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APPLICATION OF SUBMERGED MEMBRANE BIOREACTOR FOR CONVERTING HIGH STRENGTH WASTEWATER INTO CLEAN WATER

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SCHOOL OF CIVIL AND ENVIRONMENTAL ENGINEERING

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Master of Engineering

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ABSTRACT

The high biomass submerged membrane bioreactor (MBR) showed exceptionally high performance in organics and nutrients removal for a high strength industrial wastewater feed. During the 300 days of continuous operation, chemical oxygen demand (COD) values of the permeate fell to less than 10 mg-L^{-1} after just 100 days. This would represent an excellent organic reduction of 99%. It was found from the study that the biological process of the MBR was responsible for 90-98% of COD removal while the membrane separation contributed to further 2-10% of COD removal. Total nitrogen (TN) removal also showed high reductions. Quality of the permeate were better than local tapwater and typical clean water microfiltration effluent presented an exciting opportunity for the reuse or recycle instead of discharge into open waters. The high quality of the permeate was found to be due to the formation of a “biomembrane” that had a higher rejection rate than the membrane itself. This “biomembrane” was observed to be a result of a biofilm layer formed. The original microfiltration (MF) ceramic membrane had served as a supporting structure to the “biomembrane” layer that had higher selectivity, analogous to morphology of a hollow fibre asymmetric ultrafiltration (UF) membrane. Sludge generation was also very low in the submerged MBR system and sludge yield, Y_G of the MBR system was $0.115\text{ gVSS-gCOD}^{-1}$, twice less than the lower value reported for conventional activated sludge system.

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LIST OF ABBREVIATIONS

BOD	biological oxygen demand
BOD ₅	5 day biological oxygen demand
BOM	biodegradable organic matter
CAS	conventional activated sludge system
COD	chemical oxygen demand
CP	concentration polarization
CR	controlled release
DO	dissolved oxygen
DOC	dissolved organic carbon
ED	electrical driven (electrodialysis/electrolysis)
EMBR	extractive membrane bioreactor
EPS	extracellular polymeric substances
F/M	food to microorganism ratio
GS	gas separation
HD	haemodialysis
HF	hollow fibre
HRT	hydraulic retention time
IC	inorganic carbon
IX	ion exchange
MBR	membrane bioreactor
MF	microfiltration
MLSS	mixed liquor suspended solids
MLVSS	mixed liquor volatile suspended solids
MST	membrane sewage treatment
N.D.	non detectable
NF	nanofiltration
NOM	natural organic matter
NTU	nephelometric turbidity unit
PUB	Public Utilities Board, Singapore
PV	pervaporation
PVDF	polyvinylidene fluoride

RO	reverse osmosis
SEM	scanning electron microscope
SMP	soluble microbial product
SRT	solid retention time or mean cell residence time
SS	suspended solids
SVI	sludge volume index
TC	total carbon
TMP	transmembrane pressure
TN	total nitrogen
TOC	total organic carbon
TP	total phosphorous
UF	ultrafiltration
UV	ultraviolet
VLR	volumetric loading rate
VOC	volatile organic carbon
VSS	volatile suspended solids

LIST OF NOMENCLATURE

λ	wavelength of light, nm
b	endogenous decay coefficient, d^{-1}
C	organic concentration, $gCOD \cdot L^{-1}$
C_e	effluent organic concentration, $gCOD \cdot L^{-1}$
C_i	influent organic concentration, $gCOD \cdot L^{-1}$
E	process efficiency, %
I_s	intensity of the scattered light, cd
J	flux, $m \cdot s^{-1}$
K_d	decay coefficient, d^{-1}
K_s	saturation constant, $mg \cdot L^{-1}$
n	number of particles
η	viscosity, $kg \cdot m^{-1} \cdot s^{-1}$
θ	SRT or mean cell residence time, d
Δp	change in pressure, kPa
P_x	sludge production, $kgVSS \cdot d^{-1}$
Q	flow rate, $L \cdot d^{-1}$
Q_i	influent flow rate, $L \cdot d^{-1}$
R_b	biofilm resistance, $m \cdot kg^{-1}$
R_c	cake resistance, $m \cdot kg^{-1}$
R_d	sludge growth rate, $gVSS \cdot L^{-1} \cdot d^{-1}$
R_m	intrinsic membrane resistance, $m \cdot kg^{-1}$
R_p	pore resistance, $m \cdot kg^{-1}$
R_t	filtration resistance, $m \cdot kg^{-1}$
$-R_o$	organic degradation rate, $gCOD \cdot L^{-1} \cdot d^{-1}$
S	substrate concentration, $mg \cdot L^{-1}$
S_e	substrate concentration in effluent, $mg \cdot L^{-1}$
t	time, d
T	HRT, volumetric loading, d
μ	specific growth rate, d^{-1}
μ'	net specific growth rate, d^{-1}
μ_m	maximum specific growth rate, d^{-1}
V	volume, m^3

X	sludge concentration, $\text{gVSS}\cdot\text{L}^{-1}$
X_r	sludge concentration in the bioreactor, $\text{gVSS}\cdot\text{L}^{-1}$
Y	observed sludge yield, $\text{gVSS}\cdot\text{gCOD}^{-1}$
Y_m	maximum yield coefficient, $\text{mg}\cdot\text{mg}^{-1}$
Y_G	theoretical sludge yield, $\text{gVSS}\cdot\text{gCOD}^{-1}$

CHAPTER 1 INTRODUCTION

1.1 BACKGROUND

Rapid industrialization during the last century has improved the life of millions of people around the globe. However, with industrialization and a surging population growth, the demand for clean and potable water is exponentially raised. This places an enormous stress on the limited water supply to meet the ever rising demand for clean water. Singapore with her small size and limited natural water resources is no exception to support its growing water demand. Even a country with vast land area like China is presently facing water shortage due to rapid modernization of its cities.

Concurrent with the rising clean water demand, huge amount of wastewater is also generated from municipal and industrial sources. This large amount of wastewater greatly exceeds what can be degraded naturally and could threaten to offset the delicate balance of the natural environment. Greater awareness on this issue has lead to more stringent regulation on the wastewater discharge standards to prevent contamination of clean water sources.

For the past 50 years, activated sludge process is one of the most prevailing technologies for biological wastewater treatment. However, the efficiency of this conventional technology is restricted by the difficulty of separating solids (biological sludge or biomass) from the effluent by gravitational settling, which limits the solids concentration to about $5 \text{ g}\cdot\text{L}^{-1}$, and consequently the required reactor volumes are large. In addition, the process generates large quantities of excess sludge and its treatment and disposal represent 50-60% of total wastewater treatment cost (Egemen *et al.*, 2001). Therefore, there is plenty of scope for higher efficient systems to be developed. Also, in an effort to reduce reliance on conventional clean water supplies, there are increasing interests in the development of alternative water resources, such as water reclamation especially within industries. Many of which are also interested in evaluating new and emerging technologies for wastewater treatment which might provide cost advantages for water reclamation projects. Prominent among these technologies is the membrane bioreactor (MBR).

MBR is devised to overcome these constraints, in which the large-size settling tank is replaced by a membrane filtration unit permitting the extraction of clean water. An advantage of a MBR is having a higher biomass concentration than most conventional activated sludge process (Shim *et al.*, 2002; Hong *et al.*, 2002). This results in a higher rate of removal of organic, nitrogen and phosphorous (Trouve *et al.*, 1994; Côté *et al.*, 1997; Seo *et al.*, 1999; Ghyyoot and Verstraete, 2000; Shim *et al.*, 2002). It is also capable of a smaller excess or zero sludge production (Chaize and Huyard, 1991; Muller *et al.*, 1995; Rosenburger *et al.*, 2002; Sun *et al.*, 2003). Moreover, the space occupied by the biological wastewater treatment plant is substantially reduced due to the absence of settling tanks and the reduction in bioreactor size is made possible by the higher biomass concentration (Huang *et al.*, 2001). This will economize the wastewater treatment process especially to places where land is a limited resource as in the case of Singapore.

However, the development and applications of MBR is nevertheless limited by membrane fouling and the unclear mechanism of biological process under higher biomass condition are not yet fully delineated and controlled. A literature review indicated that a number of research activities have been reported in the last 15 years. These major reported researches include a combination of MBR using hollow fiber membrane in bioreactor, and a combination of MBR using inorganic membrane either internally or externally configured (Muller *et al.*, 1995; Côté *et al.*, 1997; Rosenburger *et al.*, 2002; Sun *et al.*, 2003).

Currently, most of researchers are focusing on the MBR with a submerged configuration. The main advantage of this configuration is the cost effectiveness comparing with the external (side stream) configuration (Ueda *et al.*, 1996; Dijk and Roncken, 1997; Gander *et al.*, 2000). Despite the fact that numerous journals have reported on various MBR issues, there is still much room for investigations because of limited understanding in this field. Many researchers have reported their MBRs based on different hydraulic retention times (HRT) and sludge retention times (SRT) in external configuration but only a few of them had discussed on the feature of submerged MBR system. Even when the submerged MBR was investigated, the experiments were often based on relatively low strength influent such as municipal wastewater.

1.2 RESEARCH OBJECTIVES

The implementation of MBR to replace conventional activated sludge process especially in high strength industrial wastewater treatment is a very promising application. However, this has not been actively investigated. In order to further understand the MBR process and further application of such system into industries, there is an urgent need for this kind of research work. The main objective of this project was to set up a laboratory scale submerged membrane bioreactor and examined its performance in treating the high strength industrial wastewater.

The scope of study included the following:

1. Study of the overall efficiency of submerged MBR system in the treatment of high-strength wastewater and its performance in terms of organics removal, nutrients removal and permeate quality. The effect of inorganic material on the biological process was also studied;
2. Study of the bio-process mechanisms associated with membrane separation especially in the sludge generation of submerged MBR system and the effect of a 200 day SRT on the sludge yield;
3. Study of the membrane performance in a 200 day SRT submerged MBR system and the effect of membrane cleaning on operational performance;
4. Study of the existence of a biomembrane layer and proposed a theoretical biofouling structure.

The research work was however limited to the study of the objective with a fixed HRT and fixed SRT due to the cost and space of constructing multiple laboratory scale reactors for concurrent studies.

1.3 ORGANIZATION OF THESIS

The thesis is divided into 6 chapters. Chapter 1 provides a general introduction of the conventional activated sludge process and its limitations. The first chapter also gives a general background on the MBR, the solution to the limitations of the conventional process and also the aims of the project. Chapter 2 is the literature review which discusses the two phases in a MBR process, the biological and membrane. It is followed by a review of current MBR research developments and its advantages and disadvantages. The methodology, design, experimental procedure and analysis methods are presented in Chapter 3.

Chapter 4 presents experimental results from the performance of the laboratory scale MBR. Chapter 5 will discuss on the membrane performance and membrane fouling phenomenon observed. Finally, Chapter 6 will draw conclusions on this research work based on the results obtained and recommend further studies to the current work.

1.4 LIST OF PUBLICATIONS

The following is a list of publications that the author had relating to his scope of study.

1. Sun, Darren Delai, Tay, Joo Hwa, Zeng, Luhai, Hay, Choon Teck (2003) **“Converting High Strength Wastewater into Clean Water Using Membrane Bioreactor with Prolonged Solid Retention Time”** Sino-Singapore Joint Symposium on Environmental Protection Technologies and Environmental Hydraulics and First Asian Environmental Research Alliance Partnership Symposium, Taipei, Taiwan, ROC. 6-7 January, 2003.
2. Sun, Darren, Hay, Choon Teck, Khor, Swee Long (2004) **“The Influence of 200 Days Sludge Retention Time on System Performance of a Submerged Ceramic Membrane Bioreactor”**, J. Mem. Sci, submitted and under review in December 2004.
3. Hay, Choon Teck, Khor, Swee Long, Darren, D. Delai and James, O. Leckie (2005) **“Minimized Sludge Production Using a Membrane Bioreactor”**, Singapore-Stanford Symposium, NTU, Singapore, May 2005.
4. Hay, Choon Teck, Sun, Darren, Khor, Swee Long and James O Leckie (2005) **“Effect of 200 Days Sludge Retention Time on Performance of a Pilot Scale Submerged Membrane Bioreactor for High Strength Industrial Wastewater Treatment”** IWA International Conference on Sustainable Development of Chemical Industries with the Environment Chemical Industries 2005: Waste and Wastewater Management, Tsukuba & Kashima, Japan, July 14-16, 2005.
5. Hay, Choon Teck, Khor, Swee Long, Sun, Darren Delai (2005) **“Use of Microfiltration Membrane Bioreactor for Ultrafiltration Quality Water Production”**, International Desalination Association World Congress on Desalination and Water Reuse, Singapore, September 11-16, 2005, submitted in December 2004 and accepted on July 2005.

6. Hay, Choon Teck, Sun, Darren, Khor, Swee Long (2005) **“Characterisation of the Biological and Membrane Behaviours in a 200-day Sludge Retention Time Pilot Scale Submerged Membrane Bioreactor”**, Wat. Res., to be submitted July 2005.
7. Sun, Darren, Hay, Choon Teck, Khor, Swee Long (2005) **“The Role of Biofilm for the Production of Ultrafiltration Water in a Submerged Microfiltration Ceramic Membrane Bioreactor”**, J. Mem. Sci., to be submitted August 2005.

CHAPTER 2 LITERATURE REVIEW

2.1 BIOLOGICAL FUNDAMENTALS

2.1.1 Conventional Activated Sludge Process

Wastewater treatment is the largest biotechnology industry in the world. Generally, it is the handling and disposing of domestic and industrial wastewaters so they present no threat to the general population and the environment. The treatment of wastewater is first done in primary clarification (settling) tank where the solids are removed before the biological treatment. In biological process, the organic matters, which have carbon substrates measured as biochemical oxygen demand (BOD) or chemical oxygen demand (COD), are degraded by microorganisms. The microorganisms that grow on the organic matters in the wastewater are then separated from the water by further settling of the “treated” wastewater in the sedimentation tank, leaving a relatively clean effluent as the treated effluent (Stephenson *et al.*, 2000). The treated effluent will then be discharged into environment or channeled for further tertiary treatment or for reuse. This biological treatment is by far the most common treatment process for municipal and industrial wastewaters.

The biological wastewater treatment processes are designed to reduce the following parameters to an allowable concentration level for discharge or reuse:

- BOD/COD
- suspended solids (SS)
- nitrogen (N) and phosphorous (P)
- fecal coliforms

The main purpose of secondary treatment is to reduce the BOD/COD value which does not benefit as much as SS from primary clarification. In other words, secondary treatment should be a process that is capable of biodegrading the organic matters into non-polluting end products, H_2O , CO_2 and biomass (sludge). Then the discharge of biologically treated wastewater should meet the environmental requirements.

The mechanisms of removal of organic matters include (Kiely, 1998):

- Air stripping
- Adsorption
- Biodegradation

Adsorption of non-degradable organics onto biomass is not significant but it does occur for some specific organics. Heavy metals will also adsorb to biomass and bio-accumulate. Air stripping of volatile organic carbons (VOCs) occurs in aerobic systems. The breakdown of carbonaceous material by aerobic degradation generates CO₂ and other VOCs into the atmosphere.

Biodegradation is the most dominant mechanism of organics removal for municipal and most industrial wastewaters. Biological processes are primarily designed for the removal of dissolved and suspended organic matters from wastewaters by microbial metabolism. It involves the use of living microscopic organisms, which include bacteria and protozoa, to consume dissolved and colloidal organic materials as food. The large microbial surface permits initial adsorption of colloidal and soluble organics together with synthesis of cells so that after a relatively short contact time, the liquid phase of the wastewater contains little residual organic matter. The adsorbed organic matters are then oxidized to normal aerobic end products (Tebbutt, 1998).

