort *et al.*, 1994; Schafer *et al.*, 2000). The membrane rejection is highly related with the pore size of the membrane since a smaller membrane pore size resulting in a higher membrane rejection.

The results suggested that biofouling layer on MF membrane would increase the MF membrane rejection performance up to the UF rejection efficiency. This rejection enhancement clearly related to the structure of formed biofouling layer on the MF membrane which was mainly associated with the EPS in the biogel layer and cake layer.

Figure 7.7 Rejection performances versus MF membrane fouling in MBR with SRT of 300 days, MLSS concentration of 12,000 mg/L and membrane flux of 26 L/m².hr.

7.3.4 The relationship of membrane rejection and biofouling layer

The experimental results revealed that membrane rejection performance was related to the formation of biofouling layer (biogel and cake layer) throughout the filtration process. Therefore, the biofouling layer must be taken into consideration as part of filtration performance. Thus the rejection capability of membrane in MBR can be expressed in Equation 7.1,

$$R \text{ (Rejection)} = R_0 \text{ (membrane rejection)} + R_b \text{ (biofouling layer rejection)} \text{ (7.1)}$$

In order to explore the correlation between filtration rejection performance and biofouling layer, the changes of filtration rejection and fouling degree (TMP) as a function of time for imposed at flux at 18 L/m².hr and 26 L/m².hr are presented in

Figure 7.8, respectively. Both figures revealed a two-stage membrane fouling, where a slow fouling stage followed with a fast fouling stage. Additionally, the rejection performance increased rapidly at slow fouling stage and subsequently stable at 83-86% of rejection percentage during the fast fouling stage. This suggested that the rejection performance was significantly related to the membrane fouling steps. Cho and Fane (2002) observed a two stage membrane fouling, and suggested that the first fouling stage (slowing fouling stage) was due to the deposition of EPS, while the second fouling stage (TMP jump) was caused by the increased local flux. Moreover, some researchers report that the EPS matrix was the main matrix that formed the biofilm and determines the biofilm structure and play a role for determinate the pore size and porosity of biofilm (Nielsen *et al.*, 1997; Flemming and Wingender, 2001). Therefore, the sharp increase of rejection percentage during the slow fouling stage can be related to the formation of biogel layer where EPS deposited onto the membrane surface and hence modified the membrane properties. Subsequently, the stable rejection percentage achieved when equilibrium of biogel layer, cake layer and reactor hydrodynamic has been reached.

The great enhancement of rejection performance by the biofouling layer during the early filtration followed by a slight enhancement in rejection throughout the entire filtration process can be mathematically expressed by logarithm regression as shown in Equation 7.2,

$$R_b = b * \ln[TMP] + c \quad (7.2)$$

The overall MF rejection performance can be summarized as Equation 7.3,

$$R = R_o + (b * \ln[TMP] + c) \quad (7.3)$$

To verify the correlation between MF rejection and biofouling layer (represent by TMP value) in this experimental condition, the experimental data collected from operations under 18 L/m².hr and 26 L/m².hr membrane flux and the theoretical data derived from Equation 7.3 were compared in Figure 7.9. The results indicated that the relationship between MF rejection performance and TMP could be described by the Equation 3 with coefficient of determination (R^2) higher than 0.85.

Figure 7.8 Changes of filtration rejection and fouling degree (TMP) as a function of time for imposed flux at (a) 18 L/m².hr and (b) 26 L/m².hr in MBR with SRT of 300 days and MLSS concentration of 12,000 mg/L

Figure 7.9 Rejection performance versus degree of fouling for imposed flux at (a) 18 L/m².hr and (b) 26 L/m².hr in MBR with SRT of 300 days and MLSS concentration of 12,000 mg/L

7.4 Summary

The biofouling layer on MF membrane has been studied in the aspect of surface morphology, EPS distribution and rejection performance. The formation of biofouling layer could be visually defined as biogel and cake layers. It was found the attachment of polysaccharides was the only contributor forming the biogel layer which formed on top of membrane surface (adhesive attachment). The protein, polysaccharides and bioparticles were the main substances forming the cake layer (cohesive attachment). As exhibited in SEM photos and permeate quality, the formed EPS matrix and cake layer changed the membrane surface properties such as the pore and porosity, and hence produce the better permeate quality. These formed biofouling layer on MF membrane increased the MF membrane rejection performance up to the UF rejection efficiency. It is presumed that the rejection enhancement was related to the structure of formed biofouling layer which was mainly associated with the EPS matrix and cake layer. The rejection enhancement by the biofouling rejection can be described by logarithm function with the degree of membrane fouling where a great enhancement of rejection performance at the early filtration followed by a slight enhancement in rejection throughout the entire filtration.

CHAPTER 8

FOULING BEHAVIOR IN MICROFILTRATION MBR

8.1 Introduction

Membrane fouling was influenced by the properties of membrane, mixed liquor characteristics and hydrodynamic conditions of the MBR process (Choi *et al.*, 2002; Kang *et al.* 2002; Le-Clech *et al.*, 2003; Lee *et al.*, 2001a; Lee *et al.*, 2003; Nagaoka *et al.*, 1996; Shin and Kang, 2003; Tardieu *et al.*, 1998; Tardieu *et al.*, 1999; Le-Clech *et al.*, 2006). Cho and Fane (2002) conducted the flat sheet microfiltration anaerobic MBR and reported that the initial and gradual TMP rise is believed to be caused by the slow deposition of EPS, and the sudden rise in TMP is believed to be caused by increasing local flux in some regions of the membrane. Ognier *et al.* (2004) applied the local flux concept to model the two stages of TMP increase where they hypothesized that the increase of local flux was due to the successive blocking of membrane pores. Although many efforts have been made to reduce fouling in MBR, the phenomenon continues to be a serious problem due to the complexity properties of mixed liquor.

In investigating the fouling behavior, mathematical tool provide an alternative way to explore the fouling mechanisms. Several fouling models have been developed and applied to identify the membrane fouling mechanisms such as pore blocking, pore constriction, intermediate blocking and cake formation mechanisms (Hermia, 1982; Bowen and Gan, 1991; Hlavacek and Bouchet, 1993). Tracey and Davis (1994) reported that initial and subsequent fouling of 0.2 μm track etched membranes by BSA could fit by standard or complete model and cake model, respectively. Jacob *et al.*, (1998) conducted the study on the structural modification of MF membrane associated with the membrane fouling kinetics. The authors found that the single fouling model (e.g. complete, standard, intermediate or cake blocking) was insufficient to describe the fouling phenomenon of MF membrane. The MF fouling was occurred according to a successive or simultaneous coexistence of two

or more of the models. Ho and Zydney (2000) developed a fouling model that described the filtrate flux which accounted for initial fouling by pore blockage and subsequently fouling due to the growth of protein cake over these initially blocked regions. This combined model was in good agreement with experimental data obtained during the stirred cell filtration of bovine serum albumin solutions through polycarbonate track-etched microfiltration membranes over the entire course of the filtration. Using the knowledge of blocking laws and cake formation theory, the MF fouling behavior of monodisperse suspensions (protein, BSA) can be predicted well. However, little information is available for the incorporation of blocking laws and cake filtration theory in explaining the polydispersity suspensions in MF long SRT MBR system consisting of high mixed liquor concentration with a wide range of bioparticle and colloidal.