Most biological treatment plants now use the conventional activated sludge process. The activated sludge process has proved useful for the treatment of many organic wastes which were at one time thought to be toxic to biological systems (Tebbutt, 1998). In general, the activated sludge process is a treatment technique in which wastewater and reused biological sludge full of living microorganisms is mixed and aerated. This process is based on the aeration of wastewater with flocculating biological growth, followed by separation of treated wastewater from this growth. This process depends on the use of a high concentration of microorganisms present as a “floc” kept suspended by agitation, either mechanically or aeration. The activated sludge is constantly growing and more is produced that can be returned for reuse in the aeration basin. Some of this sludge must,

therefore be wasted to a sludge handling system for further treatment and disposal. Usually, the separation of the growth from the biologically treated wastewater is performed by settling. The microorganisms are mixed thoroughly with the incoming organic as food. As they grow and are mixed with air, the individual organisms clump together (flocculate). Once flocculated, they settle more readily in the secondary clarifier. Figure 2.1 shows the schematic diagrams of an activated sludge system.

Figure 2.1. Schematic diagrams of an activated sludge systems (Metcalf and Eddy, 2003)

The activated sludge system, in simplicity, comprises of an aeration tank and a secondary settling tank. The aeration tank, while also having many possible configurations, basically retains the influent wastewater for a number of hours, known as hydraulic retention time or HRT, in a well mixed and aerated environment before forwarding the effluent for further settling to the secondary settling tank where the flocculated biomass settles rapidly out of suspension to form sludge with the clarified effluent (Gray, 1990). The end products of the settling tank are clarified or treated liquid effluent, ready for discharge to open water bodies or for further treatment and reuse, and a liquid-solid sludge. A fraction

of the sludge will be returned to the aeration tank. The sludge contains a high density of live microbial mass and in returning part of the sludge; an active population of microbes are always maintained in the aeration tank.

The “mixed liquor” suspension in the aeration tank contains wastewater, living and dead microorganisms and inert biodegradable and non-biodegradable suspended and colloidal matters. The particulate fraction of the mixed liquor is called the mixed liquor suspended solids (MLSS). The volatile sub-fraction of the MLSS called the mixed liquor volatile suspended solids (MLVSS) is often used as a measure of the microbial population. The influent wastewater is the food source for the resident microorganisms in the aeration tank. The microbes biodegrade the substrates in the wastewater into new microbial cells in the presence of air. Other end products include CO_2 , NO_3^- and SO_4^{2-} . In the settling tank, the excess biomass settles out as sludge and about 80 per cent of this is removed for further treatment and subsequent disposal.

The activated sludge process is the cornerstone of sewage treatment systems. Although it is a biological process and has been in use for more than 80 years, we still lack detailed understanding of how it works and how its performance might be better controlled and manipulated. The activated sludge process in wastewater treatment technology is copied from the natural self-cleaning process of water bodies. As a result of biological decomposition and degradation processes, which run in a concentrated and controlled way, the organic material contained in wastewater is absorbed and converted or respired, respectively, into biomass. The rate of organic material in wastewater is higher than in natural water bodies. For its metabolization, it is therefore necessary to raise the concentration of microorganisms as well as oxygen supply. Metabolization or degradation of organic material means its oxidation (burning) with the help of microorganisms. This process is also called “biological burning”. Final product of this burning process is carbon dioxide.

The activated sludge process was developed around 1913 at the Lawrence Experiment Station in Massachusetts by Clark and Gage (Metcalf and Eddy, 1930) and by Arden and Lockett in 1914 at the Manchester Sewage Works in Manchester, England. Since its inception by Arden and Lockett, the activated sludge process has grown in popularity, becoming the most widely applied wastewater treatment system invented. This system

has been used as a root for different modification and alteration to improve the wastewater treatment field. One of the most significant of it in modern times will be the MBR, a hybrid process coupling the use of membranes in activated sludge process.

2.1.2 Aerobic Biological Oxidation

The primary purpose of biological wastewater treatment is to remove the organic matters present in wastewater. The organic matters are most commonly quantified in terms of BOD or COD. Sufficient contact time is required between the wastewater, heterotrophic microorganisms, oxygen and nutrients. During the initial bacteria uptake of the organic material, more than half of it is oxidized and the remainder is assimilated as new biomass, which may be further oxidized by endogenous respiration. CO₂ is produced under the aerobic process.

In biological wastewater treatment, the most widely occurring and abundant group of microorganisms are the aerobic heterotrophic bacteria. Bacteria are single celled prokaryotic organisms varying widely in size ranges from 10⁻¹ µm to 5 µm. Other microorganisms present in the aerobic biological process include protozoa and rotifiers (Horan, 1990; Ratsak *et al.*, 1996). Nuisance organisms like bacteria from genera *Nocardia* and *Microthrix* (Pitt and Jenkins, 1990), which gives bulking and foaming problems and affects the clarification process, can also develop in the activated sludge process.

Generally, their mode of reproduction is by binary fission in which the original cells are divided into two new organisms. The time required taken for each division to occur is known as the generation time. It can vary from days to even minutes.

The growth of the bacteria is promoted under suitable environmental conditions and pH. Most bacteria cannot tolerate pH above 9.5 or below 4.0. At pH greater than 9.0, microbial activity is inhibited while at pH less than 6.5, fungi dominate over the bacteria in competition for substrate. Fluctuation in the influent pH is minimized by completely mixed aeration, which offers maximum buffering capacity. If the buffering capacity is not sufficient to maintain the pH within the acceptable range, then pH adjustment will be

required. The optimum pH range for carbonaceous oxidation lies between 6.5 to 7.5. Apart from organic carbon, nitrogen and phosphorous, which are essential for bacteria growth, inorganic ions such as calcium, magnesium, potassium, iron, manganese, cobalt, etc. must be available for bacterial metabolism (Gray, 1990).

Temperature is another vital factor that influences the metabolic activities of the microbial population. Heterotrophs bacteria that are mainly use to remove carbonaceous substrate operate in the mesophilic temperature range, growing best in the temperature range 20-40°C. At higher temperature, an increase in biological activity increases the rate of substrate removal.

In addition, aeration is usually required to supply oxygen to the aerobic microorganisms in the reactor for respiration and to maintain the microbial flocs in a continuous state of agitated suspension, ensuring maximum contact between the surface of the floc and the wastewater. This continuous mixing action is crucial as it ensures a maximum oxygen concentration gradient to enhance mass transfer and at the same time help to disperse metabolic end products within the floc. Usually, a dissolved concentration between 0.2 to 2.0 mg/L is sufficient for active aerobic heterotrophic microbial activity.

2.1.3 Biological Growth Curve

The biological growth curve is a response to the bacteria environmental conditions within a closed system. In biological treatment processes, the growth phase is actually controlled by the food to microorganism ratio (F/M) or the sludge loading rate. It has been identified that the rate of organic removal is most rapid in the log growth phase where the F/M is very high. The general growth pattern of bacteria in a batch culture is illustrated in Figure 2.2 representing the six distinct phases of bacteria growth (Monod, 1949).

Figure 2.2. Biological growth curve (Monod, 1949)

Starting at time zero with substrate and nutrients in excess and only a small population of biomass exists. As the substrate is consumed, four distinct growth phase develop sequentially. In a system where an inoculum of bacteria is added to a suitable substrate containing all the necessary nutrients and growth factors, the classical biological growth curve as shown will be reproduced.

(i) The lag phase

Upon addition of the biomass, the lag phase represents the acclimatization of the microorganism to the substrate and the new environment. This is especially true for bacteria with long regeneration time. During the lag phase, the microorganisms are developing adaptive enzymes to enable them to utilize the substrate before significant cell division and biomass production can occur.

(ii) The acceleration-growth phase

After the lag phase for the adaptation to a new environment, microorganisms begin to grow during an acceleration phase.

(iii) The exponential-growth phase

Once sufficient concentration of appropriate enzymes has built up, the cells begin to divide and the population density of bacteria rapidly increases entering into the exponential or logarithmic growth phase. During the exponential-growth phase, bacterial cells are multiplying at their maximum rate, as there is no limitation due to substrate or nutrients. Extremely high rates of microbial growth can be achieved with the rate of metabolism at the maximum. . In this phase, the F/M is very high and generation time is minimal but constant. The growth rate is logarithmic and the rate of increase of microorganisms (or biomass) is proportional to the mass of microorganisms present in the system.

(iv) The declining-growth phase

Gradual decrease in substrate concentration and accumulation of metabolic products of inhibitory nature reduce growth rate during this phase.

(v) The stationary phase

The exponential phase continues until the substrate becomes limiting. The rate of microbial growth rapidly declines and the generation time increases as the substrate concentration gradually diminished. This enters the stationary phase where the biomass concentration remains relatively constant with time. In this phase, bacterial growth is no longer exponential and the amount of growth is offset by the death of cells. At this stage, the majority of cells remain viable in a state of suspended animation without the nutrients or environmental conditions to reproduce (Gray, 1990).

(vi) The endogenous (death) phase

In the endogenous or death phase, the F/M is low as the substrate has been completely depleted so that no growth is occurring and the change in biomass concentration is often observed as an approximate constant fraction of the biomass remaining that is lost each day. The condition has become unfavorable by a reduction in the food concentration and possibly also by the accumulation of toxic end products in the system, for cell survival, which leads to a microorganism death rate and a decline in the rate of substrate removal. When all the substrate has been exhausted, growth will cease and the numbers of microorganisms begin to

fall in an autodigestion. The rate of metabolism will rapidly decline until the microorganisms are in the endogenous respiration where cells lysis and resynthesis taking place. The nutrients remaining in the dead cells diffuse out to furnish the remaining cells with food. Endogenous respiration occurs at an exponentially declining rate which is analogous to decay of radioisotopes.

2.1.4 Biological Growth Kinetics

When a biodegradable organic food source is applied to a heterotrophic (utilizing organic materials for energy, as distinct from autotrophic which uses CO₂ as the carbon source) microorganism population in a well aerated environment, the response is as follows (Ekama and Marais, 1984):

- (i) The readily soluble COD goes through the cell wall and is metabolized quickly.
- (ii) The slowly biodegradable particulate COD is absorbed on to the organisms and stored. This quick reaction removes all the particulate and colloidal COD. Over time the stored COD is broken down by extracellular enzymes, transferred through the cell wall and metabolized. The rate limiting step in the overall synthesis is the enzymatic breakdown at rates of about ten percent of the readily biodegradable COD rate.
- (iii) Some of the COD metabolized is converted to new cells, while the reminder is lost as heat in the energy process required for the new cells synthesis. Oxygen externally supplied is used up in this energy process, such that the amount of oxygen utilized is proportional to the COD lost.
- (iv) At the same time, there is a net loss of live biomass, termed endogenous mass loss, where some of the organisms utilize as food their own stored food materials and dead cells. This endogenous degradation is continuous and relatively constant at about ten to twenty percent per day.

The performance of biological processes use for wastewater treatment depends on the dynamics of substrate utilization and microbial growth. The effective design and operation of such systems require an understanding of the biological reactions occurring and understanding of the basic principles governing the growth of microorganisms. Further, the need to understand all of the environmental conditions that affect the substrate utilization and microbial growth rate cannot be over-emphasized and it may be necessary to control such conditions as pH and nutrients to provide effective treatment.

In aerobic oxidation, the conversion of organic matter is carried out by mixed bacterial cultures in general accordance with the stoichiometry shown as

Oxidation and synthesis:

Endogenous respiration:

COHNS is used to represent the organic matters in the wastewater, while $\text{C}_5\text{H}_7\text{NO}_2$ is used as the general formula for bacteria cells in the reactor.

The behaviour of biological processes can be characterized by considering the kinetics of microbial growth. It is assumed that a constant fraction of microorganisms within the biological treatment unit will remain viable. In both batch and continuous culture systems, the relationship to the rate of growth of bacteria cells during the growth phase can be defined by means of a differential equation as follows:

$$\frac{dX}{dt} = \mu X \quad (2.1)$$

where X = biomass concentration, $\text{mg}\cdot\text{L}^{-1}$

μ = specific growth rate, d^{-1}

t = time, d

Laboratory studies of the batch and continuous culture systems have shown that the quantity of new cells produced to be reproducible for given substrate. The following relationship has been developed between the rate of substrate utilization and the rate of bacterial growth: The growth expression combined with the equation defining the yield relationship between bacterial growth and substrate removal:

$$\frac{dX}{dt} = -Y_m \frac{dS}{dt} \quad (2.2)$$

where Y_m = maximum yield coefficient, $mg \cdot mg^{-1}$

$\frac{dS}{dt}$ = substrate utilization rate, $mg \cdot L^{-1} \cdot d^{-1}$

Monod (1949) has related this bacteria growth to substrate utilization in the application of wastewater treatments. He observed that the growth rate dX/dt was not only a function of microorganism concentrations but also of some limiting substrate or nutrient concentration. It was discovered that in all continuous flow treatment processes in biological wastewater treatment, microorganisms are continuously cultivated but the overall rate of metabolism is controlled by the substrate concentration.

The Monod kinetics equation is given as:

$$\mu = \mu_m \frac{S}{(K_s + S)} \quad (2.3)$$

where μ_m = maximum specific growth rate, d^{-1}
 S = growth limiting substrate concentration, $mg \cdot L^{-1}$
 K_s = saturation constant, substrate concentration at one half the maximum growth rate, $mg \cdot L^{-1}$

The graphical representation of Equation (2.3) is illustrated in Figure 2.3

Figure 2.3. Monod's growth curve

Combining the bacterial growth rate into Monod kinetics equation, the rates of microbial growth and substrate utilization can be expressed as follows:

$$\frac{dX}{dt} = \mu_m \frac{SX}{K_s + S} \quad (2.4)$$

The expression of the yield can be combined with the Monod function in Equation 2.4 and the rate of substrate utilization (dS/dt) can be defined as:

$$\frac{dS}{dt} = -\frac{\mu_m SX}{Y_m (K_s + S)} \quad (2.5)$$

In bacterial systems used for wastewater treatment, the distribution of the cells ages is such that not all cells in the system are in logarithm growth phase. To account for the biomass losses, a decay coefficient, K_d (d^{-1}) is used in model describing the kinetics in wastewater. This coefficient incorporates a large number of mechanisms including endogenous metabolism (maintenance), death, predation and lysis. This loss of biomass is considered independent of growth rates. The microbial growth rate (dX/dt) can be modified to incorporate this decrease in the cell mass referred to as the endogenous decay:

$$\frac{dX}{dt} = (\mu - K_d)X \quad (2.6)$$

This endogenous decay is taken into consideration to obtain the net specific growth rate, μ' (d^{-1}) for the microorganisms in the wastewater. This expression is given as:

$$\mu' = \frac{\mu_m S}{K_s + S} - K_d \quad (2.7)$$

Under steady state conditions of an aerated tank, mass balance technique has been performed (Metcalf and Eddy, 2003). In biological wastewater treatment, if the HRT is too short, there will be progressive reduction in BOD removal as in sufficient time is available for adsorbed materials to stabilize. The HRT must be sufficiently long to allow the organic matter to be oxidized into simple end products while the remainder is synthesized into new cellular material. The general application of the kinetics of biological growth and substrate removal gives the effluent substrate concentrations as:

$$X = \frac{Y_m (S - S_e)}{(1 + K_d \tau)} \quad (2.8)$$

where S = substrate concentration in influent, $\text{mg}\cdot\text{L}^{-1}$
 S_e = substrate concentration in effluent, $\text{mg}\cdot\text{L}^{-1}$
 K_d = endogenous metabolism activities, d^{-1}
 τ = HRT, volumetric loading, d

The food/microorganisms (F/M) ratio affects the rate of metabolism of the microorganism. It controls the rate of biological oxidation as well as the volume of microbial biomass produced by maintaining microbial growth either in logarithm, declining or exponential growth phase (Gray, 1990). A system achieved equilibrium when the food substrate and the microorganisms consuming it are in balanced. With the biomass actively removing the organic fraction of the wastewater, it follows that the BOD loading should be related to the amount of activated sludge in the reactor. The sludge loading rate is usually within 0.2 to 0.5 and is defined as:

$$\frac{F}{M} = \frac{SQ}{VX} \quad (2.9)$$

where Q = influent flow rate, $\text{m}^3\cdot\text{d}^{-1}$
 V = volume of reactor, m^3

The F/M is ultimately controlled by the sludge age and can then be defined as:

$$\frac{1}{\theta} = Y_m \left(\frac{F}{M} \right) \frac{E}{100} - K_d \quad (2.10)$$

where θ = SRT or mean cell residence time, d
 E = process efficiency, %

The sludge ages for activated sludge plants treating municipal wastewater are typically in the range of 5 to 15 days, with F/M ratio ranging from 0.2 to 0.5 kgBOD·kgMLVSS⁻¹·d⁻¹. Equation (2.10) shows that at long sludge ages, the MLSS is higher. This reveals a potential advantage of MBR, which has the ability to operate at high SRT, high biomass concentrations (MLSS) and a low F/M ratio, thereby, reducing the sludge yield.