A more detailed understanding of MF fouling in long SRT MBR system is needed to reduce the fouling, predict a priori and the optimal operating conditions for the membrane filtration unit and significantly reduce the economic drawbacks associated with fouling of membranes. The aim of this study was to identify the fouling behavior in the microfiltration long SRT MBR system in order to obtain better insight and understanding of the fouling mechanisms sequence in MBR system. Four kinds of fouling mechanism models are applied to verify the fouling tendency and behavior during the filtration time. A conception of MF fouling behavior in MBR system will also be established based on the analytical results.

8.2 Theoretical background

(a). Complete/Pore blocking model for constant flux system

In complete blocking model, it is assumed that each particle arriving at the membrane participates in blocking some pores with no superposition of particles (Hlavacek and Bouchet, 1993; Agustin Suarez and Veza, 2000). The basis for the complete/pore blocking model is developed from Poiseuille's law (equation 8.1). In the constant flux mode, flow of filtrate is related to the membrane's pressure drop and physical properties as shown in equation 8.1:

$$Q = \frac{\pi \Delta P}{8 \mu L} d_p^4 N_p \quad (8.1)$$

Where μ is fluid viscosity, L is the length of membrane, r_p is the membrane pore size, N_p is the number of open pores (Hlavacek and Bouchet, 1993; Agustin Suarez and Veza, 2000). N_p is a function of the initial number of open pores and of the number of blocking particles per unit volume of filtrate as shown in equation 8.2:

$$N_p = N_{p0} - k_1 V \quad (8.2)$$

Where k_1 is the pore blockage efficiency, and with placing equation 8.2 into equation 8.1 yields:

$$\frac{1}{\Delta P} = \frac{1}{\Delta P_0} - \frac{\pi k_1 r_p^4}{8 \mu L} t \quad (8.3)$$

$$\text{or } \frac{1}{\Delta P} = \frac{1}{\Delta P_0} - K_1 t \quad (8.4)$$

Equation 8.4 shows that the pressure drop is inversely proportional to time. As time increases, the right hand side of the equation becomes smaller, the pressure drop increases dramatically.

(b). Standard blocking/Pore constriction model for constant flux system

Standard blocking laws presumed that membrane is supposed to consist of a set of equal cylindrical pores, and each particle arriving at the membrane is deposited onto the internal pore walls, thus leading to a decrease of the pore volume. Similar to the pore blocking model, the basis for the pore constriction model is also developed from Poiseuille's law (equation 8.1). In the standard blocking model, foulants such as colloids and solutes enter and adsorb onto the pore walls decreasing the pore diameter while the number of pores remains constant. During a time interval, dt , the volume of filtered suspension is $dV = Qdt$. The reduction of the free volume of N pores (subtract the initial pore volume from the volume of deposited foulants) is expressed by (Hlavacek and Bouchet, 1993; Agustin Suarez and Veza, 2000):

$$-N_p(2\pi r dr)L = c_1 dV \quad (8.5)$$

Where c_1 is the volume of deposit by unit of volume of filtered suspension. The integration of equation 8.5 leads to:

$$r_p^2 = r_{p0}^2 - \frac{c_1 V}{\pi L N_p} \quad (8.6)$$

For a constant flux system, combining equations 8.1 and 8.6, gives the expression for pore constriction model:

$$\frac{1}{\sqrt{\Delta P}} = \frac{1}{\sqrt{\Delta P_0}} - \frac{c_1 V}{\sqrt{8\pi N_p \mu L^3 Q}}$$

or $\frac{1}{\sqrt{\Delta P}} = \frac{1}{\sqrt{\Delta P_0}} - K_2 t \quad (8.7)$

As time increases, the right hand side becomes smaller, but unlike the linear case for the pore blocking model, this pressure drop increases much more dramatically.

(c). Intermediate blocking model for the constant flux system

Intermediate blocking model presumed that each particle can settle on other particle previously arrived and already blocking some pores or it can also directly block some membrane area as expressed by (Hlavacek and Bouchet, 1993; Agustin Suarez and Veza, 2000):

$$\frac{dN_p}{dV} = -\frac{kN_p}{N_{p0}} \quad (8.8)$$

By integrating equation 8.8, yield,

$$N_p = N_{p0} \exp -k_3 V \quad (8.9)$$

Substitute equation 8.9 into equation 8.1, provides the expression of intermediate blocking model:

$$\Delta P = \frac{8Q\mu L}{\pi r_p^4 N_{p0}} \exp k_3 V$$

$$\text{or } \Delta P = \Delta P_0 \exp K_3 t \quad (8.10)$$

This equation states that the pressure drop is exponentially with increasing function of time.

(d). Cake formation model for the constant flux system

It is assumed that each particle locates on others already arrived and already blocking some pores and there is no room for directly obstructing some membrane area. Cake formation model is developed from Darcy's law (Ho and Sirkar, 2001) which states that the flow of filtrate passing through the membrane is related to the system pressure and the membrane resistance. This is shown in equation 8.11:

$$Q = \frac{\Delta P A}{\mu R} \quad (8.11)$$

Where R is the sum of the membrane resistance and the resistance of the built up particulate cake. The function of R is expressed as:

$$R = \frac{\alpha C_b V}{A} + R_0 \quad (8.12)$$

Where α is the specific cake resistance, C_b is the concentration of particles in the feedwater. Substituting equation 8.11 into equation 8.12 leads to the following equation:

$$\Delta P = \Delta P_0 + \frac{Q_0^2 \mu \alpha C_b}{A^2} t$$

$$\text{or } \Delta P = \Delta P_0 + K_4 t \quad (8.13)$$

This equation states that the pressure drop is linear with increasing function of time.

A summary of constant flux membrane blocking laws and cake filtration models in their linearized form are given in Table 8.1. All the characteristic equations are linear. By plotting ΔP , ΔP^{-1} , $\Delta P^{-1/2}$ versus time, the model which more accurately reflects the actual process can be determined.

Table 8.1 Summary of constant flux membrane blocking models in their linearized form

Model	Equation	Linearized form
Pore blockage/ Complete blocking	$\frac{1}{\Delta P} = \frac{1}{\Delta P_0} - \frac{\pi k_p r_p^4}{8 \mu L} t$	$\frac{1}{\Delta P} = a + bt$
Pore constriction/ Standard blocking	$\frac{1}{\sqrt{\Delta P}} = \frac{1}{\sqrt{\Delta P_0}} - \frac{c_1 V}{\sqrt{8 \pi N_p \mu L^3 Q}}$	$\frac{1}{\sqrt{\Delta P}} = c + dt$
Intermediate blocking	$\Delta P = \Delta P_0 \exp K_3 t$	$Ln(\Delta P) = e + ft$
Cake formation	$\Delta P = \Delta P_0 + \frac{Q_0^2 \mu \alpha C_b}{A^2} t$	$\Delta P = g + ht$

(adapted from Hlavacek and Bouchet, 1993; Agustin Suarez and Veza, 2000)

8.3 Design of Experiments

8.3.1 MBR system

The detailed description of MBR setup was presented in Chapter 3. Table 8.2 provides the information on the operating conditions of MBR with SRT of 10 days and 300 days.

Table 8.2 Operating condition for MBR with SRT of 10 days and 300 days

Parameters	MBR	
	SRT of 10 days	SRT of 300 days
HRT (hour)	24	8
pH	7-7.5	6.5-7.5
COD removal (%)	98%	99%
MLSS (mg/L)	1500±100	16000±500
MLVSS (mg/L)	1400±100	15000±500
Organic loading (kg/m ³)	1	3

8.4 Results and Discussion

8.4.1 Observation of MF fouling rate in 300-day SRT MBR

The MF membrane was submerged into the stabilized MBR system (with SRT of 300 days) and operated with membrane flux of 25 L/m².hr. The TMP increase resulting from the membrane fouling was monitored through the entire experiment as shown in Figure 8.1. In order to identify the fouling behaviour in MF MBR system, the function of fouling rate is plotted versus the filtration time and shown in Figure 8.2. Two stage of membrane fouling can be distinguished from Figures 8.1 and 8.2, namely slow fouling stage and fast fouling stage. The slow fouling stage was occurred during 0 to 10 hours, which the increase of TMP was slow at 3-13 Pa/min. Whereas, the fast fouling stage was observed after the 10 hours of filtration run where a dramatically TMP increase occurred (15-140 Pa/min). These two different fouling stages could be due to the different fouling mechanisms take place during the filtration run. The similar fouling trend was observed by Cho and Fane (2002) who reported a two stages membrane fouling in ultrafiltration MBR system

where the first fouling stage was gradually increased, and the second stage was a sudden TMP jump.

Figure 8.1 Changes of TMP versus time in MF MBR with SRT of 300 days and membrane flux of 25 L/m².hr

Figure 8.2 The function of fouling rate versus filtration time in MF MBR with SRT of 300 days and membrane flux of 25 L/m².hr

8.4.2 *Fouling analysis for MF MBR with SRT of 300 days*

8.4.2.1 *Single stage fouling analysis*

In order to understand the fouling mechanism of MF membrane in 300-day SRT MBR, the fouling data from this study was inserted into membrane models as presented in Figure 8.3. According to Equations 8.4, 8.7 8.10 and 8.13, a linear regression model should be obtained for ideal fitting in each case and the best fit linear regression was determined by minimizing the sum of the squared residuals between the filtration TMP data and the linear regression model.

The results showed that the complete blocking model provided the most fitted linear regression with the experimental data, with coefficient of determination, R^2 at 0.9904. Subsequently, the standard blocking and intermediate blocking models provided the R^2 of 0.9626 and 0.9185, respectively. Lastly, the cake formation model presented the least coefficient value R^2 at 0.7588. This illustrated that the complete, standard blocking and intermediate blocking models were in good agreement with the experimental data compared with cake formation model. Based on this data analysis, the overall fouling phenomenon was greatly related with the reduction of number of pore available and the pore size. Furthermore, it is interesting to note that despite the membrane fouling in MBR system was due to the deposit of bioparticles, and it was thought that external fouling (cake layer) to be the dominant fouling for the entire experiment, nevertheless, regression of the data revealed that cake filtration model was insufficient to describe the entire fouling behavior. As the cake filtration model presumed the cake filtration is non compressible (constant specific cake resistance). This implied that biofouling layer may experienced a compression effect throughout the filtration period. In order to further understand the MF fouling in MBR, the filtration data was divided into two stages based on the fouling rate (Figure 8.2), and analyzed with the fouling models.

Figure 8.3 Fouling analysis using (a) complete blocking model, (b) standard blocking model, (c) intermediate blocking model and (d) cake filtration model

8.4.2.2 Two-stages fouling analysis

8.4.2.2.1 Slow fouling stage

According to the analysis of fouling rate, the MF membrane fouling in MBR system can be classified into two stages, (i) slow rate of fouling stage (ii) high rate of fouling stage. The four blocking models were applied to identify the fouling behavior in the slow fouling stage as shown in Figures 8.4a, 8.4b, 8.4c and 8.4d, respectively. The results revealed that complete blocking and intermediate blocking models provided that close fitted linear regression, followed cake filtration and finally the standard blocking model. This revealed that different fouling mechanisms involved in the membrane fouling phenomenon, hence single fouling model was not able to fully describe the fouling behavior.

It is clear from the Figures 8.4a-d that the initial slow TMP increase can be attributed to the complete blocking of some of the pores (complete blocking), superimposed of particles on fouling layer (intermediate blocking) and increase of fouling layer (cake filtration) were the major fouling mechanism in the first stage of membrane fouling. Belfort *et al* (1994) suggested that the initial MF fouling was due to the fast adsorption of macromolecules into the membrane pore and onto the membrane surface, and forming a single layer of foulant, subsequently cake formation take place. However, the stage of fast adsorption of macromolecule and formation of single first fouling layer was insignificant in Figures 8.4a-d. This can be presumed that the adsorption of macromolecule onto the membrane pore and formation of first fouling layer occurred within a short period in the biological system. Therefore, it is difficult to detect their occurrence during the initial fouling period.

Figure 8.4 Fouling analysis for slow fouling stage using (a) complete blocking model, (b) standard blocking model, (c) intermediate blocking model and (d) cake filtration model

8.4.2.2.2 *Fast fouling stage*

As shown in Figures 8.5a, 8.5b, 8.5c and 8.5d, the standard, complete and intermediate blocking models provide well fitted linear regression, whereas cake formation model was least fitted. Based on the results, the agreement to the experimental data is much better when standard and intermediate blocking models are considered, with a correlation coefficient R^2 higher than 0.99. It implied that the sharp increase of TMP was mainly due to a partial pore plugging and superimposed of the particles on the fouling layer which cause the reduction of pore diameter. The analysis also revealed that cake filtration model was not excellently for expressing the fouling behavior in the second stage of fouling. It can be concluded that the sharp TMP increase was insignificantly related with the deposition of bioparticles on the biofouling layer. This revealed that the assumption of non compression of cake layer (constant specific cake resistance) in cake filtration model was not an appropriate model to describe the biofouling in fast fouling stage. The result showed that compression effect may significantly relate to the fast fouling stage. It is suggested that during this period, the biofouling layer experience the high pressure force, hence induced the compression of cake layer, and further incur the reduction of cake porosity and reduces the available effective pores.

Figure 8.5 Fouling analysis for fast fouling stage using (a) complete blocking model, (b) standard blocking model, (c) intermediate blocking model and (d) cake filtration model

8.4.3 *Fouling behavior for MF MBR with SRT of 10 days and 300 days under super-critical flux, critical flux and sub-critical flux conditions*

In order to understand the fouling behavior in submerged MF MBR system, membrane flux was operated at super-critical flux, critical flux and sub-critical flux under two different SRT MBR systems (SRT of 10 days and 300 days). Flux step method has been applied to measure the critical flux, the selection of the critical flux was based on the fouling rate which is lower than 10 Pa/min. The critical flux was 16 L/m².hr and 27 L/m².hr for 10-day and 300-day SRT MBR, respectively. Therefore, the imposed flux for 10-day SRT MBR was designed at 25 L/m².hr (super-critical), 20 L/m².hr (super-critical), 15 L/m².hr (critical) and 10 L/m².hr (sub-critical). While the imposed flux for 300-day SRT MBR was selected at 35 L/m².hr (super-critical), 25 L/m².hr (critical), 15 L/m².hr (sub-critical) and 10 L/m².hr (sub-critical).

The fouling tendency as a function of imposed flux in MBR with SRT of 10 days and 300 days are displayed in Figures 8.6 and 8.7, respectively. Two distinct fouling phases were observed during the filtration with different imposed flux under different SRT condition. It was apparent that a slow fouling stage occurred at the early filtration stage and followed by a fast fouling stage. The results showed that two stage fouling phenomenon was obviously the main fouling behavior for the submerged MBR with SRT of 10 days and 300 days.