2.2 MEMBRANES

A definition of membrane can be “a material through which one type of substance can pass more readily than others, thus presenting the basis of a separation process”, by Prof George Solt, Former director of the School of Water Sciences, Cranfield (Judd and Jefferson, 2003). In simple terms, they are thin films of synthetic organic (polymeric) or inorganic (ceramic or metallic) materials, which can bring about a selective separation between a fluid and its component.

However, the definition of a "membrane" can be a bit fuzzy, and any definition requires some mention of the application or function. A functional classification of membranes includes such diverse categories as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO), electrodialysis and electrolysis (commonly gathered under the term "electrically driven" or ED), haemodialysis (HD), gas separation (GS), pervaporation (PV), ion exchange (IX), and controlled release (CR). Membranes can be biological or synthetic, and organic or inorganic. Membrane geometry is also diverse as well, but commonly used forms include hollow fibers, films, tubes, composites, and flat sheets configured as "plate and frame" or "spiral wound" cartridges. The microstructure in cross-section can be homogeneous, asymmetric, or composite.

The key interest in selecting and designing membrane separation systems is the inherent property of the membrane to separate components of the water to be treated. Although the membrane may act as a medium to extract pollutants from the wastewater, or to transfer gas to the wastewater, for most processes, the membrane acts to reject the pollutants, which may be suspended or dissolved. Physically filtering wastewater with various types of membranes can be very effective in creating recycled water for secondary purposes (Bhattacharyya *et al.*, 1978). Various membrane separation processes include MF, UF and RO are capable for the removal of different size materials resulting in permeate free from suspended solids and pathogenic microorganisms.

The principle objective in membrane manufacture is to produce a material of reasonable strength which can maintain a high desired permeate with a high degree of selectivity. A high selectivity is normally achieved using a membrane with small pores, which results inherently high hydraulic resistance. The permeability is directly proportional to density

of pores and inversely proportional to the thickness of membrane. Therefore, the optimum physical structure for any membrane material is based on a thin layer of material with narrow range of pore size and a high surface porosity. In this way, the membranes can remove the passage particles either larger or smaller than membrane pores effectively.

The range of available membrane materials is very diverse. They can vary widely in chemical composition and physical structure, but the most fundamentally important property is the mechanism by which separation is actually achieved. On this basis, membranes may be categorized as either dense or porous (Stephenson *et al.*, 2000). The former relies on the physiological interactions between the permeating components and the membrane material to separate the particles from water while the latter, which is normally used in membrane bioreactors (MBRs) to retain suspended solids materials, mainly biomass, achieves separation mechanically and thus are closer to conventional filtration processes. Examples of separation by dense membranes include reverse osmosis, electrodialysis and nanofiltration processes.

In general, most of the MBR applications were initiated with organic membranes, which are cheaper compared to their ceramic counterparts. Membrane manufacturing cost is substantially reduced for organic membranes due to their simplicity in production. Inorganic membranes are formed by the pressing and sintering of fine powders onto a pre-prepared porous support. This sophisticated forming process tends to be very costly, particularly if a membrane layer of even thickness and narrow size distribution is to be produced. Polymeric membranes, on the other hand, are easily produced by the stretch of partly crystalline sheets perpendicular to the orientation of crystallites (Stephenson *et al.*, 2000). However, in recent years, research has been focused on ceramic membranes due to their proposed longer service life and higher permeates flux than polymeric membranes. Full-scale applications of ceramic MBRs for industrial wastewater have been very recent. In France, an aerobic bioreactor coupled with ceramic UF membrane was used for treatment of cosmetics processing effluents at Lancome plant (Degremont, France). The high quality of treated water obtained enabled direct reuse on the same facility (Manem and Sanderson, 1996).

Membrane science began emerging as an independent technology only in the mid-1970s, and its engineering concepts still are being defined. Many developments that initially

evolved from government-sponsored fundamental studies are now successfully gaining the interest of the industries as membrane separation has emerged as a feasible technology.

2.2.1 Brief History of Membranes

The word “membrane” comes from Latin word, “membrana” that means a skin (Jones, 1987). In today’s context, the word has been used to describe a thin sheet or film of natural or synthetic material that acts as a selective boundary between two phases due to its semi permeable properties. Physically a membrane could be solid or liquid and function as a selective separation agent. Membrane separation occurs because of differences in size, shape, chemical properties, diffusivity coefficient, solubility or electrical charge of the substances to be separated. Micro-porous membranes control separation by size, shape and charge discrimination, whereas nonporous membranes depend on sorption and diffusion. The performance of the membrane is determined by the degree of separation of fluid mixtures and permeation rate, better known as permeate flux (Singh, 1998).

Membranes are one of the most common features of the biological world. All cells composing living things, including ours are surrounded with membrane. With the exception of some viruses, all living things depend in one way or another on membranes. They surround cells and separate cellular contents from the external environment. Membranes also form special spaces, or compartments, within the cytoplasm that separate various cellular processes. Without membranes, life as we know it would likely not exist.

Biological membranes (membrane cells) are very selective that transfer only particular species. Synthetic membrane history began in 1748 when Frenchman Abbé J.A. Nollet discovered osmosis and osmotic pressure, a pressure that develops in a solution separated from a solvent by a membrane permeable only to solvent. Nollet demonstrated semipermeability for the first time with a pig bladder which had let water through and not alcohol. It took more than 100 years later before Fick published his phenomenological law of diffusion, which we still use today as a first-order description of diffusion through membranes. He was also the first man to prepare and study artificial semi-permeable

membranes. These membranes were made from an ether-alcohol solution of cellulose called “collodion”. Many researches were done after this and many inventions were found using membranes including the likes of dialysis, different permeability of gases at rubber, osmotic pressure, and Donan’s ion equilibrium phenomena.

For the first time in 1950, Sartorius Werke GmbH, Germany manufactured industrial scale membranes, MF membranes. Before that, membranes were developed in small scale for laboratory applications (Lonsdale, *et al.*, 1982). However, the most fundamental breakthrough in membrane technology, which also started the golden age of membrane technology (1960-1980), came in late 1950s, when Loeb and Sourirajan invented the first asymmetric integrally skinned cellulose acetate RO membrane. This development simulated both commercial and academic interest, first in desalination by RO, and then in other membrane application and processes. During this period, significant progress was made in virtually every phase of membrane technology: applications, research tools, membrane formation processes, chemical and physical structures, configurations and packaging. Kesting and Fritzsche (1993) describe the significant development of this golden age in more details in their literature. Table 2.1 gives a chronological breakdown on some of the important historical development of the membrane technology before the Golden Age of membrane technology.

Nowadays membrane applications spread over various industries: metal industries (metal recovery, pollution control, air enriching for combustion), food and biotechnology industries (separation, purification, sterilization and byproduct recovery), leather and textile industries (sensible heat recovery, pollution control and chemicals recovery). Other industries that also use membrane technology are pulp and paper industries (replacing evaporation process, pollution control, fiber and chemicals recovery), and chemical process industries (organic material separation, gas separation, recovery and recycle chemicals). Medical sector including health-pharmaceutical-and medical industries (artificial organs, control release (pharmaceutical), blood fractionation, sterilization and water purification), and waste treatment (separation of salt or other minerals and deionization).

Table 2.1. Historical development of membranes

Year	Events
1748	Abbe Nollet – water diffuses from dilute to concentrated solution
1846	The first synthetic (or semisynthetic) polymer studied by Schoenbein & produced commercially in 1869.
1855	Fick employed cellulose nitrate membrane in his classic study <i>Ueber Diffusion</i> .
1866	Fick, Traube, artificial membranes (nitrocellulose)
1907	Bechhold, pore size control, "ultrafiltration"
1927	Sartorius Company, membranes available commercially
1945	German scientists, methods for bacterial culturing
1957	USPH, officially accepts membrane procedure
1958	Sourirajan, first success in desalinating water

Generally, there are several processes to synthesize membrane; some of them are sintering, stretching, track-etching, phase inversion, and coating. There are several ways to classify membranes. Based on their materials, membranes are classified as polymeric membrane, liquid membrane, solid (ceramics) membrane and ion exchange membrane. Based on their configuration, membranes are classified as flat (sheet) membrane, spiral wound, tubular, and emulsion. Based on what they do and how they perform, membranes are classified as fine filtration (MF, UF, NF, and RO), dialysis, ED, GS, carried-mediated transport, control release, membrane electrode, and PV.

2.2.2 Classifications of Membranes

Biological membranes, with the exception of cell membranes, are thin sheets of tissue that cover various organs of the body or plants. Of the hundreds of biological membranes, the mucous membrane is one of the more familiar. It lines the canals and cavities of the body, including the respiratory tract. The mucous membrane functions as a barrier to prevent toxic components from coming in contact with tissue. This property of selective passage is mimicked by synthetic membranes. This directory does not deal with biological membrane for the most part.

Synthetic membranes possess unique flux and selectivity properties, which allow them to be used for a wide variety of industrial and biomedical applications. Synthetic membranes can be classified by function, media, structure, morphology, and geometry. Media or materials may be an organic or inorganic polymer (cellulose acetate, polyamide, polyester), ceramic or metal. In this study of submerged MBR, an aerobic bioreactor coupled with ceramic MF membranes was used.

MF has two common forms: crossflow separation, and dead-end filtration. In crossflow, a fluid stream runs parallel to a membrane, which causes a pressure differential. Crossflow MF is often used as a prefiltration step, or as a process to separate fluid from a process stream.

In dead-end filtration, or perpendicular filtration as it is sometimes called, all of the fluid passes through the membrane, and all of the particles that cannot fit through the pores of the membrane are stopped. Dead-end MF is commonly used in stopping particles in either prefiltration or final filtration before a fluid is to be used.

MF can be defined as the separation of particles of one size from particles of another size in the range of approximately 0.01 μm through 20 μm . The fluid may be either a liquid or a gas. MF media are available in a wide variety of materials and methods of manufacture, and are rated either as "absolute" or "nominal" depending upon the percentage of capture of particles of the same size or larger than the retention rating of the media.

2.2.3 Membrane Processes

Membrane processes can be classified based on various driving forces, some use pressure difference (MF, UF, RO and piezodialysis), while others use other driving forces such as concentration difference (GS, PV, liquid membrane and dialysis), thermal (membrane distillation, thermo osmosis) and electric (ED).

The three principal advantages of membrane processes compared to other conventional separation processes are

1. Separation is achieved as a result of different rate of transfer between each substance in membrane and not a result of phase equilibrium, unlike distillation and therefore is more energetically efficient. Phase change may also affect the quality of materials and products. Therefore, membrane technology is suitable for the pharmaceutical, biochemical and food industries.
2. Under steady state condition, it can operate continuously with little or no accumulation taking place in the process and therefore eliminate the need for regeneration cycles, unlike absorptive separation processes. This also makes membrane technology a “clean technology”, in which no additive materials such as extractor and absorber to attain the separation, which may be potential pollutants.
3. Addition of chemicals which may later become pollutants is usually not required, unlike conventional clarification which generally relies on the addition of chemical coagulants and flocculants (Judd and Jefferson, 2003).

Other factors include simplicity and environmental friendliness. Designs of membrane module are very simple, compact and easy-to-use. In addition, not much auxiliary equipment is needed. There is a unique phenomenon in membrane where the scale of process and operating costs are related proportionally. This phenomenon may be caused by the modular-nature of membrane. This nature distinguishes membrane processes from other processes such as distillation, in which an increase in the process scale is followed by a decrease in cost until economical condition is reached. Not only in cost spent, but

also in operating condition. Adding several modules including its auxiliary to existing system can do scaling up membrane processes.

Apart from the advantages described above, membrane processes also do possess several disadvantages, such as flux optimization and selectivity, material sensitivity, fouling and dependability. However, there have been several studies conducted to overcome the disadvantages and drawbacks in membrane processes.

Flux and selectivity problems arise as an increase in flux is usually followed by a decrease in selectivity, while we aim at increasing both. Therefore membrane processes are suitable for very selective separation in which flux is not concerned such as that carried out in pharmaceutical industries.

The dependability problems arise as the characteristics of membrane differ from each other. It is due to the different characteristics of each membrane that a direct scale up of membrane processes is virtually impossible. Before a process is applied in an industrial scale, it is suggested to have a laboratory assessment of the membrane. In this way we may have better prediction on process performance.

Other major problems are material sensitivity and fouling. Polymeric membranes have limited stability (chemically, physically, and biologically), which restrict the conditions of membrane processes applied. Ceramic membranes, on the other hand, can overcome these constraints although at a higher cost (Manem and Sanderson, 1996; Cicek *et al.*, 1999b). Fouling causes a decline in performance of membrane processes, in which flux (performance) is very high initially but then decline drastically as materials of foulant accumulate on membrane surface. Solutions to the problem may lie in the hydrodynamic of the process and pretreatment processes.

2.2.4 Membrane Performance

Membrane resistance is the product of pore size, pore density, pore depth, the materials' wettability, and the hydrodynamic resistance of the device holding the membrane. The interaction forces between solute, solvent, and membrane material play an important role

as well. The final resistance also depends on the bulk fluid's viscosity. Lower viscosity means higher flow. Increasing temperature, which lowers viscosity, can increase production if the heat does not degrade biological or other sensitive molecules in the feed. The most critical parameter affecting the filtration membrane performance is the membrane pore size, which should have diameter smaller than the microorganisms. However, it was discovered that membrane with the same nominal sizes might provide different rejections. This phenomenon can be explained due to the availability of some openings in the membrane larger than the nominal pore size or imperfections of the membranes (Jacangelo *et al.*, 1989). The performance of a given membrane process is represented by rejection and specific permeate flux or permeability. The former is expressed as a function of the ratio of the respective concentrations of the target contaminant in the feed and the permeate product while the latter refers to the quantity of material passing through a unit area of membrane per unit time and pressure. Flux and rejection are interdependent (Waters and Fane, 1981) with the general expectation of enhancing the rejection by reducing the flux.

2.2.4.1 Rejection

Rejection is the removal of particles, including biological and non-biological colloids and macromolecules in the bioreactor either by sieving or adsorption. In sieve retention, porous membrane acts as a barrier for particle penetration. Particle size larger than the membrane pores are accumulated on the membrane surface forming a cake layer that grows in thickness as the filtration progresses. Because low molecular weight substances or sub-micron colloids particles could be rejected and biodegraded by the dynamic membrane composed of living microorganisms (Yamagiwa *et al.*, 1995), the dynamic membrane would provide small molecules with fewer chances of interaction with the membranes, thereby alleviating the rate of membrane fouling.