Figure 8.6 Changes of TMP versus time in MF MBR with SRT of 10 days, MLSS concentration of 1,500 mg/L and critical flux of 16 L/m².hr

Figure 8.7 Changes of TMP versus time in MF MBR with SRT of 300 days, MLSS concentration of 16,000 mg/L and critical flux of 27 L/m².hr

8.4.3.1 MF fouling mechanism in MBR with SRT of 10 days under super-critical flux, critical flux and sub-critical flux conditions

As discussed in Chapters 8.4.1 and 8.4.2, two stage fouling analysis managed to provide an in-depth explore into the occurrence of fouling mechanisms through entire filtration period. The fitting performance of blocking and cake formation models toward the slow fouling stage for MF filtration in 10-day SRT MBR is presented in Figure 8.8. With imposed flux at super-critical level (20 and 25 L/m².hr), the complete and standard blocking models provided the best fitting models to explain the fouling trend. While as the imposed flux was operated at critical flux level (15 L/m².hr), the complete blocking model offered the best fitted filtration model. When the imposed flux operated at sub-critical flux condition, all the four fouling models (standard, complete, intermediate blocking and cake formation) managed to describe the filtration trend of 10-day SRT MBR.

The analysis of fast fouling stage revealed that intermediate blocking models provided the best fitting regression model for the fast fouling stage for the imposed flux at super-critical, critical and sub-critical condition in MF MBR with SRT of 10 days as displayed in Figure 8.8b. Whereas, complete blocking and cake formation presented the least fitted regression models compared with intermediate blocking and standard blocking models with respect to the fouling behavior during the fast fouling stage.

The overall results suggested that standard blocking and complete blocking models were the dominant fouling mechanisms during the slow fouling stage of the MBR with SRT of 10 days. In the fast fouling stage, intermediate blocking model appeared to be the key fouling mechanism. The imposed flux magnitude was insignificantly affecting the fouling mechanisms in both fouling stages (slow and fast fouling). However, the imposed flux magnitude was related with length of

filtration period were the imposed flux under the sub-critical condition provided the longer filtration period compared with critical flux and super-critical flux conditions.

Figure 8.8 The fitting performance of blocking and cake formation models toward the MF filtration in 10-day SRT MBR for (a) slow fouling stage and (b) fast fouling stage.

8.4.3.2 MF fouling mechanism in MBR with SRT of 300 days under super-critical flux, critical flux and sub-critical flux conditions

The fitting performance of blocking and cake formation models toward the slow fouling stage for MF filtration in 300-day SRT MBR is presented in Figure 8.9a. At the super-critical flux level (35 L/m².hr), all the blocking models and cake formation model provided a well fitted regression model to the slow fouling stage in the MBR with SRT of 300 days. When the imposed flux operated at the critical flux level (25 L/m².hr), the complete blocking model offered the best fitted filtration model with coefficient of determination, R^2 at 0.9940. While during the sub-critical flux condition (10 and 15 L/m².hr), intermediate blocking and cake formation models presented well fitted regression model for the slow fouling stage in 300-day SRT MBR.

Whereas, the analysis of fast fouling stage revealed that intermediate blocking models provided the best fitting regression model for the fast fouling stage for the imposed flux at super-critical, critical and sub-critical condition in MF MBR with SRT of 300 days as displayed in Figure 8.9b. The results suggested that slow fouling stage was significantly affected by the selection of imposed flux where different fouling mechanism dominated in the imposed flux at sub-critical, critical and super-critical flux condition. On the other hand, intermediate blocking model was the crucial fouling mechanism during the fast fouling stage of 300-day SRT MBR.

Figure 8.9 The fitting performance of blocking and cake formation models toward the MF filtration in 300-day SRT MBR for (a) slow fouling stage and (b) fast fouling stage.

8.4.4 Discussion on fouling behavior in MF MBR

The results from this study showed a two stages membrane fouling through the MF filtration at sub-critical flux, critical flux and super-critical flux conditions. In addition, the phenomena of two stages fouling also demonstrated under the membrane filtration in 10-day and 300-day SRT MF MBR. This was in agreement with some researchers who also reported the two stages fouling in biological system where a slow TMP rise followed by the dramatically TMP rise of the membrane filtration (Nagaoka *et al.* 1996; Cho and Fane, 2002 and Ye *et al.*, 2005). The authors suggested that the initial and gradual TMP rise were caused by the slow deposition of EPS, and the increase of specific cake resistance, whereas the sudden rise in TMP was due to the local flux in some regions of the membrane increasing. Ognier *et al.*(2004) applied the local flux concept to model the two stages of TMP increase where hypothesized that the increase of local flux was due to the successive blocking of membrane pores.

Under the stage of slow fouling, the operation of imposed flux at various conditions (super-critical flux, critical flux and sub-critical flux) provided different fouling behavior. Additionally, the lower the imposed flux, the longer the period of slow fouling stage, which extend the usage of membrane. This can be explained by the critical flux concept, which imposes flux that operated at the higher than critical flux (super-critical flux) will tend to cause more foulant deposit on or into the membrane. While, little or least foulants deposit on to the membrane if the impose flux is below critical flux value (sub-critical flux) (Field *et al.*, 1995, Howell, 1995; Le-Clech *et al.*, 2003; Le-Clech *et al.*, 2006).

Furthermore, the results from this study revealed different fouling performance under different SRT conditions (10 days and 300 days). This may likely due to the complexity of mixed liquor composition which consists of microorganisms, cell

debris, EPS, and etc. The composition of mixed liquor is varying with operating condition employed (such as reactor configuration, aeration, SRT) and the influent wastewater compounds (Chang *et al.*, 2002). Many studies revealed that EPS play a major role that caused the membrane fouling where the higher the suspended EPS concentration, the lower the filtration flux (Chu and Li, 2005). The measured EPS concentration for MBR with SRT of 10 days and 300 days was 232 and 139 mg/g, respectively. This is consistent with Pollice *et al.* (2005) who reported that EPS concentration tends to decrease with the increase of SRT for a biological reactor. EPS are considered as the key components that determine the structural and functional integrity of microbial aggregates, where it form a three dimensional, gel like, highly hydrated and locally charged biofilm matrix, in which the microorganisms are more or less immobilized (Flemming and Wingeder, 2003). As a summarize, it is presumed that the deposit of EPS on the membrane surface will provide an additional filtration layer on the membrane surface and the filtration properties such as effective pore size, number of pore available will be greatly related with the matrix or structure of the EPS.

During the fast fouling stage, intermediate blocking provided a well fitted regression to the MF fouling trend in MBR with SRT of 10 days and 300 days. The intermediate blocking model also emerged to be the key fouling mechanism for the fast fouling stage under sub-critical, critical and super-critical flux conditions. This implied that the fast fouling stage was highly related to the reduction of available membrane pore. Shiau *et al.* (2003) presented a two stages fouling in a dead end microfiltration of BSA solution. They concluded the fast fouling stage was caused by the cake compression hence incur the reduced of cake porosity. Therefore, it is presumed that the fast fouling stage was significantly caused by the cake compression which reduces the available membrane pore and porosity.

8.4.5 Hypotheses of membrane fouling steps in MBR

Based on experimental data from this study and previous research works done by other researchers on MBR membrane fouling, it may be presumed that fast internal sorption of macromolecules and build up of first biofouling layer occurred in a very short period in the initial filtration run. It followed by the build of multi-sublayer of biofouling, and finally the fully blockage of the available membrane pores, inducing the sharp TMP increment. A simple perception model had been explored according to the experimental data. It provided an understanding the MF membrane fouling development in MBR system. As shown in scheme of Figure 8.10, the filtration process developed through the following phases:

During the first period, the bioparticles (biomass, lysed cell, EPS, etc.) deposit on the membrane pore and surface, building up a single biofouling layer. The biofouling layer is suggested to be mainly structured by EPS, where polysaccharides form the main matrix of the biofouling layer. As a result, the membrane surface is modified by the biofouling layer, hence provokes a reduction in the number of pores open to the filtrate flow. However, in the biological system, this stage occurs in a very fast moment at the initial filtration period, hence it is hard to identify the occurrence of this stage.