The second mechanism involves the entry and capture of the particles into the membrane matrix. At this stage, smaller particles may be absorbed inside the membranes pores when arriving at the membrane without any interruption and therefore reduces the pore density of the membrane. This in turn deteriorates the permeability of membrane. Generally, the particles can be removed by both mechanisms onto the cake layer that has been formed over the membrane surface. On the whole, the rejection of particles depends on the

membrane loading and is lower at higher loadings. It also depends on particle size, membrane pore size and membrane thickness (Ho and Sirkar, 1992). In conventional perm-selective MBR, membrane rejection of suspended materials and oxygen demand is normally very high. Membrane rejection is quantitatively defined as:

$$R = \frac{(1 - C_p)}{C} \times 100 \quad (2.11)$$

where C_p = permeate concentration, $\text{mg}\cdot\text{L}^{-1}$
 C = concentration of the matter under consideration with respect to both
suspended and oxygen demanding materials, $\text{mg}\cdot\text{L}^{-1}$

2.2.4.2 Permeate Flux

Flow rate through the membranes depends on a number of complex inter related parameters including directly on driving force, membrane permeability, membrane area and hydrodynamic conditions (e.g. shear stress) at the filtration region. Permeate flux is the flowrate divided by the area of the membranes and is normally expressed in standard units of $\text{m}\cdot\text{s}^{-1}$ or also $\text{L}\cdot\text{m}^{-2}\cdot\text{hr}^{-1}$.

Membrane permeability is closely dictated by pore size, but depends on the feed being filtered. It is critically affected by the fouling phenomenon on the internal and external structures of the membrane. This increases the overall resistance to filtration (Belford *et al.*, 1994) and commensurate increases the energy demand. The flux is determined by both the driving force (a transmembrane pressure gradient as with filtration) and the membrane permeability and the interfacial region adjacent to it. The resistance of the membrane is fixed unless it becomes partly clogged (or fouled internally) by components in the feed water. The interfacial region resistances is, on the other hand, a function of both feed water, composition and permeate flux since for a conventional pressure driven process, the materials rejected by the membranes tend to accumulate within the interfacial region at a rate dependent on the flux. The process operational efficiency is therefore determined by the extent to which the forces opposing the driving predominate

(Stephenson *et al.*, 2000). In filtration processes, the flux decline rate generally decreases with time but increases with increasing operating pressure.

In most membrane filtration processes, there consist of three streams: feed, retentate and permeate stream. The retentate stream is unpermeated product. The two different operating conditions of MBRs are illustrated in Figure 2.4.

Figure 2.4. (a) dead end filtration (b) crossflow filtration

The first is dead-end or full flow operation occurs when there is an absence of a retentate stream. This is normally restricted to low-solids water, such as UF for apyrogenic water production or cyclic operation with frequent backwashing such as Merncor MF process. In this operation, the suspended solids in the feed are assumed to end up on the membrane surface forming a filter cake, which normally offers a higher hydraulic resistance than membranes itself.

The alternative to dead end operation is cross flow or tangential flow operation, in which the feed water flows parallel to the membrane surface at crossflow velocity. Crossflow velocity is the speed with which fluid flows past a given point on the membrane surface; it is higher at the inlet than at the outlet, since some material is being removed continuously as it passes the membrane surface. Higher crossflow velocities typically result in a higher flux, since they relate directly to increased removal of accumulated materials from the membrane interfacial region (Stephenson *et al.*, 2000). Crossflow operation helps reduce concentration polarization, and is a technique most commonly associated with ultrafiltration and microfiltration. It is also usually preferred in MBR

systems since the feed flow velocity aids in removal of the fouling layer unlike dead end filtration where the particles retained on the membrane has to be removed by other cleaning methods (Engelhardt *et al.*, 1998).

2.2.4.3 Membrane Fouling

The effectiveness of a membrane filtration process can be limited by fouling, which results in loss of flux and altered rejection. Fouling can occur from pore blocking and plugging, or from the formation of external cakes. Usually, blocked pores precede cake formation on the exterior of the membrane.

Fouling resistance builds as deposits chemically bind to the membrane. Fouling is distinct from polarization, in which the interfering layer is held against the membrane by hydrodynamic forces. If increasing the tangential flow increases flux, the effect is polarization. If increasing the flow decreases the flux in a non-concentrating run, the effect is due to fouling. The phenomenon can occur through a number of physiochemical and biological mechanisms, and is exacerbated by concentration polarization as this increases the concentration of foulants in the vicinity of the membrane (Stephenson *et al.*, 2000). Additionally, the fouling is in close association with solute rejection as it could be originated from the adsorption of organic species and adhesion of microbial cells on the membrane surfaces.

Concentration polarization (CP) is the term given to describe the tendency of the solute to accumulate at the membrane/solution surface within a concentration boundary layer or liquid film (Stephenson *et al.*, 2000). Rejected materials thus build up in the region adjacent to membrane, increasing their concentration over this bulk liquid region. The thickness of the boundary layer is determined entirely by the system hydrodynamics, especially decreasing in thickness when turbulence is promoted. Thus, it is very much desirable to suppress CP by promoting turbulence and/or operating at a flux below that at which CP starts to be significant.

Although all membranes are subject to CP, the degree of impact is varying for the different membrane processes. In UF processes, precipitates of sparingly soluble organics at the membrane/surface interface form a gel layer. This gel or dynamic layer often has a

lower permeability and permselectivity often greater than membrane itself. This layer will eventually determine the process performance with respect to the hydraulics and product water quality. In MF processes the effect of CP is quite minimal.

In general, physiochemical fouling (fouling unrelated to biological growth) is attributed to the presence of proteins and colloids or particulate materials in the feed. Palacek and Zydney (1994) have discovered that the former can cause excessive fouling in MF membranes particularly hydrophobic polymers such as polypropylene with irreversible deposition onto and penetration into the bulk membrane material. The binding of protein and bacteria to hydrophobic polymeric surfaces has been extensively studied and deleterious effect of such hydrophobicity on permeability is evident. Several studies have shown that hydrophilic membranes tend to suffer less flux decline than hydrophobic membrane. Similarly, Pouet and Grasmick (1995) have identified the supracolloidal fraction with particle size above 1 μm to be responsible for the fouling of a side stream ceramic MF membrane of sub-micron pore size.

Biofouling caused by biofilm formation is often unavoidable in membrane operation. Biofilm formation results from a rapid formation of an organic layer and the onset of one is normally starts in the first few minutes of operation and will be followed by microbial adhesion and further entrapment of solid matter which co-deposits with the microorganisms. This film can be existing organic matter from the feedwater such as natural organic matter (NOM) or microbial products, namely extracellular polymeric substances (EPS). The overall thickness of biofilm thickness will depend on the hydrodynamics. Increasing turbulence will decrease the thickness of the biofilm layer (Ridgeway, 1988)

Membrane fouling results in a flux decline and reduce the effectiveness filtration area under a constant pressure pump, while in a constant flow rate filtration, it will cause an increase in pressure drop across the membrane (Bicknel *et al.*, 1985). In addition to a flux decline, fouling reduces overall plant efficiency, shortens membrane useful life and increases cleaning frequency. Recent studies have quantified the fouling caused by each fractions of the sludge (suspended solids, colloids and solutes) and shown that colloids are of prime importance in the process of MF (Wisniewski and Gramick, 1998). In MF

systems, membrane fouling takes place with deposition being the most deleterious to performance with regards to flux decline.

2.2.4.4 Fouling Amelioration

At some point in the filtration process, permeate flux decline may reach a point where there is no longer economical to continue filtration, necessitating membrane cleaning. Various techniques have been explored to suppress membrane fouling and improve the permeate flux.

The first mechanism involves the operation of MBRs under turbulent aeration conditions (Wisniewski and Gramick, 1998). This turbulence introduced within the MBR promotes scouring of the membrane surface to limit the thickness of the hydrodynamic boundary layer. In submerged MBRs, reduction of the flux can be proposed to reduce the fouling phenomenon. This has brought forward the emergence of critical flux concept. This hypothesis is 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. Gander *et al.* (2000) has discovered that the rate of fouling was greatly reduced by selecting the correct initial flux or TMP. Moreover, Defrance and Jaffrin (1999) has pointed out that the sub-critical operation of the MBR process leads to non-fouling, low energy consumption and then substantial reduction of cleaning requirements and operational costs.

Studies on membranes operated on protein solutions has suggested that improved performance in filtration is obtained using hydrophilic in place of hydrophobic membrane. Fane *et al.* (1981) used hydrophilic and hydrophobic PVDF membranes, operated at 1 bar, for filtrating bacteria suspensions and reported results for the flux recovery of approximately 50% for a hydrophobic membrane compared to almost 100% recovery for hydrophilic membrane.

Membrane regeneration, which involves chemical washing, is the last mechanism that is commonly used. The chemicals to be used vary accordingly to the membrane material. All these cleaning techniques incur additional cost, either ostensibly operational or capital. Usually, side stream systems require more frequent and rather more aggressive cleaning

than submerged MBRs as the flux and the fouling rate is much higher (Gander *et al.*, 2000). This inevitably, results in an increased cost of operating side stream systems, thus submerged MBR is preferred and is gaining popularity in wastewater treatment (Ueda *et al.*, 1996; Dijk and Roncken, 1997; Gander *et al.*, 2000).

2.3 MEMBRANE BIOREACTOR

MBR is an example of a hybrid process, combining the activated sludge aerobic biotreatment process and membrane filtration (Stephenson *et al.*, 2000). It has been developed markedly in recent decades and possibly the most successful implemented membrane process for wastewater treatment, especially following the improvement of UF and MF membranes. In such applications, membranes are used to separate the activated sludge from the treated water and therefore replacing the secondary settling tank in conventional activated sludge process. This hybrid process has also been known under many different names such as a membrane bioreactor (Trouve *et al.*, 1994), a membrane separation bioreactor (Brindle and Stephenson, 1996) and a membrane separation activated sludge process (Aya, 1994).

2.3.1 Development of Membrane Bioreactor for Wastewater Treatment

The pioneer research into combining membranes with biological processes for wastewater treatment began over 30 years and membrane bioreactors have been commercially tried for past 20 years. The earliest reports of MBRs were presented by Smith *et al.* in 1969 (Brindle and Stephenson, 1996) and by Hardt *et al.* (1970). Smith *et al.* (1969) reported the combination of biological treatment with ultrafiltration process in activated sludge. The combined process is free from limitations imposed by the usage of the settling tank in conventional treatment plant and a much improved effluent quality can be achieved. On the other hand, Hardt *et al.* (1970) used a 10 litres aerobic bioreactor to treat a synthetic sewage with a dead end ultrafiltration membrane for biomass separation. It was discovered that the mixed liquor suspended solids concentration was high compared to conventional aerobic systems at 23 to 3000 mg·L⁻¹. COD removal efficiency for permeate was at 98% with membrane flux of 7.5 L·m⁻²·h⁻¹.

Although their original ideas were to combine a membrane with an aerobic bioreactor, membranes can be coupled with both aerobic and anaerobic bioreactors (Stephenson 1997). Anaerobic MBRs have been applied mainly for treating concentrated industrial wastewater (Ross and Strohwald, 1994; Brindle and Stephenson, 1996), such as maize

processing effluent (Ross *et al.*, 1992), brewery effluent (Strohwald and Ross, 1992), alcohol-distillery wastewater (Choo and Lee, 1996) and dairy effluents (Li *et al.*, 1985).

Meanwhile aerobic MBRs have been applied to both municipal and industrial wastewater (Brindle and Stephenson, 1996). However, applications in municipal and domestic wastewater were more common. Besides the above-mentioned MBR, there is yet another category of MBRs named “membrane aeration bioreactor”, in which membranes provide bubbleless aeration for achieving high oxygen mass transfer (Brindle and Stephenson, 1996; Brindle *et al.*, 1998, 1999)

In 1960s, Dorr-Oliver Inc. developed the Membrane Sewage Treatment (MST) process (Bemberis *et al.*, 1971). In this system, wastewater entered a suspended growth bioreactor where flow was continuously withdrawn via a rotating drum screen to an ultrafiltration membrane module. The membrane configuration was plate and frame, operating air inlet and outlet pressures of $345 \text{ kN}\cdot\text{m}^{-2}$ and $172 \text{ kN}\cdot\text{m}^{-2}$ respectively, achieving a flux rate of $16.9 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$.

The membrane technology was only introduced into the Japanese market through a licence agreement between Dorr-Oliver and Sanki Engineering Co. Ltd. in 1970s. However, by 1993, 39 of these external membrane bioreactor systems have been reported for use in sanitary and industrial application (Aya, 1994). Today, there has been a widespread application of MBR in Japan where the focus is in domestic wastewater and reuse.

Around the same time, Thetford systems, now part of Zenon Environment also launched their version of an external membrane separation system. The “Cycle-LET” process for aerobic treatment of domestic wastewater. In the late 1980s to early 1990s, Zenon Environmental continued the early development of Dorr-Oliver in developing the systems for industrial wastewater treatment, resulting in two successful patent applications (Tonelli and Behmann 1996).

In 1989, the Japanese government, in view of the great marked potential of MBR, joined ventures with several companies to invest in the development of small footprint, high product quality process that would be suitable for water recycling. This was part

demonstrated through the Aqua Renaissance Programme 1990 (Kimura, 1991). It was at that time, Kubota, one of the participating companies developed a flat plate submerged MBR (Churchouse and Wildgoose, 1999).

Today, over 500 commercial membrane bioreactors have been commissioned for the treatment of industrial and municipal wastewaters, as well as in building treatment and reuse of grey water, with many more proposed or currently under construction. Full scale commercial aerobic MBR processes first appeared in North America in the late 1970s and then in Japan in the early 1980s. The introduction of aerobic MBRs into Europe did not occur until the mid-1990s. Commercial MBRs have proliferated in Japan, which has approximately 66% of the world's processes with the rest predominantly in North America and Europe. Over 98% of these systems coupled the membrane separation process to an aerobic biological rather than to an anaerobic bioreactor. The aerobic MBR process has successfully treated effluents from a range of industrial wastewater, including paper and pulp, pharmaceuticals, metal fabrication rendering and chemical manufacture.

2.3.2 Classification of Membrane Bioreactors

Membrane filtration unit coupled with biological reactors for the treatment of wastewaters has led to the development of three generic membrane bioreactors. The first type when coupled to biological processes is used for separation and retention of solids. The second type, which is, refers to as an oxygen mass transfer membrane bioreactor is used in mass transfer of gases. Lastly, the extractive membrane bioreactor (EMBR) is used for controlled transfer of nutrients into a bioreactor. The EMBR enables the transfer of degradable organic pollutants from hostile industrial wastewater, via a dense silicone membrane, to a nutrient medium for subsequent biodegradation (Livingston, 1994). To date, the solid-liquid separation MBR has drawn great attention in research due to its enormous market potential with the latter two types yet to be commercially exploited.

In membrane processes, there are three possible streams; a feed, a retentate and a permeate stream. The retentate stream is unpermeated product. If there is no retentate stream then operation is termed dead end or full flow. Such operation is normally restricted to low solids loading and/or membranes of limited permeability, it is not

desirable to try and convert all of the feed to permeate product in a single passage through a module. In such cases, crossflow operation is employed whereby some of the feedwater is collected as a retentate stream. This expedites the removal of accumulated materials from the membrane surface; provided by the scouring action of the retentate flowing over it.