In the second period, the mass transfer coefficient for permeate flow mainly involved the deposition of additional EPS, biomass, lysed cell on the biofouling layer rather than the membrane properties modification. As the permeate flow is controlled at a constant rate throughout the experiment, this reduction of the area open to the flow is expressed as a slow increase in TMP. The further deposit of bioparticles induced the formation of multi sublayer of biofouling where the thickness of biofouling layer will be controlled by the hydrodynamic conditions, such as aeration and solid concentration.

During the third period, it is presumed the compression of biofouling layer occur and severely reduce in number of pores that are available for filtrate flow, translating to very high hydraulic resistance and cause the TMP increase sharply.

Figure 8.10 Changes of filtration area and fouling mechanisms

8.5 Summary

The filtration data from MF MBR system with constant flux mode presented a slow TMP increase followed by dramatic TMP increase through the entire filtration run, namely slow fouling stage and fast fouling stage, respectively. These two distinct fouling stages occurred in the membrane filtration in 10-day and 300-day SRT MF MBR. Under the slow fouling stage, different fouling behavior was found at various imposed flux operation (super-critical flux, critical flux and sub-critical flux). This was affected by the composition of mixed liquor composition which consists of microorganisms, cell debris, EPS and etc. While, under the fast fouling stage, intermediate blocking model provided the best fitted regression model for 10-day and 300-day SRT MF MBR system under the imposed flux of sub-critical, critical and supercritical flux conditions. It is suggested that during this period, the biofouling layer experience high pressure force, hence induced the compression of cake layer, and further incur the reduction of cake porosity and reduces the available effective pores. A simple perception of membrane fouling steps in MBR has been established based on the experimental data from this study and previous researchers work.

CHAPTER 9

EFFECT OF INTERMITTENT PERMEATION AND CAKE COMPRESSIBILITY ON MEMBRANE FOULING

9.1 Introduction

Membrane fouling which reduces the permeate flux or increases the TMP has limited it to be widely applied in water industry. Many efforts have been done in this field to overcome membrane fouling by operate the membrane flux below critical flux, membrane modification, gas bubbling, intermittent permeation, backwashing, mechanical and chemical cleaning (Cote *et al.*, 1997; Cui *et al.*, 2003; Schoeberl *et al.*, 2005; Sofia *et al.*, 2004; Yu *et al.*, 2005; Psoch and Schiewer, 2006). Nevertheless, the fouling problem still remains in MBR system due to the interaction between membrane and the mixed liquor (Judd, 2004).

Among these prevention and cleaning techniques, intermittent permeation operation method provides the membrane cleaning with less energy consumption where the permeation is suspended periodically. It allows relaxation and reduces compression of the cake layer, thus resistance is reduced and better permeability is then maintained (Yamamoto *et al.*, 1989). Particles deposited on the membrane could be removed by the crossflow when the TMP that held the particles is negated during the suspension of permeation. Howell *et al.* (2004) conducted the MBR study with a MF flat sheet membrane, and reported the intermittent permeation was an effective technique that allows long-term sustainability even when operated above the critical flux. Similar conclusion was also reported by Ndinisa *et al.* (2006) who studied the use of gas-liquid two-phase flow as a fouling control mechanism for submerged flat sheet membrane bioreactors. They concluded that the use of intermittent filtration as an operating strategy was more effective than continuous filtration and it also reduced energy consumption.

Chapter 8 clearly indicates that two stages fouling (slowing fouling stage followed by a fast fouling stage) occurred on MF membrane in MBR system, where the fast

fouling stage was presumably related to cake compression. Thus, more comprehensive study is needed to provide a better understanding on the correlation between intermittent permeation and the membrane fouling particularly for 300-day SRT MBR, and hence facilitating the optimization of design and operation of submerged reactor treatment plants. This study was designed to further elucidate the effect of intermittent permeation timing on the fouled membrane. The relationship between the cake compressibility under different membrane flux was also studied.

9.2 Material and Methods

9.2.1 Experimental apparatus and system

The schematic diagram for the intermittent filtration and recording system is shown at Figure 9.1. The testing unit consists of a unit of reactor with ultrapure water, membrane unit, digit pressure switch (Model: ISE50-T2-22L, SMC), suction pump (Masterflex pump), on off timer, data logger (HOBO micro station).

Figure 9.1 Schematic diagram for the intermittent filtration and recording system

9.2.2 Experimental procedures

A series of experiments were designed to measure the TMP changes at various intermittent filtration timing for a fouled membrane. First, a fouled membrane was prepared (as described below). Subsequently, the fouled membrane was transferred to a reactor which fills with ultra pure water and proceeds with intermittent permeation filtration as display in Figure 9.1.

9.2.3 Preparation of fouled membrane with TMP of 40 kPa

A tubular ceramic MF membrane made by diatomaceous earth material with 0.9 μm was operated with a constant imposed flux in a 300-day SRT MBR system. When the TMP value reached 45 kPa, the fouled membrane was transferred to the intermittent filtration testing unit (Figure 9.1). The detailed 300-day SRT MBR performance is summarized in Table 9.1. The operation procedures are presented in Section 3.2.

Table 9.1 System performance of long SRT MBR

Parameter	Value
Organic loading Rate ($\text{kg COD/m}^3\cdot\text{day}$)	3
Influent COD (mg/L)	1000
MBR permeate COD (mg/L)	<20
COD removal (%)	<98%
Working volume (L)	20
HRT (hour)	8
SRT (day)	300
MLSS (mg/L)	16000
DO (mg/L)	>3
Temperature ($^{\circ}\text{C}$)	23-25
pH	6.9-8.0
Airflow rate (L/min)	6
Membrane Flux ($\text{L/m}^2\cdot\text{hr}$)	26

9.2.4 Intermittent permeation

Table 9.2 shows the operating condition for the intermittent permeation cycle that implied in this study.

Table 9.2 Operating condition of the intermittent permeation

Subject	Condition
Effect of relaxation time of intermittent permeation cycle to TMP	60/15 minutes, 60/30 minutes, 60/120 minutes
Effect of permeation time of intermittent permeation cycle to TMP	360/60 minutes, 180/60 minutes, 30/60 minutes, 15/60 minutes
Effect of relaxation time of fast intermittent permeation cycle to TMP	60/300 seconds, 60/60 seconds, 60/30 seconds, 60/10 seconds
Effect of permeation time of fast intermittent permeation cycle to TMP	1/5 minutes, 10/5 minutes, 50/5 minutes

Note: 60/15 minutes = 60 minutes of permeation follow by 15 minutes of relaxation, similar condition apply to other intermittent permeation cycle.

9.3 Results and Discussion

9.3.1 The function of imposed flux to cake compressibility

Three fouled membranes (45 kPa) were prepared with imposed flux of 10, 15 and 25 L/m².hr, respectively. The fouled membrane was transferred to a reactor filled with ultrapure water, and operated with various flux for assessing the cake compressibility. The assessment result is shown in Figures 9.2, 9.3 and 9.4. At the lower flux condition, the TMP displayed a stable and consistent state; while at the higher flux, the TMP increased gradually. It showed the effect of cake

compressibility during the higher flux condition. This phenomenon can be interpreted by viscoelastic model which is used to express the instantaneous variation of cake porosity during cake compression:

$$\frac{\varepsilon_t - \varepsilon_i}{\varepsilon_f - \varepsilon_i} = 1 - \exp\left(\frac{-t}{\tau}\right) \quad (9.1)$$

Where ε_i is the local cake porosity before compression ($t=0$), ε_f is the local cake porosity at equilibrium after compression ($t \rightarrow \infty$), ε_t is the local cake porosity at time t , and τ is the retardation time, which can be determined from curves plotted using the cake porosity versus time (Lu *et al.*, 2001; Hwang and Hsueh, 2003). Many cake materials such as microbial cells are highly compressible which compressible cakes exhibit a decrease in void volume and an increase in the specific resistance as the compressive pressure is increased. The relationship between cake porosity and specific cake resistance can be interpreted by Carman-Kozeny equation (Baker *et al.*, 1985):

$$\alpha = \frac{180(1 - \varepsilon)}{(\rho_p d_p^2 \cdot \varepsilon^3)} \quad (9.2)$$

Figure 9.2 The function of imposed flux to the cake compressibility for fouled membrane at TMP of 45 kPa with membrane flux of 10 L/m².hr in 300-day SRT MBR

Figure 9.3 The function of imposed flux to the cake compressibility for fouled membrane at TMP of 45 kPa with membrane flux of 15 L/m².hr in 300-day SRT MBR

Figure 9.4 The function of imposed flux to the cake compressibility for fouled membrane at TMP of 45 kPa with membrane flux of 25 L/m².hr in 300-day SRT MBR

Where α is the specific cake resistance, d_p is the particle diameter, ε is the porosity of cake layer and ρ is particle density. Under the simplest operational conditions, the pressure driven permeate flux can be describe by Darcy's law (Ho and Sirkar, 2001) as

$$J = \frac{1}{A} \frac{dV}{dt} = \frac{\Delta p}{\mu(R_m + \alpha m)} \tag{9.3}$$

where J is filtrate flux, Δp is the TMP, μ the fluid viscosity, and R_m the membrane resistance, α the specific cake resistance and m is the mass of cake per unit membrane area. If we define the ultimate transmembrane pressure of the steady state as TMP_f , the following equation is modified from equation 9.1, to predict

transmembrane pressure (TMP_i) under the non steady states:

$$\frac{\Delta P_t}{\Delta P_f} = 1 - \exp\left(\frac{-t}{\tau}\right) \quad (9.4)$$

This gives that at $t \rightarrow \infty$, $\Delta P_t / \Delta P_f \rightarrow 1$, where τ is the coefficient of the retarding time,

h. Based on this equation, the experimental data was evaluated for the retarding effect of cake layer using computer statistical software, Statistical Package for Social Sciences (SPSS) as displayed in Figures 9.5, 9.6 and 9.7. The results show that the equation 9.4 was able to portray the TMP trend under different imposed flux condition. This implied that the changes of TMP were due to the retarding effect of the biofouling layer. The cake retarded model was in good agreement with the data from three fouled membrane which operated at different membrane flux. The best fit values of the model parameter for the equation 9.4 under different imposed condition are presented in Table 9.3. The data indicated that as the imposed flux increased, the P_i , P_f and τ values also increased. This revealed the retardation effect on the fouled membrane was more significant at conditions of higher imposed flux. Due to this retarding effect, the biofouling layer does not react instantly with the imposed flux, hence demonstrated the gradually increased of TMP through the filtration period. The higher the imposed flux, the greater the retarding effect onto the biofouling layer.

Figure 9.5 The function of imposed flux to the cake compressibility for fouled membrane at TMP of 45 kPa with membrane flux of 10 L/m².hr in 300-day SRT MBR. The blue line is the experimental data while pink line is calculated from the Equation 10.4.

Figure 9.6 The function of imposed flux to the cake compressibility for fouled membrane at TMP of 45 kPa with membrane flux of 15 L/m².hr in 300-day SRT MBR. The blue line is the experimental data while pink line is calculated from the Equation 10.4.

Figure 9.7 The function of imposed flux to the cake compressibility for fouled membrane at TMP of 45 kPa with membrane flux of 25 L/m².hr in 300-day SRT MBR. The blue line is the experimental data while pink line is calculated from the Equation 10.4.

Table 9.3 Best fitted model parameters of cake retard model

(a) Fouled membrane at 45 kPa under 10 L/m ² .hr			
Flux, L/m ² .hr	P _f -P _i , kPa	τ, h	P _i , kPa
2	1.2690	0.1761	1.05
5.5	2.6300	2.5884	13.355
7	3.2361	3.2384	23.8
9	7.8500	5.3482	32.845

(b) Fouled membrane at 45 kPa under 15 L/m ² .hr			
Flux, L/m ² .hr	P _f -P _i , kPa	τ, h	P _i , kPa
4	0.4326	0.0063	4.79
5.5	2.5656	4.6044	12.44
7	6.1377	5.7272	14.2
11	44.7206	23.5941	14.88

(c) Fouled membrane at 45 kPa under 25 L/m ² .hr			
Flux, L/m ² .hr	P _f -P _i , kPa	τ, h	P _i , kPa
7	1.0034	0.3053	2.30
10	7.7442	5.1385	6.85
16	10.4491	11.7705	12.295
22	23.3180	12.0037	14.075

Note: (a) the fouled membrane at 45 kPa under membrane flux of 10 L/m².hr, (b) the fouled membrane at 45 kPa under membrane flux of 15 L/m².hr, and (c) the fouled membrane at 45 kPa under membrane flux of 25 L/m².hr.

9.3.2 *The relationship between cake retarding effect and intermittent permeation cycle operation*

The Chapter 9.3.1 illustrated the occurrence of retarding effect on biofouled membrane, where the cake layer does not react immediately when pressure applied. The retarding time can be ranged from 0 to 24 hours depending on the operating conditions as shown in Table 9.3. Since the cake layer does not react instantly with the pressure applied, hence this lag time can be seen as an advantage in optimizing the membrane usage. In this study, intermittent permeation was used to identify the

effect of cake retarding to the biofouled membrane. Fouled membrane (45 kPa) was prepared from a MBR with $10 \text{ L/m}^2\text{.hr}$ membrane flux, and transferred to a reactor which fills with ultrapure water. The fouled membrane (45 kPa) was operated with $9 \text{ L/m}^2\text{.hr}$ in the ultrapure water reactor to identify the effect of intermittent permeation cycle on the fouled membrane. This study was divided into two sections, mainly to identify the effect of intermittent permeation cycle (more than 60 minutes is needed for a cycle) and fast intermittent permeation cycle (one cycle is completed within 60 minutes) on the fouled membrane.

9.3.2.1 Effect of relaxation time of intermittent permeation cycle on TMP

Relaxation experiments were conducted to examine the reversibility of cake layer at different relaxation period. Figure 9.8 displays the measured TMP changed as the function of relaxation period of 60/15, 60/30 and 60/45 (where 60/15 is referring to the 60 minutes filtration, followed by 15 minutes relaxation time, similar condition applied to the 60/30 and 60/45) at membrane flux of $9 \text{ L/m}^2\text{.hr}$. The results showed that TMP of fouled membrane (membrane with biofouling layer) was insignificantly affected by the relaxation time of 15 to 45 minutes during the intermittent permeation of 60/15, 60/30 and 60/45. Although different relaxation time was applied, the TMP of the membrane was constantly at 45 kPa. During the relaxation time, the TMP was decreased from 45 kPa to zero within 15 minutes. This suggested that relaxation of 15 minutes was sufficient for the recovery of compressed cake layer to rebound back to its original stage.