In a crossflow MBR, the membrane modules are allocated outside the bioreactor and the mixed liquor is driven into the membrane modules by a recirculation pump. The circulation pump generates high cross flow velocity where the permeate is discharged and the retentate is returned into the bioreactor. The biomass is pumped at high speed so as to slow down the deposition of suspended solids at the membrane surface and reduce the frequency of membrane cleaning. Though this type of membrane bioreactor is stable and easy to use, it requires significant energy due to the use of recirculation pump, which leads to higher power consumption than the submerged membrane bioreactor. In addition, the intensive recirculation into the membrane units modified the composition and characteristics of the biological suspension and size distribution of the particles present. Seyfried and Brockman (1995) has reported that high shear stresses generated in the membrane units and in the recirculation pumps can contribute to the destruction of bioflocs, which has been linked in recent studies to the loss of biological activity.

Figure 2.5. Types of MBR configuration (a) side stream (b) submerged

Biomass separation membrane bioreactors are the amalgamation of a suspended growth reactor membrane filtration device into a single unit process. It can exist in two different

configurations, one with the low pressure membrane modules replacing the clarifiers downstream the bioreactor (in series), and the second with the membrane submerged within the bioreactor as illustrated in Figure 2.5.

The submerged MBR has been recently developed out of a need to reduce operating costs. In these new configurations, the membrane modules are immersed directly in the reactor containing the biological sludge and the treated permeate is extracted. The driving force for filtration is achieved by pressurizing the bioreactor or creating a suction on the permeate side. The membrane surfaces induce a moderate shear stress, which generates the back transport of filtered colloids particles from the membrane surfaces (Shimizu, *et al.*, 1996). This effect promotes scouring of the membrane surfaces and suppresses fouling layer formation and flux decline. The submerged MBR is superior to a cross flow MBR in regard to power consumption since the suction pressure in the former is generally lower than that in cross flow due to the absence of recirculating pumps. Therefore, the submerged MBR has the potential to be applied effectively to small wastewater treatment plants that need low cost treatment systems (Ueda *et al.*, 1997).

2.3.3 Advantages of Membrane Bioreactor Process

The water quality improvement profession has witnessed some exciting advancements recently in the development of new and innovative technologies to treat wastewater. One notable example is the use of MBR as a modification of the activated sludge process. Since early reports in 1969, MBR's are increasingly being used in the municipal and industrial wastewater sectors due to their ability to achieve exceptionally high effluent quality. Given the increased focus on effluent discharge requirements and the emergence of new membrane suppliers competing for market share, the use of membrane technology in municipal and industrial wastewater applications is likely to increase. Other advantages of MBR over conventional activated sludge processes will be discussed below.

One of the most striking features of the MBR system is the absence of sedimentation tank. Instead, liquid and solid separations are accomplished by MF or UF membranes. This means that MBRs could almost completely remove substances that are larger than the pore size, such as SS and bacteria. In addition, several reports claimed that a cake/gel

layer deposited upon the membrane partly removes substances that are even smaller than the pore size (dynamic membrane layer), such as macro-molecular dissolved organic matter (Yamamoto *et al.*, 1989) and viruses. . From an operator's perspective, the elimination of the clarifier and all the potential problems (e.g. sludge bulking) associated with it is perhaps the most appealing aspect of the technology. Indeed, a significant number of effluent quality problems result from issues with clarifier settling. Removing these problems represents a real potential for advancement in the way wastewater treatment plants operate. The footprint of the plant would also be substantially reduced (Stephenson *et al.*, 2000).

MBR is readily adaptable to retrofit applications without major modifications of the existing plant due to the modular design of the membranes, which also allow for a phased approach as membrane modules can be added to accommodate increases in influent flows. Since system sizing is based almost exclusively on hydraulic factors, utilization of existing tankage makes MBR cost competitive with other technologies. High MLSS concentrations also enable the use of smaller tank structures thereby increasing organic capacity in retrofit applications (Huang *et al.*, 2001).

Many studies have reported high and stable removal of organic substances with an MBR (Yamamoto *et al.*, 1989; Suwa *et al.*, 1989; Chiemchaisri *et al.*, 1992; Trouve *et al.*, 1994; Côté *et al.*, 1997). COD removal rates greater than 90% have been commonly observed. This was attributed to the high efficiency of removal by the activated sludge and complete rejection of SS

As for nitrogen and phosphorous, although MF and UF membranes cannot remove these nutrients by themselves, MBR can remove these nutrients through manipulations of its biological process.

One example would be that nitrification tends to deteriorate at low temperatures but by intensifying the aeration, it could be sustained. (Chiemchaisri and Yamamoto, 1993b). Another example, denitrification would not take place when dissolved oxygen (DO) is high in the reactor. Therefore, an anoxic condition can be provided in the reactor by intermittent aeration which provided a low DO and mixing effect to enhance denitrification (Yamamoto *et al.*, 1989; Chiemchaisri *et al.*, 1992; Suwa *et al.*, 1992;

Ueda *et al.*, 1996; Nagaoka, 1999; Yeom *et al.*, 1999). Denitrification also needs a sufficient source of carbon and augmentation of carbon sources is an effective option (Suwa *et al.*, 1992; Ueda *et al.*, 1996). Suwa *et al.* (1989) reported that, in an MBR, simultaneous nitrification and denitrification occurred under a high DO concentration possibly because, at a very high MLSS concentration, micro anoxic/anaerobic zones formed within flocs thereby stimulating denitrifying bacteria.

Phosphorous removal efficiency would be affected by the amount of excess wasted and the duration of a non-aeration period, as phosphorous uptake by sludge was the only major route to remove phosphorous from a liquid phase (Ueda *et al.*, 1996; Côté *et al.*, 1997; Seo *et al.*, 1999). Cicek *et al.* (1999a) found that excess load of phosphorous could reduce a removal efficiency of organic matters and concluded that phosphorous was an important factor in the operation of an MBR.

An additional benefit of MBR is the reduced biosolids production through high mixed liquor concentrations and long sludge retention time or SRT. MBR enable complete sludge retention within the bioreactor, because activated sludge shows minimal leakage from an MBR. This means that sludge retention time (SRT) can be manipulated independently of the HRT (Trouve *et al.*, 1994). Therefore, SRT can be kept long or even infinite. This would translate to low or even zero sludge discharge.

Another advantage of the long SRT is that microorganisms with relatively slow growth rates, such as nitrifying bacteria, are easily retained in the MBR (Chiemchaisri and Yamamoto, 1993b). This is especially beneficial for nitrification. Moreover, MBR can overcome bulking, which often caused serious problems in the operations of conventional activated sludge process, as sludge sedimentation is not required.

MBR can be operated at very high concentrations of MLSS than conventional activated sludge process. Due to the long SRT, MLSS of up to 40 g/L can be achieved by certain MBR systems (Stephenson *et al.*, 2000). The high concentration of MLSS promotes the treatment of high COD wastewater such as those from industrial source. Moreover, the high MLSS removes substrates faster (Shim *et al.*, 2002; Hong *et al.*, 2002), thereby reducing HRT. As a consequence, MBR can be more compact than conventional processes.

From the advantages listed above, the MBR can be summarized as a system having a high concentration of MLSS, a long or infinite SRT and a low F/M ratio. Under such conditions, the endogenous respiration rate of activated sludge is often competitive to its substrate assimilation rate. Thus excess sludge production is minimized in MBRs (Chaize and Huyard, 1991; Muller *et al.*, 1995; Rosenburger *et al.*, 2002; Sun *et al.*, 2003). Ghyyoot and Verstaete (2000) reported that an MBR yielded a 20 to 30 % lower sludge production than a conventional activated sludge under similar conditions of SRT and organic loading rate.

Côté *et al.* (1997) reported that sludge production in a pilot scale MBR was 0.25 kgSS/kgCOD.d, which was about 50% lower than a conventional activated sludge process. Some studies also reported that MBR can be operated without excess sludge wasting (Yamamoto *et al.*, 1989; Muller *et al.*, 1995; Benitez *et al.*, 1995). Rosenburger *et al.* (1999a) reported that zero net sludge production was achievable at an F/M ratio of 0.07 d^{-1} for the municipal wastewater treatment.

The unique operational characteristics of an MBR could affect the properties of activated sludge within the MBR. Zhang *et al.* (1997) investigated floc-sized distributions of MBR sludge using particle sedimentation technique. They found out that the floc size of MBR sludge was mostly less than $30\mu\text{m}$, which was substantially smaller than that of conventional activated sludge. Rosenburger *et al.* (1999b) carried out direct microscopic observation of MBR sludge and revealed that it contained a high number of suspended cells and filamentous bacteria but a few protozoa. However further studies would be necessary to understand the characteristics of MBR sludge.

2.3.4 Drawbacks of Membrane Bioreactor Process

Despite the many advantages of MBR, the cost of MBR has so far inhibited their widespread inauguration. One of the major costs would be the membrane modules in the MBR system. Owen *et al.* (1995) reported that the most significant factors influencing the overall cost were the membrane costs, membrane replacement frequency and power requirements and that widespread uses of MBR will depend on the availability of cheaper membranes. Davies *et al.* (1998) estimated that membrane modules accounted for 85% of

the capital cost and membrane replacement cost for 40% to 75% of the running cost of the MBR.

As discussed, the power consumption of recirculating pumps could lead to relatively high requirements for electrical power within an external MBR (Chaize and Huyard, 1991). Therefore a submerged MBR which does not necessitate recirculation pumps would reduce external MBR requires 3 to 5 kWh of electricity per 1 m³ of treated water, which is about ten times that of a conventional process (Aya, 1994; Côté and Thompson, 1999). In contrast, Côté and Thompson (1999) reported that the energy consumption of a Zenon submerged MBR (hollow fibre membranes) was between 0.3 to 0.6 kWh/m³. Similarly Ueda *et al.* (1996, 1999) found that the power consumption of a submerged MBR was reduced to 2.0 (hollow fibre membranes) to 2.4 (flat membranes) kWh/m³.

One of the most significant problems for MBR is the fouling of the membranes. Membrane fouling either increases filtration pressure at constant flux operation or reduce membrane flux at constant pressure operation. Backflushing or membrane washing would alleviate this problem. Membrane cleaning is accomplished in a number of ways. During normal operation, some systems rely on the continuous scouring action of the aeration diffusers while others use a combination of air scouring and periodic backflushing (or backpulsing) from the permeate pumps. Some also include a provision for in-place cleaning with a bleach solution. Eventually, however, membranes must be removed from the process for a more thorough cleaning. This would include mechanical and/or chemical washing of the membranes. However, the search for optimum operating procedures for minimizing membrane fouling and effective ways of membrane washing still has been an important ongoing research objective.

Activated sludge, which is to be separated by membrane, is a complicated mixture of suspended and dissolved solids. Therefore several substances that caused membrane fouling have been identified and include (1) attached biomass (2) inorganic precipitation (Choo and Lee, 1996) and (3) macromolecular organic substances such as polysaccharides, proteins (Judd and Jefferson, 2003), glycoproteins (Fukagawa *et al.*, 1992) and bacterial extra-cellular polymers (Liu *et al.*, 1993; 1995; Nagaoka *et al.*, 1996).

Membrane fouling is affected by several operating conditions, which consist of physical and biological parameters within an MBR. Physical parameters include (1) flux and (2) crossflow velocity. Recent studies have claimed that there exist a “critical flux” below which there is no fouling by colloidal particles (e.g. Howell, 1995); Defrance and Jaffrin, 1999). Vigneswaran *et al.* (1999) constructed a force balance model, which took into account several forces acting upon a particle approaching a membrane surface and predicted a practical critical flux. Li *et al.* (1998) demonstrated that a critical flux could be deduced from a direct microscopic observation of particle deposition on membrane. The concept of critical flux is becoming increasingly important in designing an MBR plant. A number of experiments have been conducted for determining a practical crossflow in an external MBR, as it affects power consumption of a recirculating pump (Baker *et al.*, 1985; Riesmeier and Kroner, 1987; Magara and Itoh, 1991; Nishimura *et al.*, 1992; Tardieu *et al.*, 1998). On the other hand, a submerged MBR uses rising bubbles for generating a crossflow. Therefore aeration intensity in a submerged MBR could affect membrane fouling (Yamamoto *et al.*, 1994; Shimizu *et al.*, 1996; Ueda *et al.*, 1997).

Meanwhile biological parameters affecting membrane fouling include (1) MLSS concentration (e.g. Magara and Itoh, 1991) and (2) sludge viscosity (Nagaoka *et al.*, 1996; Ueda *et al.*, 1996). Rosenburger *et al.* (1999a) reported that sludge viscosity in an MBR was a function of shear stress, a MLSS concentration and structure and composition of activated sludge biomass.

Despite previous efforts for reducing membrane fouling within MBR, it might be impossible to totally eliminate it over a long term operation. Therefore effective means of washing membranes must be developed for a successful operation of an MBR. The most effective and convenient way of reducing membrane fouling may be by intermittent suction of treated water, involving a periodic cessation of transmembrane flow (Yamamoto *et al.*, 1989; Benitez *et al.*, 1995; Choo and Lee, 1996; Ueda *et al.*, 1997). It was assumed that the cake layer deposited on membrane might be depressurized and partially detached during a cessation of suction.

Membrane fouling was also removed effectively by (1) jet aeration inside a bioreactor (Chiemchaisri *et al.*, 1992; 1993a) and (2) periodical backflushing by air (Scott and Smith, 1997; Visvanathan *et al.*, 1997) or by permeate water (Pankhania *et al.*, 1994; Yamamoto

et al., 1994; Côté *et al.*, 1998). Such on-site washing of membranes needs less time because it does not displace the membranes out of the bioreactor.

As membrane fouling proceeds, however, chemical washing of membranes is often needed to recover the membrane flux. The chemicals that have been used for membrane washing include sodium hypochlorite (Muller *et al.*, 1995; Visvanathan *et al.*, 1997; Churchouse and Wildgoose, 1999; Ueda and Hata, 1999), hydrogen chloride (Yamamoto *et al.*, 1994), sodium hydroxide (Judd and Jefferson, 2003) and surfactant (Ueda *et al.*, 1996). The duration of chemical treatment and the temperature of the chemical solution, as well as the chemicals used, were important factors for successful membrane washing.

CHAPTER 3 MATERIALS AND METHODOLOGIES

3.1 EXPERIMENTAL DESIGN

The research study was divided into three phases. The first phase was the cultivation of activated sludge. The second phase was the setting-up of the laboratory scale MBR. The third and final phase was a 300 days experimental run and collection of necessary results to fulfill the main objective of this research project.

3.1.1 Experimental Setup and Materials for Cultivation of Activated Sludge

The activated sludge used in the project was acquired from the Jurong Water Reclamation Plant. The biomass was then cultivated in a 4-litre cylindrical tank using high strength synthetic wastewater, which has a COD value of 2000 mg·L⁻¹. The composition of the synthetic wastewater is given in Table 3.1.

Table 3.1. Composition of synthetic wastewater

Nutrient components	Concentration (mg·L ⁻¹)
Glucose	1400
Peptone	400
Beef Extract	250
Ammonia Chloride (NH ₄ Cl)	200
Potassium Phosphate (K ₂ HPO ₂)	45
Calcium Chloride (CaCl ₂ ·2H ₂ O)	30
Magnesium Sulphate (MgSO ₄ ·7H ₂ O)	25
Iron (II) Sulphate (FeSO ₄ ·7H ₂ O)	20

The cultivation was done by feeding the biomass in the reactor once per day. During feeding, the aeration was stopped for half an hour to allow the biomass to settle. The supernatant was then discharged and the reactor was topped up to its initial volume with fresh synthetic wastewater.

The cultivation period lasted for two weeks and the synthetic wastewater was subsequently replaced by industrial wastewater from Wyeth Pharmaceutical. The change from synthetic wastewater to industrial wastewater was done by increasing the percentage of industrial wastewater gradually. At first, industrial wastewater was added to the synthetic wastewater at 25% concentration (e.g. 250 mL of industrial wastewater was added to 750 mL of synthetic wastewater). The mixture was then fed to the biomass. The industrial wastewater was increased by 250mL every week. Therefore, by the end of 4 weeks, the biomass was fed on 100% industrial wastewater.

Throughout the cultivation period, the aeration in the reactor was monitored and dissolved oxygen (DO) was maintained at above $4.0 \text{ mg}\cdot\text{L}^{-1}$ to maintain aerobic conditions while temperature was kept at room temperature of about 25°C . The pH in the cultivation reactor was found to be near to neutral. Therefore, no additional chemicals were needed to adjust the pH. The set-up for the cultivation reactor is shown in Figure 3.1. The acclimated sludge was later used for the laboratory scale experiments.

Figure 3.1. Schematic diagram of the cultivation reactor

3.1.2 Laboratory Scale Experimental Setup

The schematic illustration shown in Figure 3.2 is the laboratory scale experimental setup of a submerged membrane bioreactor (MBR) system. This system consisted of an activated sludge bioreactor having submerged membrane modules.

Figure 3.2. Schematic setup for laboratory scale submerged MBR

The bioreactor was separated into 3 sections by baffles. The 3 sections were named the 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 additional scouring of membrane surfaces to reduce fouling layer formation. 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 (Heidolph) was used to provide the mixing. All aerations were supplied by compressed air from an air blower (GAST 1/3 HP)

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 from McMillan Co.

An ultrasonic level sensor (FLOWLINE®) 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 (Masterflex peristaltic pump) to start and wastewater will be fed into the system.

From the schematic diagram, the wastewater will be 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-tank by means of a recirculation pump from DOSEURO. The HRT of each compartment will make up the total HRT. DO and pH were measured online in the system using DO and pH probes from Mettler Toledo.

A suction pump (Masterflex peristaltic pump) was used to obtain the membrane filtered permeate. The HRT of the system was controlled by the permeate flux. A backwash pump (Masterflex peristaltic pump) was also provided for the backwashing phase of the membrane module. The flowrates were measured using digital flowmeters (McMillan Co.) with signal feedback to the PLC. Pressure in the membrane was measured using a digital pressure switch with signal feedback from SMC®. Permeate collected from the system will be stored in an acrylic permeate tank beside the reactor.

The ceramic membranes used in the laboratory scale experiments were of MF type and have an effective pore size of 0.9 μm . 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. Figure 3.3 shows a picture taken from the operational laboratory scale submerged MBR in the laboratory.

Figure 3.3. Laboratory scale submerged MBR

3.2 EXPERIMENTAL PROCEDURE

In the experimental run, the membrane permeate flux was fixed at $26 \text{ Lm}^{-2}\cdot\text{hr}^{-1}$ to obtain a HRT of 8 hours. The characteristics of the high strength industrial wastewater fed to the reactor were as in Table 3.2. As the COD of the industrial wastewater was at a high strength of $1000 \text{ mg}\cdot\text{L}^{-1}$, the volumetric loading rate expressed in COD can then be calculated to be at a value of $3 \text{ kgCOD}\cdot\text{m}^{-3}\cdot\text{d}^{-1}$. Total organic carbon (TOC) and dissolved organic carbon (DOC) of the industrial wastewater were also determined to be $334 \text{ mg}\cdot\text{L}^{-1}$ and $209 \text{ mg}\cdot\text{L}^{-1}$, respectively. Sludge from the bioreactor was only discharged for analytical purposes twice a week and then once a week subsequently after stable state operation was achieved. Sludge from non-destructive tests was returned to the MBR system. The amount of sludge discharge will worked out an SRT of 200 days.

Table 3.2. Characteristics of the industrial wastewater

Component	Concentration
COD ($\text{mg}\cdot\text{L}^{-1}$)	1000
Soluble COD ($\text{mg}\cdot\text{L}^{-1}$)	543
Particulate COD($\text{mg}\cdot\text{L}^{-1}$)	456
TOC ($\text{mg}\cdot\text{L}^{-1}$)	334
DOC ($\text{mg}\cdot\text{L}^{-1}$)	209
TN ($\text{mg}\cdot\text{L}^{-1}$)	10
TP ($\text{mg}\cdot\text{L}^{-1}$)	1.35
pH	7.0-7.5
SS ($\text{mg}\cdot\text{L}^{-1}$)	200
VSS ($\text{mg}\cdot\text{L}^{-1}$)	197

DO in the COD-tank was kept above $4.5 \text{ mg}\cdot\text{L}^{-1}$ by air stones producing fine bubbles, while DO in the MBR-tank can only be kept above $3.5 \text{ mg}\cdot\text{L}^{-1}$. This was due to the coarse bubbles produced by coarse air diffusers which helped to reduce fouling but was poorer in oxygen diffusion. The DO concentration needed to be held above $2.0 \text{ mg}\cdot\text{L}^{-1}$ for heterotrophic microbial activity. When the dissolved concentration decreased with increase in the MLSS concentration, the aeration intensity was increased. This ensured that sufficient oxygen was supplied to maintain the bacteria in the aerobic condition since the biomass concentration was higher. The aeration in the system was kept running for 24

hr daily. DO in the N/P-tank was generally below $0.5 \text{ mg}\cdot\text{L}^{-1}$. this was made possible by intermittent aeration.

As the growth of the bacteria would be promoted under suitable pH and temperature range, the temperature was kept constant at 25°C in the mesophilic temperature range in the bioreactor suitable for the growth of heterotrophic bacteria. The pH of the mixed liquor was maintained in the range of 6.5 to 8.0.

The pressure indicator was connected in parallel to the permeate pipeline to obtained the tranmembrane pressure. As the experiment is based on a fixed flux operation, the transmembrane pressure is monitored continuously to monitor the membrane performance.

Additionally, at the initial startup of the MBR system, a series of analytical tests was conducted daily to monitor the overall performance of the MBR system. This was necessary to monitor the performance of the MBR to ensure that the system was running smoothly and efficiently at the initial stage to achieve the desired quality effluent. However, the frequency of the experiments was subsequently reduced to twice weekly as the system reached a more stable stage producing a more consistent effluent quality.

Detailed operating conditions of the experimental runs are summarized in Table 3.3 shown.

Table 3.3. Operating conditions of the laboratory scale submerged MBR

Parameters	value
Duration (d)	300
Working volume (L)	20
HRT (hr)	8
SRT(d)	200
Flux ($\text{L}\cdot\text{m}^{-2}\cdot\text{hr}^{-1}$)	26
VLR ($\text{kgCOD}\cdot\text{m}^{-3}\cdot\text{d}^{-1}$)	3
Temperature ($^{\circ}\text{C}$)	25
pH	6.5 - 8.0

3.3 MEMBRANE CLEANING PROCEDURES

Whenever the suction pressure exceeded a predetermined pressure depending on different experimental needs, it indicated that there was substantial fouling on the membrane surface, which hindered the permeate to be extracted. As a result, mechanical cleaning method was carried out to remove the fouling layer formed on the membrane surface. If internal fouling had occurred, chemical cleaning was performed after mechanical cleaning to remove the internal foulants.

During cleaning phases, the membranes were first taken out of service. Then each ceramic membrane was jet-washed to remove the fouling layer. If only mechanical method was employed, the membrane was jet-washed before washing with a soft sponge. After which, the surface of the membrane was rinsed with distilled water for a few minutes before placing back in service.

If chemical cleaning was used, the membranes were soaked in 0.5% sodium hypochlorite (NaOCl) for one hour after mechanical washing was performed. After which, the membranes were rinsed with tapwater and finally soaking in distilled water together with slight agitation for an hour to remove the sodium hypochlorite before placing back in service.

Thereafter, the permeate flux will be monitored for 30 minutes after membrane washing (mechanical or chemical) to ensure that the system after membrane regeneration was stable.

3.4 ANALYTICAL METHODS

The Standard Methods for Examination of Water and Wastewater (AWWA, 1998) was used for all sample analysis. The following list encompasses the tests that were performed at a regular basis to evaluate the performance of the laboratory scale MBR system:

- Chemical Oxygen Demand (COD)
- Total Organic Carbon (TOC) / Dissolved Organic Carbon (DOC)
- Mixed Liquor Suspended Solids (MLSS)
- Mixed Liquor Volatile Suspended Solids (MLVSS)
- Sludge Volume Index (SVI)
- Size Distribution of Activated Sludge
- Total Nitrogen (TN)
- Scanning Electron Microscopy (SEM)
- Optical Microscopy
- Turbidity
- Colour₂₅₄

Chemical Oxygen Demand

The COD test is used to measure the oxygen equivalent of the organic material in wastewater that can be oxidized chemically using a dichromate in a boiling sulphuric acid solution (150°C), as illustrated in the following equation, when the organic nitrogen is in the reduced state (Sawyer et al., 1994)

$$\text{where } d = \frac{2n}{3} + \frac{a}{6} - \frac{b}{3} - \frac{c}{2}$$

Based on Method 5220D (AWWA, 1998) closed reflux, colorimetric method, sample placed in digestion culture tubes before addition of digestion solution and sulfuric acid reagent in the presence of silver catalyst. Then the tubes are to be placed in preheated digester at 150°C and reflux for 2 hours. The samples are then analyse with a spectrophotometer and recorded in units of absorbency (abs). The abs units can then be correlated to COD values predetermined from a calibration curve.

Mixed Liquor Suspended Solids

The components of the mixed liquor concentration in the submerged MBR can be divided into soluble fraction and suspended solids including biomass and colloids. The former consists of residual influent substrate and organic compounds that are released into bulk solution from the substrate metabolism and biomass decay. Suspended solids (SS) analysis is used to determine the total biomass concentration. The organic biomass is measured by means of volatile suspended solids (VSS) analysis. VSS is a collective parameter which reflects, in addition to active biomass, all particulate organics entrapped in the activated sludge flocs. Based on Method 2540D (AWWA, 1998), the concentration in the MLSS could be determined. The sludge sample of known liquor were first centrifuged at 3000 rpm for 15 min, thereafter, it was filtered through 1.2µm Whatman GFC filter paper and weighing it after drying it in an oven at 103°C. The increased in weight of the filter represents the total suspended solid present in the reactor. This represents the total suspended solids (MLSS). The following equation is used to determine the MLSS:

$$MLSS(mg / L) = \frac{(A - B)}{\text{sample size}(mL)} \times 1000\left(\frac{mL}{L}\right) \quad (3.2)$$

where

A = weight of filter and dried residue, mg

B = initial weight of the filter before filtration, mg

Mixed Liquor Volatile Suspended Solids

Based on Method 2540E, the residue from Method 2540D (AWWA, 1998) is ignited at 550°C to obtain a constant weight. The remaining solids represent the total fixed suspended solids and the volatile portion can be obtained from the weight loss during the ignition. The mixed liquor volatile suspended solids (MLVSS) can be determined as:

$$MLSS(mg / L) = \frac{(C - D)}{\text{sample size}(mL)} \times 1000 \left(\frac{mL}{L} \right) \quad (3.3)$$

where C = weight of residue before ignition, mg
 D = weight of the residue after ignition, mg

Sludge Volume Index

Based on Method 2710D (AWWA, 1998), SVI is measured by filling a 1 liter graduated cylinder with mixed liquor obtained from the bioreactor and allowing the sample to stand undisturbed for 30 mins settling. SVI is typically used to monitor settling characteristics of activated sludge and other biological suspension. Sludge settleability is dependent on the microbiological and physiochemical properties of the sludge. A sludge sample with SVI below 100 mL·g⁻¹ will settle well. However, a high SVI above 150 mL·g⁻¹, indicates settling problems and possible sludge bulking. The value of the sludge volume index can be obtained through:

$$SVI = \frac{\text{settled sludge volume}(mL / L)}{\text{suspended solids}(mg / L)} \times 1000 \quad (3.4)$$

Size Distribution of Activated Sludge

The Malvern particles size analyzer was employed to determine the size distribution of the particles present in the mixed liquor of the MBR. The analyzer measures particles size analysis based on the principle of Laser Diffraction in the range of 0.05 to 550 μm .

Total Organic Carbon / Dissolved Organic Carbon

Based on Method 5310A (AWWA, 1998), a sample was analysed by a TOC analyzer for the TOC value. For DOC reading, the sample is first filtered through 0.45 μm glass-fiber filter before the filtrate was analysed by a TOC analyser. The TOC analyser used in this experiment was the Shimadzu TOC analyser, Model 5000. For this analyser, the total carbon (TC) content is measured by reaction of sample with the oxidative catalyst at a temperature of 680°C. The inorganic carbon (IC) content is obtained from the IC reaction tube where the IC reactant (acid liquid) reacted with the inorganic carbon at around 150°C. The value for TOC could then be obtained from the difference between the TC and IC.

Total Nitrogen

The TN test is measured using a TN analyzer from Lachat Instruments, Inc. It uses an in-line digestion followed by flow injection analysis method. Nitrogen compounds in the samples are oxidized in-line to nitrate using alkaline persulfate/ultraviolet digestion. Oxidation of nitrogen containing compounds to nitrate is achieved at 95°C with additional energy supplied by exposure to ultraviolet light (UV). The digestion occurs prior to the injection valve.

After digestion, nitrate is quantitatively reduced to nitrite by passage of the sample through a copperized cadmium column. The nitrite (reduced nitrate and original) nitrite is then determined by diazotization with sulfanilamide under acidic conditions to form diazonium ion. The diazonium ion is coupled with N-(1-naphthyl)ethylenediamine

dihydrochloride. The resulting pink dye absorbs at 540 nm and is proportional to total nitrogen.

Scanning Electron Microscopy

The SEM was used to study the surface morphology of membrane. The Leica Steroscan 420 comprises of an electron microscope, a cryo coating workstation and an image analyzer. The microscope can view up to magnification of 300kx. This instrument works on a principle that a constant current of electrons that is produces from the column first impinges on the sample. Then this primary electron beam generates secondary electrons from the surface of the sample. The number of electrons escaping from the sample is directly related to the topography of the sample.

The SEM was used to view the morphology before and after the onset of fouling on the membrane surface. Several preparation steps were taken before looking at the samples especially after the onset of fouling. The fouling layer was first fixed onto the surface of the membrane by soaking them in 2% of glutaraldehyde for 1-4 hours. The chemical was then removed from the samples by washing them with 0.10M sodium cacodylate buffer for an interval of 20 minutes. This procedure was repeated 3 times before dehydrating the samples in series of 10 minutes washer in 50, 70, 85 and 95% strength of ethanol. This was followed by storing the samples in 100% strength of ethanol for overnight. The purpose of this was to remove the water content from the fouling layer that consists of largely organic or biological materials, which would hinder the viewing process. Finally, the samples were dried using Critical Point Drying method before a layer of Au was coated on the surface. The sample would then be ready for viewing.

Optical Microscopy

An optical microscope was used to view the physical state of the microorganisms in the activated sludge. The activated sludge samples had to be dripped onto slide plates previously cleaned with ethanol of 75% strength before viewing. The microscope model

used in this experiment was Reyence VH-8000 and had magnification capability of 75-750 times when used with a Reyence VH-Z75 lens.

Turbidity

Turbidity is a test used to indicate the quality of a sample with respect to colloidal and residual suspended matter. It is a measure of the light-transmitting properties of water as a result of the scattering and absorption of light by suspended solids. The turbidity values of samples were measured using Hach 2100N turbidimeter.

Colour₂₅₄

A Spectrophotometer, type of Lambda Bio 20, having 10 mm absorption cells and an effective operating range from 190 to 800 nm was used for the measurement of colour. The wavelength was scanned at 254 nm. The manufacturer's instructions were followed for analyzer assembly, testing, calibration, and operation.