9.3.2.2 Effect of permeation time of intermittent permeation cycle on TMP

Figure 9.9 represents the effect of filtration time to the intermittent permeation with 60 minutes relaxation time for the fouled membrane (membrane with fouling layer).

The correspondent of TMP toward the intermittent permeation of 360/60, 180/60, 30/60 and 15/60 minutes were 38.7, 38.4, 31.1 and 27.8 kPa, respectively. This result indicated that the shorter the filtration timing the lower the TMP value for the intermittent permeation with 60 minutes relaxation time. This can be explained by the cake retarding concept, where the applied force on the fouled membrane did not cause an instant reaction from the biofouling layer, hence it needs more time to achieve the equilibrium state. Therefore, applying a shorter filtration time, a lower TMP value can be maintained.

Figure 9.8 Effect of relaxation time of intermittent permeation cycle on TMP for the fouled membrane (TMP of 45 kPa)

Figure 9.9 Effect of permeation time of intermittent permeation cycle on TMP for the fouled membrane (TMP of 45 kPa)

9.3.2.3 Effect of relaxation time of fast intermittent permeation cycle on TMP

Figure 9.10 represents the effect of relaxation time to the intermittent permeation with 1 minute filtration time for the fouled membrane (membrane with fouling layer). The correspondent of TMP toward the intermittent permeation of 60/300, 60/60, 60/30 and 60/10 seconds were 10.8, 14.2, 15.4 and 17.9 kPa, respectively. The results indicated that the TMP could be reduced by the applying the longer relaxation time (more than 300 seconds) during the fast intermittent permeation cycle. The TMP decreased from 12 kPa to zero value during the relaxation period of 60/300 seconds intermittent permeation cycle, while the TMP did not decrease to the zero value during the relaxation period of 60/60, 60/30 and 60/10 seconds. The results suggested that the biofouling layer require sufficient relaxation time to return to their origin state (zero TMP value), otherwise the pressure will build up in the biofouling layer and cause the higher TMP value during the next filtration period.

9.3.2.4 Effect of permeation time of fast intermittent permeation cycle on TMP

The effect of filtration time to the intermittent permeation with 5 minutes relaxation time for the fouled membrane (membrane with fouling layer) is presented in Figure 9.11. Without the implementation of intermittent permeation cycle, the TMP was gradually increased from 25 kPa to 40 kPa during the continuous 34 hours of filtration. While the correspondence of TMP toward the intermittent permeation of 1/5, 10/5 and 50/5 minutes were 13.5, 22.6 and 25 kPa, respectively. The result indicated that the intermittent permeation cycle help to reduce the TMP value. The shorter the filtration timing the lower the TMP value for the intermittent permeation with 5 minutes relaxation time. In other words, shorter filtration timing could help to reduce the build of internal pressure of biofouling layer and hence lower the TMP that needed for water to pass through the membrane.

Figure 9.10 Effect of relaxation time of fast intermittent permeation cycle on TMP for the fouled membrane (TMP of 45 kPa)

Figure 9.11 Effect of permeation time of fast intermittent permeation cycle on TMP for the fouled membrane (TMP of 45 kPa)

9.3.2.5 The usage of cake retarding effect into the intermittent permeation cycle

The results from this study showed the existence of retarding effects in the filtration of fouled membrane (Figure 9.2) and the intermittent permeation cycle could also be explained with the cake retarding concept. Based on the results, the retarding time was an important fact to be considered in the selection of a fast intermittent permeation, for the reduction of TMP and enhancement the membrane life span. The TMP trend of fouled membrane (45kPa) as the function of intermittent permeation cycle is shown in Figure 9.12. Solid line represents the TMP value during the continuous filtration run and dots represent the TMP at the specific intermittent permeation cycle. The results showed that fast intermittent permeation cycle (1 cycle is completed within 60 minutes) managed to reduce the TMP value compared with the intermittent permeation cycle (more than 60 minutes/cycle). This was due to the usage of the cake retarding effect where biofouling layer react slowly with the imposed force, hence the short filtration timing follow with a proper relaxation time was sufficient to maintain the TMP at a low value. The results suggested that fast intermittent permeation cycle was able to maintain the TMP at low level due the cake retarding effect and with a proper relaxation time.

Figure 9.12 The TMP trend of fouled membrane (45kPa) as the function of intermittent permeation cycle. (Solid line represents the TMP value during the continuous filtration run and dots represent the TMP at the specific intermittent permeation cycle)

9.4 Summary

The results revealed the occurrence of retarding effect on the fouled membrane. This may be due to the compressibility of fouling layer which comprises of highly compressible bioparticles. An equation was established to portray the phenomenon of cake retarding effect on the fouled membrane. The study on intermittent permeation revealed that a fast intermittent permeation cycle was able to keep the TMP at a low level, hence longer the usage of membrane. The execution of fast intermittent permeation cycle was based on the cake compressibility and retardation effect on the biofouled membrane. The results suggested that the cake retarding effect is an important parameter for selection of a proper intermittent permeation cycle, hence longer the membrane life span. The outcome of this study provides a better elucidation for the membrane fouling control based on cake compression and retarding effects. Furthermore, the implementation of fast intermittent permeation can be conducted in-situ, without disturbing the MBR operation as compared with mechanical and chemical cleaning methods.

CHAPTER 10

CONCLUSIONS AND RECOMMENDATIONS

10.1 Conclusions

In this work, the sustainability of 300-day SRT MBR in term of biological performance was studied. Furthermore, the performance of membrane filtration in 300-day SRT MBR also investigated. Based on the results obtained from this work and theoretical analyses, the following conclusions were drawn.

(a). Biological performance and stability of long SRT MBR

A lab scale 300-day SRT MBR was operated for over 2.5 years to assess its sustainability and performance in the treatment of dairy wastewater. The overall removal efficiency of COD was more than 99%. MLVSS/MLSS ratio indicated that no accumulation of inorganic compounds occurred in the 300-day SRT MBR system. Due to the formation of biofouling layer, permeate water quality was higher than the expected microfiltration membrane. The observed sludge yield for 300-day SRT MBR was $0.02277 \text{ gVSS.gCOD}^{-1}$, which was nearly 20 to 40 times lower than the CAS. The reason was most likely related to the energy usage by microorganism during endogenous phase where most of the energy will goes to the cell maintenance rather than cell synthesis. The microbial activity was performed stably in the 300-day SRT MBR system. The results indicated that the 300-day SRT MBR was able to provide a stable and sustainable treatment efficiency for the wastewater treatment in term of degradation, microbial activity and process stability.

The comparison of MBR with different SRT condition (5 days, 10 days and 300 days) illustrated that membrane filtration play a significant role as second purification line in producing a consistent and excellent quality of treated effluent. The 300-day SRT MBR posed a great ability to degrade the inert organics and SMP and provided the extremely low sludge yield compared with 5-day and 10-day SRT

MBR. SOUR results indicated the low consumption of oxygen occurred in the 300-day SRT MBR. It revealed that smaller amount oxygen was sufficient to achieve high degree of organic degradation during the 300-day SRT MBR condition. The results from this study implied that the high efficiency of catabolic reactions (high organic degradation rate with low oxygen consumed) can be achieved in the 300-day SRT MBR system.

(b). Influence of membrane bioreactor (MBR) mixed liquor in cake resistance

This study presented the involvement of mixed liquor and supernatant with SRT of 10 days and 300 days in UF filtration. The correlation among MLSS, supernatant, cake resistance and specific cake resistance in UF membrane was studied. Additionally, the fouling tendency of MF and UF membranes in dealing with mixed liquor from 300- day SRT MBR was also been investigated.