CHAPTER 4 PERFORMANCE OF LABORATORY SCALE SUBMERGED MBR

4.1 OPERATIONAL PERFORMANCE PARAMETERS

4.1.1 MLSS & MLVSS Behaviour during 300 Days of Operation

The biomass (solids) in a bioreactor is commonly measured as TSS and VSS. The mixture of solids resulting from combining recycled sludge with influent wastewater in the bioreactor is termed MLSS and MLVSS. MLSS analysis is used to determine the total biomass concentration. The organic biomass is classically measured by MLVSS. The ratio of MLVSS/MLSS is often used to characterize the wastewater with respect to amount of organic matter present.

Figure 4.1. Variation of MLSS growth in submerged MBR system.

(Initial average MLSS=4,500mg·L⁻¹; HRT=8hr; SRT=200d)

The growth of MLSS is a very important indicator to the stability of the submerged MBR system. Figure 4.1 clearly shows that the average MLSS rose from an initial value of $4,500 \text{ mg}\cdot\text{L}^{-1}$. This was contributed by the initial cultivated sludge inoculation and industrial wastewater. The average MLSS concentration then increased rapidly to $12,000 \text{ mg}\cdot\text{L}^{-1}$ on day 40 before increasing slowly to $14,500 \text{ mg}\cdot\text{L}^{-1}$ at the end of the experimental period on day 300. Due to the complete sludge retention of all suspended solids by the membrane, the MBR has the advantage of a higher biomass concentration than most conventional activated sludge process (Shim *et al.*, 2002; Hong *et al.*, 2002).

MLSS in the various sub tanks were also recorded. MLSS is initially higher in the MBR-tank than those in the COD-tank and N-tank. This was due to sludge washed out by the overflow design. However, with sludge recirculation from MBR-tank to COD-tank, the difference was not great. To solve this problem, the height of the air blower in the MBR-tank was raised on day 43 and the MLSS in the MBR-tank fell below those recorded for COD-tank and N-tank. This was the original intention to concentrate the sludge in the COD-tank to alleviate fouling in the MBR-tank due to a higher MLSS concentration.

Figure 4.2. Variation of MLVSS growth in submerged MBR system
(Initial average MLVSS= $4,000 \text{ mg}\cdot\text{L}^{-1}$; HRT=8hr; SRT=200d)

MLVSS indicated by Figure 4.2 also shows a similar trend to MLSS. As MLVSS is classically used as a direct indicator of the quantity of bacteria present in the system, higher concentrations of MLVSS in the submerged MBR could mean a higher concentration of bacteria and therefore promote the removal of substrates faster.

The similarity in values of MLSS and MLVSS indicates a high MLVSS/MLSS ratio and little accumulation of inorganic solids. From Figure 4.3, MLVSS/MLSS ratio was higher in MBR-tank than COD-tank and N-tank indicating less accumulation of inorganics in the MBR-tank. The reason could be due to the recirculation of sludge from MBR-tank to COD-tank and inorganics having specific gravity heavier than water would remain in the COD-tank. However, due to constant aeration and subsequent mixing in the COD-tank, complete retention of all inorganics was not possible and therefore some will still overflow into neighboring tanks as depicted by a slow decreasing MLVSS/MLSS ratio. Average MLVSS/MLSS fell from an initial 93% to 90% at the end of the experimental.

Figure 4.3. Variation of MLVSS/MLSS in submerged MBR system
(Initial average MLVSS/MLSS=89%; HRT=8hr; SRT=200d)

4.1.2 Inorganic Accumulation

Accumulation of insoluble inorganic materials might be a major obstacle for zero sludge production (Yoon *et al.*, 2004). Inorganic accumulation can be determined from the MLVSS/MLSS ratio. The lower the ratio would mean less active microorganisms in the system and more accumulation of inert materials or rather inorganics. As the results shown in Figure 4.3, average MLVSS/MLSS ratio in the experiment MBR decreased from 93 to 90% during the 300 days of operation. This amount of decrease was lower than what most researchers reported (Yasui *et al.*, 1996; Sakai *et al.*, 1997). Moreover, the quality of the permeate were not unaffected by this change.

Based on the results, a material balance was taken to determine how much inorganic solids had accumulated in the reactor. The accumulation of inorganic solids in the reactor was calculated by considering the difference between TSS and VSS in the sludge and the cumulative difference in the influent wastewater (Pollice *et al.*, 2004). At the end of the experimental run, the inorganic solids in the sludge were about 28.2g and the total non volatile solids that had entered the reactor were about 54g. This showed that 52% of the influent inorganic solids that entered the reactor were accumulated which was close to the observation by Yasui *et al.* (1996). The rest of the inorganic solids were considered to be gone with the effluent. The reason was probably due to hydrolysis or enzymatic solubilization producing compounds having molecular size compatible with permeation (Yasui *et al.*, 1996; Sakai *et al.*, 1997; Pollice *et al.*, 2004; Yoon *et al.*, 2004).

4.1.3 Food/Microorganism Ratio

The F/M ratio is commonly used to characterize process designs and operating conditions. Apart from sludge age or SRT, F/M ratio is one of the two important parameters for operation of a biological wastewater treatment process (Ronald, 1997).

Figure 4.4. Variation of F/M ratio in submerged MBR system

(Initial F/M ratio=0.5; HRT=8hr; SRT=200d)

Figure 4.4 shows the F/M variation throughout the 300 operation days. As reviewed in Sections 2.1.3 and 2.1.4, the biomass was in the growth phase where the F/M was very high at 0.5 d^{-1} . As the biomass entered the endogenous or death phase, the F/M declined and stabilized at 0.17 d^{-1} when the substrate has been completely depleted so that no growth is occurring. Many previous studies on submerged MBR have been performed at an F/M ratio of less than 0.1 d^{-1} but their target wastewater was of municipal source and contains lower organic concentrations (Chiemchaisri *et al.*, 1993a; Ueda *et al.*, 1999). Also reviewed in Section 2.3.3, Rosenburger *et al.* (1999a) reported that zero net sludge production is achievable at an F/M ratio of 0.07 d^{-1} for the municipal wastewater treatment. The submerged MBR's F/M ratio was higher than what was reported by Rosenburger *et al.* (1999a). However, this could be explained by the 200 day SRT of the experimental submerged MBR system which resulted in a higher F/M ratio from Equation (2.10) reviewed in Section 2.1.4.

4.1.4 Sludge Volume Index

The SVI is an indicator of the quality of the sludge. Although, the MLSS in MBR system may be too high to use the index quantitatively, it is especially useful as a qualitative gauge to determine if sludge bulking had occurred due to errand operational parameters before the reactor stabilized. From Figure 4.5, the SVI decreased drastically for all 3 tanks to a stabilized value of 80. A value of less than 100 would mean good settling sludge with little or no filamentous bacteria growth while a value above 150 indicates settling problems and possible sludge bulking (AWWA, 1998). However, this test was ceased after day 60 when MLSS was too high. The settled volume in the measuring cylinder became too clouded to be determined visually.

Figure 4.5. SVI stabilizing with time

(Initial COD-tank SVI=277; Initial N-tank SVI=244; Initial MBR-tank SVI=154;
HRT=8hr; SRT=200d)

4.2 LOW SLUDGE GENERATION IN THE SUBMERGED MBR SYSTEM

Sludge production has been proven to be major obstacle in biotechnology applications in conventional wastewater treatment plants. In conventional wastewater treatment process, the treatment and disposal of excess sludge often represent 50-60% of the total wastewater treatment cost (Egemen *et al.*, 2001). Therefore, one of the key areas for present time research has been to develop system to minimize sludge production

A way to reduce excess sludge is to retain the sludge completely in the bioreactor, which can be achieved by a membrane separation process. As reviewed in Section 2.3.3, the MBR is capable of a smaller excess or zero sludge production. The control of the bacteria environment through efficient solid and liquid separation and operation of the biological processes with high biomass concentrations are likely to affect cell metabolism and limit bacteria growth and therefore lower sludge production (Chaize and Huyard, 1991; Suwa *et al.*, 1992). By operating the processes at low organic loading rate, it is possible to divert the utilization of polluting compounds from biosynthesis to non-growth energy demanding activities, favour the utilization of substrates for maintenance of bacterial vital functions and limit the net growth (van Houten and Eikelboom, 1997; Low and Chase, 1999). This is the concept of “maintenance energy”, first introduced by Pirt in 1965. It can be defined as the amount of energy strictly necessary for endogenous respiration (Pirt, 1965). The sludge concentration is expected to stabilize at the level at which energy supplied is fully utilized for maintenance purpose.

Another way to reduce sludge production is to exploit the organisms in the process that predate on bacteria (sludge), by promoting their growth in an extra “grazing stage”. Reduced sludge production can be achieved by higher organisms such as protozoa and metazoa in the activated sludge processes that predate on the bacteria whilst decomposition of substrate remains unaffected (Ratsak *et al.*, 1996; Ghyoot and Verstraete, 2000). The increased amount of bacterivorous protozoa and metazoa could also probably be responsible for decreased sludge yield.

4.2.1 Effect of 200 Day SRT on Sludge Yield

Figure 4.1 shows the sludge concentration changes in the MBR over the experimental period. The average MLSS concentration increased rapidly to 12,000 mg·L⁻¹ at day 40 before increasing slowly to 14,500 mg·L⁻¹ at the end of the experimental period of 300 days. A sufficiently high sludge concentration will ensure good performance in pollutant removal and better effluent quality (Shim *et al.*, 2002; Hong *et al.*, 2002). This value was obviously higher than that of the conventional activated sludge process, implying that MBR can be operated at higher organic loading and the equipment volume can thus be reduced (Huang *et al.*, 2001). On the other hand, the ratio of average VSS/SS stabilized at a range 0.90-0.93, almost constant over the whole entire operation period. It indicated low accumulation of inorganic matter in the bioreactor.

For a biological wastewater treatment system, the sludge concentration in the bioreactor depends on both microbial growth and endogenous respiration. Consequently, a kinetic model for sludge growth in a biological treatment process can be derived as follows (Horan, 1990),

$$\frac{1}{Y} = \frac{1}{Y_G} + \frac{b}{Y_G} \frac{1}{\mu} \quad (4.1)$$

$$Y = \frac{R_d}{-R_o} \quad (4.2)$$

$$\mu = \frac{R_d}{X_r} \quad (4.3)$$

where, R_d = sludge growth rate, gVSS·L⁻¹·d⁻¹
 $-R_o$ = organic degradation rate, gCOD·L⁻¹·d⁻¹
 X_r = sludge concentration in the bioreactor, gVSS·L⁻¹
 μ = sludge specific growth rate, d⁻¹
 Y_G = theoretical sludge yield, gVSS·gCOD⁻¹
 Y = observed sludge yield, gVSS·gCOD⁻¹
 b = endogenous decay coefficient, d⁻¹

For the submerged MBR, mass balances with respect to organic matter, suspended solids and water amount could be represented as Equation (4.4) to (4.6), respectively.

$$V \frac{dC_s}{dt} = Q_i C_i - Q_e C_e - Q_w C_s + R_o V \quad (4.4)$$

$$V \frac{dX_r}{dt} = Q_i X_i - Q_e C_e - Q_w X_r + R_d V \quad (4.5)$$

$$Q_i = Q_e + Q_w \quad (4.6)$$

where, V = volume of MBR, L
 C = organic concentration, gCOD·L⁻¹
 Q = flow rate, L·d⁻¹
 X = sludge concentration, gVSS·L⁻¹

Subscripts i, e, w, s and r represent the system influent, effluent, discharged sludge, supernatant and mixed liquor in the bioreactor, respectively.

With the assumption that the membrane-filtered effluent is free of SS and the influent X_i is negligible, then R_d and $-R_o$ can be represented as follows by combining Equation (4.5) and (4.6), and Equations (4.4) and (4.6), respectively.

$$R_d = \left(\frac{Q_w X_r}{V} + \frac{dX_r}{dt} \right) \quad (4.7)$$

$$-R_o = \left[\frac{Q_e (C_i - C_e)}{V} + \frac{Q_w (C_i - C_s)}{V} - \frac{dC_s}{dt} \right] \quad (4.8)$$

The SRT (θ) and the HRT (τ) can be written as

$$\theta = V/Q_w \quad (4.9)$$

$$\tau = V/Q_e \quad (4.10)$$

Consequently, Equation (4.9) and (4.10) can be transformed as

$$R_d = \left(\frac{X_r}{\theta} + \frac{dX_r}{dt} \right) \quad (4.11)$$

$$-R_o = \left[\frac{(C_i - C_e)}{\tau} + \frac{(C_i - C_s)}{\theta} - \frac{dC_s}{dt} \right] \quad (4.12)$$

Using the experimental data, R_d and $-R_o$ at any operation time could be calculated from Equation (4.11) and (4.12). Furthermore, Y and μ could be obtained based on Equation (4.2) and (4.3). The reciprocals of these two factors held a linear relationship.

Substituting the values of the submerged MBR system into Equation (4.11) and (4.12) and consequently obtaining values for R_d and $-R_o$, Y and μ was obtained. The reciprocals of the latter were plotted versus each other as depicted in Figure 4.6. Based on Equation (4.1), Y_G and b were calculated to be $0.115 \text{ gVSS} \cdot \text{gCOD}^{-1}$ and 0.024 d^{-1} from the slope and intercept in Figure 4.6.

Figure 4.6. Correlation of $1/Y$ versus $1/\mu$
(MBR system; $HRT=8hr$; $SRT=200d$)

Huang *et al.* (2001) attained a relationship as in Equation (4.13) between endogenous decay coefficient, b and SRT. They concluded that the sludge decay coefficient, b decreased exponentially and this phenomenon might be related to oxygen transfer in the bioreactor. When SRT was short, the sludge concentration in the bioreactor was low. This condition was conducive to oxygen transfer and subsequent enhancement of sludge endogenous respiration. As for longer SRT, the decrease in sludge endogenous decay was probably due to impeded oxygen transfer at high sludge concentration associated with long SRT.

$$b = 0.85.\theta^{-0.62} \quad (4.13)$$

Substituting the SRT of 200 days for the submerged MBR into Equation (4.13), a sludge decay coefficient, b of 0.032 d^{-1} is obtained which is close to the submerged MBR calculated value of 0.024 d^{-1} .

For the conventional activated sludge (CAS) process for treating domestic wastewater, sludge yield and endogenous decay is normally in the range $0.25\text{--}0.4\text{ gVSS}\cdot\text{gCOD}^{-1}$ and $0.04\text{--}0.075\text{ d}^{-1}$ (Gu, 1993). The sludge yield, Y_G of the MBR system was $0.115\text{ gVSS}\cdot\text{gCOD}^{-1}$ which was twice less than the lower value reported for CAS.

The endogenous decay coefficient, b value of 0.024 d^{-1} obtained from this study was twice lower than the lower value for CAS processes. The reason was probably due to different levels of aeration. Generally, in the membrane bioreactor, air supply to individual biomass is lower than that in the CAS and to the decomposing of organic compounds. Decay cells or dead cells that are still intact are unavailable to other bacteria as a food source and in this context contribute to inert biomass. However, both living and dead bacteria can be utilized in trophic reactions (as a food source) by higher bacteriovoric organisms such as protozoa, metazoa and nematodes.

Figure 4.7. Observed sludge yield in submerged MBR system
(Initial $Y=0.181\text{ gVSS}\cdot\text{gCOD}^{-1}$; $\text{HRT}=8\text{ hr}$; $\text{SRT}=200\text{ d}$)

The observed sludge yield, Y plotted against time in the MBR is shown in Figure 4.7. The observed yield was initially high at $0.181\text{ gVSS}\cdot\text{gCOD}^{-1}$ when the sludge in the MBR

system is in the exponential growth phase and fell exponentially to a value of 0.022 gVSS·gCOD⁻¹ towards the end of the experimental run. This decreasing tendency of the sludge yield for increasing sludge concentration was also observed by Rosenburger *et al.* (2002) and Pollice *et al.* (2004).