The experimental results showed that mixed liquor with SRT of 300 days posed a higher filtration resistance over the mixed liquor with SRT of 10 days. This was attributed to the high MLSS concentration in mixed liquor with SRT of 300 days where UF filtration resistance was found exponentially increasing with the increment of MLSS concentration under the high MLSS concentration ($> 8,000$ mg/L). Nevertheless, supernatant also played a major role toward the UF membrane fouling by contributing 87.3% and 50% of total resistance for 10-day and 300-day SRT, respectively.

On the other hand, the specific cake resistance test revealed that mixed liquor with SRT of 10 days posed a less filterability characteristic compared to the mixed liquor with SRT of 300 days. Supernatant was identified as the crucial factor affecting the specific cake resistance which the relative contribution of supernatant to specific

cake resistance was 50% and 80% for 10-day and 300-day SRT, respectively. While MLSS concentration was insignificantly related to the specific cake resistance for both mixed liquor with SRT of 10 days and 300 days. The comparison between specific cake resistance and EPS from the supernatant from 10-day and 300-day SRT MBR revealed that higher soluble EPS concentration provided higher specific cake resistance. Hence, it was suggested that the soluble EPS might be a key component in determining the specific cake resistance.

Furthermore, supernatant was found to be an important parameter that affected the cake resistance in MF and UF membranes. It was attributed to about 85% of the total MF filtration resistance and 53% of the total UF filtration resistance during the MF and UF filtration of mixed liquor with 300-day SRT, respectively. Furthermore, both MF and UF membranes revealed that increase of mixed liquor concentration incurred the increase of cake resistance, especially when the mixed liquor concentration is higher than 8,000 mg/L MLSS.

(c). Effect of biofouling layer on long solids retention time microfiltration membrane bioreactor

This study was conducted to investigate the effect of biofouling layer on MF filtration performance in term of critical flux trend, membrane morphology and membrane rejection performance. The experimental results revealed that formation of biofouling occurred when the imposed flux operated at critical flux and sub-critical flux conditions. This biofouling can be divided into two stages where a slow fouling stage followed by a rapid fouling stage where slow fouling stage caused a signification influence to the critical flux and rejection performance. The critical flux value decreased from 27 L/m².hr to 14 L/m².hr as the TMP increased from 0 to 10 kPa. Subsequently, critical flux decreased slowly from 14 to 5 L/m².hr

as a result of TMP increased from 10 to 45 kPa. While, the membrane rejection increased from 72% to 85% as TMP increased from 0 to 10 kPa. Subsequently, the rejection performance was maintained at 85% to 88% during 10 to 40 kPa TMP condition. A correlation between filtration pore size and rejection performance was established and used to assess the effective filtration pore size during the filtration process. The results revealed a great reduction of effective filtration pore size occurred during the slow fouling stage compared to the fast fouling stage. This explained that the great changes of critical flux and rejection performance at the slow fouling stage were due to the rapid reduction of effective filtration pore size.

(d). Biofouling development and rejection enhancement in long solids retention time microfiltration MBR

Biofouling on the membrane surface is inevitable which is caused by the nature of biological system, where microorganism and bioparticles are the main component. This study was aimed to investigate the biofouling development on MF membrane under 300-day SRT condition, EPS distribution on membrane surface and contribution of biofouling onto the permeate quality. The results demonstrated that the formation of biofouling layer could be visually defined as biogel layer and cake layer. The experimental results suggested that the formation of biofouling layer started by the attachment of polysaccharide and followed by formation of biogel layer on membrane surface. It further induced the attachment of protein, polysaccharide and bioparticles, and formed cake layer. As evidenced in SEM photos and permeate quality, the formed biofouling layer/EPS matrix had changed the properties of membrane surface such as the pore and porosity, and hence producing the better permeate quality. Due to the formation of biofouling layer on MF membrane, the MF membrane achieved UF rejection efficiency. It is presumed that the rejection enhancement was related to the structure of formed biofouling

layer which was mainly associated with the EPS matrix and cake layer. A great enhancement of rejection performance occurred at the early filtration period, and followed by a slight enhancement in rejection throughout the entire filtration. This enhancement of rejection performance by biofouling layer can be mathematically expressed by the logarithm function with the degree of membrane fouling.

(e). Fouling behavior in microfiltration membrane bioreactor

The experimental data of the microfiltration in MBR system with constant flux mode presented a slow TMP increase followed by dramatic TMP increase through the entire filtration run. The analysis of membrane filtration using four type of fouling models presented that the reduction in number of membrane pores, pore diameter and the increase of particles deposited on membrane surface took place concurrently during the slow fouling stage. Consequently, a sharp increase of TMP occurred which was caused by reduce of number of membrane pores and decrease of pore diameter. The analysis results suggested cake filtration model was inadequate to explain the fouling behavior during the fast fouling stage. This revealed that the assumption of non compression of cake layer (constant specific cake resistance) in cake filtration model was not an appropriate model to describe the biofouling in fast fouling stage. The result showed that compression effect may significantly relate to the fast fouling stage. It is suggested that during this period, the biofouling layer experience the high pressure force, hence inducing the compression of cake layer, and further incurring the reduction of cake porosity and reducing the available effective pores. A simple perception of membrane fouling steps in MBR has been established based on the experimental data from this study and previous researchers work.

(f). Effect of intermittent permeation and cake compressibility on membrane fouling

The effect of intermittent permeation timing on the biofouled membrane was investigated in this study. The experimental results presented the occurrence of cake retarding effect on the fouled membrane. Due to this retardation effect, the biofouling layer does not react instantly with the imposed flux, hence demonstrating the gradual increased of TMP through the filtration period. Additionally, the retardation effect on the fouled membrane was more significant at conditions of higher imposed flux. An equation was established to portray the phenomena of cake retarding effect on the fouled membrane. The study of the intermittent permeation showed the fast intermittent permeation cycle was able to reduce the transmembrane pressure, hence longer the usage of membrane. The execution of fast intermittent permeation cycle was based on the cake compressibility and retardation effect on the biofouled membrane.

10.2 Recommendations

The results presented in this thesis provide insights into the sustainability of the long SRT MBR. These studies also indicate the effect of long SRT mixed liquor on the specific cake resistance and membrane resistance. In addition, the effect of biofouling layer formation and compressibility also being studied. However, there are a number of important areas which require additional experimental and theoretical investigation.

(a). Microbial metabolism in the long SRT MBR

The results from this study showed that high efficiency of catabolic reactions (high

organic degradation rate with low oxygen consumed) can be achieved in the prolonged SRT MBR. The in depth study on the microbial metabolism such catabolic and anabolic reactions in long SRT condition may provide more understanding on the high catabolic efficiency with a low energy consumption and low biomass production.

(b). Characterization of the biofouling layer

The formation of biofouling layer in MBR is an inevitable process. Therefore, the understanding of the structure of cake/solution interface plays a significant role in determining cake-limited permeate flux. One of the promising areas is employing confocal laser scanning microscopic (CLSM) in conjunction with fluorescently labeled probes to explore the composition of the biofoulant. In addition to CLSM, other microscopic techniques can be employed to investigate the biofouling phenomenon.

(c). Combination of back pulsing and fast intermittent permeation

This study revealed that fast intermittent permeation was able to reduce the cake resistance and hence extend the membrane usage. It has the potential to combine the back pulsing techniques and fast intermittent permeation to reduce the membrane fouling. In addition, back pulsing and fast intermittent permeate are the in-situ cleaning method; it offers the least disruption to the process and requires the least cost to perform.

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