Given that the value for sludge yield is small and endogenous decay coefficient is also small, most of the energy provided by the substrate consumed can be deemed to be used mainly for cell maintenance. This proved the “maintenance energy” concept by Pirt is possible for the submerged MBR with a prolonged SRT of 200 days and yet maintain good effluent quality. The energy from the substrate is largely used for endogenous respiration and thus net growth is limited as time progresses. The sludge concentration had started to stabilize at the level at which energy supplied is mostly utilized for maintenance purpose when MLVSS concentration reached 12,000 mg·L⁻¹ at day 40. After which, growth of MLVSS started to retard.

Sludge production can be defined as the product of the observable sludge yield and assimilated organics. Therefore, the sludge production per day can be calculated from Equation (4.14). The results are shown in Figure 4.8.

$$P_x = Y \cdot Q_i \cdot (C_i - C_e) \times 10^{-3} \quad (4.14)$$

where, P_x = sludge production, kgVSS·d⁻¹
 Q_i = influent flow rate, L·d⁻¹
 C_i = influent organic concentration, gCOD·L⁻¹
 C_e = effluent organic concentration, gCOD·L⁻¹

Figure 4.8. Sludge production in submerged MBR system
(Initial $P_x=0.0104\text{gVSS}\cdot\text{d}^{-1}$; $\text{HRT}=8\text{hr}$; $\text{SRT}=200\text{d}$)

Sludge production in the submerged MBR was consistently low at $0.0016\text{ kgVSS}\cdot\text{d}^{-1}$ after steady state was achieved. However, as the composition of the wastewater also influences sludge production, absolute values for sludge yields, decay constant and sludge production can only be compared for treatment of the same wastewater.

4.2.2 Effect of an “Artificial Ecosystem” on Sludge Yield

A biological wastewater treatment process can be considered as an “artificial ecosystem”, and activated sludge is an ideal habitat for several organisms other than bacteria. In an activated sludge system, the grazing fauna mainly consists of protozoa and occasionally metazoa. It is well known that the presence of protozoa and metazoa in aerobic wastewater treatment processes plays an important role in keeping the effluent clear by consuming dispersed bacteria. In the past, protozoa and metazoa were usually used as important indicators of process performance and efficiency in biological wastewater treatment processes. Salvado *et al.* (1995) has demonstrated the presence of ciliated protozoa as an indicator of good effluent quality. The presence of protozoa or metazoa is

also accepted as indicators of a healthy population in wastewater treatment systems (Horan, 1990). These organisms are strict aerobes and are more sensitive to toxic conditions than bacteria. They are only found in a very stable environment and mostly in extended aeration systems with high SRT and good and stable sludge.

This predatory population in the system has been proven to enhance mineralization and reduce sludge production by many researchers. Zhang (1997) suggested that high metazoa population density leads to high mineralization rate. Moloney and Field (1991) also suggested that the higher organism could attack and consume particles according to their own body size. In that respect metazoa or worms inside a system cause the relative bigger flocs particles to go under predation pressure and in this process transformation into smaller particles increases. Small flocs inside the reactor are preferable for sludge mineralization, hydrolysis and also predation by the other predator organisms like protozoa. This could be one of the reasons for the reduction of mean floc particle size in the submerged MBR as depicted Figure 4.9. In general, particle size of an activated sludge floc ranges from 1.2-600 μm (Jorand *et al.*, 1995). The sludge reduction capacity of metazoa certainly depends on its population size. Rensink and Rulkens (1997) mentioned that if more than 20 to 30 worms per ml sludge mixture were measured, sludge reduction occurred.

Figure 4.9. Particle size of bacteria flocs in submerged MBR system
(Initial particle size=176 μm ; HRT=8hr; SRT=200d)

Samples for the submerged MBR during experimental runs were taken for microscopic examinations for the possibility of the presence of this “artificial ecosystem”. Figure 4.10 showed the microscopic image at 500 times magnification of those samples. It revealed the abundant presence of higher organisms like protozoas and rotifers apart from bacteria flocs.

Figure 4.10. Microscopic image of protozoa, rotifers and bacteria flocs at 500x magnification.

A higher organism than protozoa is the metazoa in an activated sludge system and consists of normally of rotifera and nematode. Figure 4.11 shows the microscopic images of another sample taken from the submerged MBR system. They were also taken at 500 time magnification. The organisms found were rotifers and nematode which were also present in the MBR system. Activated sludge containing many worms usually originates from sewage treatment plants (Eikelboom, 2000). The presence of these worms could have originated from inoculum sludge originating from Jurong Water Reclamation Plant. This predatory population in the system can be exploited to enhance sludge mineralization and reduce sludge production.

Figure 4.11. Microscopic images of metazoa (top) rotifers and (bottom) nematode at 500x magnification

4.2.2.1 Bacteriovoric Metabolism

Higher organisms such as protozoa and metazoa in the activated sludge processes predate on the bacteria as a food source. During energy transfer from low to high trophic levels, energy is lost due to inefficient biomass conversion and thus the predator may make a large contribution to biomass replacement (Ratsak *et al.*, 1996). The increased amount of bacterivorous protozoa and metazoa could lead to a decreased sludge yield.

Ghyoot and coworkers (1998, 2000) compared the performance a CAS reactor and a submerged MBR. The sludge yield of the two-stage submerged MBR system was 20–30% lower than that of the two-stage CAS system under similar SRT and F/M ratio. This phenomenon was attributed to more predators' presence in the MBR than those in the CAS reactor. A long sludge retention period in MBR is very suitable for the abundant growth of these higher organisms (Luxmy, 2001). The long SRT of 200 days in the experiment submerged MBR system therefore make it very susceptible for growth of these high organisms.

4.2.2.2 Nematodes

Nematodes or worms are the largest organisms observed during the microscopic investigation of activated sludge (Eikelboom, 2000), and may have more potential on sludge reduction in practical application than protozoa due to their bigger sizes. The performance of oligochaetes on sludge reduction in biological wastewater treatment is paid more attention recently.

Figure 4.12. Photo image of nematodes surfacing for air after sludge is allowed to settle in a measuring cylinder (Note: thin line is a gradation marking on the measuring cylinder)

A major worm bloom resulted in a low sludge volume index, lower energy consumption for oxygen supply and less sludge disposal in a full-scale activated sludge plant 25–50% sludge reduction (Ratsak, 1994; Ratsak, 2001). This could be the reason for the sludge reduction in the experiment submerged MBR as worm blooms were consistently observed in the system as shown in Figure 4.12.

Zhang (2000) studied the possibility of increasing worm density with membrane, and compared performances of worms on sludge reduction in different pilot MBRs fed with presettled domestic wastewater. High worm density i.e. 2600–3800 ml⁻¹ mixed liquor once occurred in the membrane separation tank of a two-stage gravitational submerged MBR system, and resulted in a low sludge yield (0.10–0.15 kgSS·kgCOD⁻¹). The sludge yield in a suction submerged MBR system varied from 0.00 to 0.12 kgSS·kg·COD⁻¹ at more than 100 worms per ml of mixed liquor. The yield for the experimental submerged MBR system was 0.022 gVSS·gCOD⁻¹. This value can be expressed in terms of SS assuming an averaged 90% MLVSS/MLSS ratio to 0.024 kgVSS·kgCOD⁻¹, which falls within the range observed by Zhang.

However, contrary to our findings, Luxmy *et al.* (2001) reported that the presence (even about 1000–2000 metazoa population per ml) or absence of the metazoa population did not have any significant effect on sludge reduction in bench scale of submerged MBRs. On the other hand, Luxmy and co-workers found out that metazoa population may play an effective role in membrane fouling control, especially those that were attached to the membrane.

4.2.2.3 Proposed Model of the “Artificial Ecosystem”

Although the populations of metazoan and protozoa were significantly observed, dead bodies of metazoan and protozoa were not usually observed. It be deduced that lysis of dead metazoan and protozoa had occurred quickly. Figure 4.13 proposed a basic model of a possible “artificial ecosystem” in the submerged MBR system. In the proposed model, waste organic matters in the industrial wastewater were assimilated by bacteria as food. The bacteria grew into flocs and were grazed and predated by protozoa and metazoan. Bacteria flocs, protozoa and metazoan lyses back into the system when they die. Taking

note that energy is lost during the transfer from low to high trophic levels (as a food source) due to inefficient biomass conversion.

Figure 4.13. Proposed model of “artificial ecosystem” in the submerged MBR

4.3 BIOLOGICAL PERFORMANCE PARAMETERS

4.3.1 Organics Removal

There are a number of organics measurements that are of use in various situations. Organics are most often assessed in terms of the oxygen required to completely oxidize the organic matters to CO_2 , H_2O and other oxidized species. Besides expressing organics in terms of a common denominator like COD, it is also practical because an important consequence of the presence of organic matters is the consumption of oxygen.

Figure 4.14. Variation of COD values in submerged MBR system
(Influent COD=1000mg·L⁻¹; HRT=8hr; SRT=200d)

Figure 4.14 shows the COD values of the supernatant (based on samples from 0.45 μm filtered centrifuged supernatant liquor) in the MBR-tank and those of the permeate from ceramic membranes in the submerged MBR system. The former were mainly due to biological degradation in the bioreactor and the latter due to both biological degradation and membrane filtration. Influent COD was at 1000 $\text{mg}\cdot\text{L}^{-1}$ and COD values of the permeate remained consistently low at less than 20 $\text{mg}\cdot\text{L}^{-1}$ after an initial startup period and fell to less than 10 $\text{mg}\cdot\text{L}^{-1}$ after 100 days of operation. This was maintained to the end

of the experimental run. Supernatant COD values were consistently higher than permeate COD and the difference was attributed to the effect of membrane separation.

Expressing the COD removal in terms of removal efficiency compared to the influent COD value in Figure 4.15, the biological removal averaged more than 90%. Total COD removal efficiency averaged at 99%. Permeate COD fell to $10 \text{ mg}\cdot\text{L}^{-1}$ after 100 days of operation as shown in Figure 4.14. A difference in COD removal between the bioreactor and the total system indicated that a fraction of dissolved COD components, probably microbial metabolic matter with a relatively large molecular weight, could be expelled by the membrane to some extent. Therefore, membrane separation plays an important role in maintaining high and stable COD removal. However, this high rejection rate is non-typical for the MF ceramic membrane with a pore size of $0.9 \mu\text{m}$. Results are closer to performance of typical UF MBR system.

Figure 4.15. COD removal efficiencies in submerged MBR system
(Influent $\text{COD}=1000\text{mg}\cdot\text{L}^{-1}$; $\text{HRT}=8\text{hr}$; $\text{SRT}=200\text{d}$)

Another important method of expressing organic is in terms of its carbon content. Carbon is the primary constituent of all organic matters. It is also more accurate to measure low

organic effluent using TOC as COD results of $20 \text{ mg}\cdot\text{L}^{-1}$ are to be used more qualitative than quantitative (AWWA, 1998). Graphical evidence of TOC removal in Figure 4.16 shows a reduction from influent wastewater of $334 \text{ mg}\cdot\text{L}^{-1}$ to less than $3 \text{ mg}\cdot\text{L}^{-1}$ in the permeate, which also corresponded to a high removal efficiency of more than 99%. These results were similar to those of COD.

Figure 4.16. TOC values and removal efficiency in submerged MBR system
(Influent TOC= $334 \text{ mg}\cdot\text{L}^{-1}$; HRT=8hr; SRT=200d)

4.3.2 High Performance of Organics Removal

Many studies have also reported high and stable removal of organic substances by MBRs. COD removal rates greater than 90% have been commonly observed (Yamamoto *et al.*, 1989; Suwa *et al.*, 1989; Chiemchaisri *et al.*, 1992; Trouve *et al.*, 1994; Côté *et al.*, 1997). However, many would also question whether the high removal rate was attributed to the membrane separation used instead of sedimentation used in conventional activated sludge process.

Figure 4.17. Mode of COD removal in submerged MBR system

(Influent COD=1000mg·L⁻¹; HRT=8hr; SRT=200d)

Figure 4.17 shows the contribution from the submerged MBR's two main processes (biological and membrane separation) contribution to COD removal. It can be seen that the bioreactor was responsible for 90-98% of COD removal. A difference of about 2–10% in COD removal between the bioreactor and the total system indicated that a small molecular fraction of dissolved COD components, probably microbial metabolic matter with a relatively large molecular weight, could be retained by the membrane to some extent. Membrane separation therefore played an important role in maintaining high and stable COD removal in the submerged MBR system.

The organic compounds in the wastewater are generally removed for sludge ages longer than 4 days. The dissolved COD remaining in the effluent is defined as refractory (Dockhorn *et al.*, 2000). It contains a variety of soluble organics including residual degradable and non or slowly biodegradable substrates in the influent as well as intermediate substrate and the end products. It has been reported that the majority of the soluble organic matter in the effluent from the biological treatment processes is actually soluble microbial product or SMP (Chudoba, 1985; Gaudy, 1985; Rittmann *et al.*, 1987; Namkung and Rittmann, 1988; Sciener *et al.*, 1998)

SMP can be defined as the pool of organic compounds that result from substrate metabolism (usually with biomass growth) and biomass decay. Molecular weight distribution (MWD) of SMP showed that the effluent contained compounds with a broad spectrum of molecular weight (<0.5–>50 kDa) and that a greater amount of high molecular weight compounds were found in many biological effluents than in the influent (Duncan and Stuckey, 1999).

MBR process is a bioreactor having a membrane separation in it. It has the advantages of perfect retention of the biomass and a more reliable effluent quality compared to that of the conventional processes. Through the use of membranes, solids including bacteria and high molecular weight by-products are efficiently retained (Urbain *et al.*, 1998). Ince *et al.*, (2000) reported that the organic concentration in the reactor was two to three times more than that of the UF membrane permeation. It is because the high molecular SMP which is larger than the molecular weight cut-off (MWCO) of the UF membrane cannot penetrate membrane pores due to size exclusion.

SMP concentration can be estimated using the biodegradable organic matter (BOM) removal (as carbon), the dissolved organic carbon (DOC) removal and the SMP biodegradation in Equation (4.15) (Carlson and Amy, 2000).

$$\begin{aligned} SMP &= BOM_{removal} - DOC_{removal} + SMP_{bio\ deg\ radation} \\ &= (BOM_{influent} - BOM_{effluent}) - (DOC_{influent} - DOC_{effluent}) + SMP_{bio\ deg\ radation} \end{aligned} \quad (4.15)$$

BOM removal represents the consumption of the influent substrate that should be equal to the DOC removal if no SMP were present. If SMP was present, the DOC removal would be reduced by the amount of SMP produced. For simplicity, it was assumed that the substrate is completely removed in the bioreactor and $SMP_{biodegradation}$ is negligible, the difference of DOC between supernatant of the MBR-tank and permeate represents the amount of observed SMP retained by the membrane as in Equation (4.16).

$$SMP_{retained} = DOC_{supernatant} - DOC_{permeate} \quad (4.16)$$

Figure 4.18. Observed SMP in supernatant and permeate of submerged MBR system
(Influent $DOC=209\text{mg}\cdot\text{L}^{-1}$; $HRT=8\text{hr}$; $SRT=200\text{d}$)

Figure 4.18 shows the observed SMP concentration in the supernatant of MBR-tank and the permeate. Initially, SMP concentrations were high and mostly likely came from the acclimated sludge that was used to start-up the MBR system. However, the SMP were quickly assimilated. After day 12, SMP quickly rose to high levels due to accumulation of non-biodegraded SMP before decreasing quickly to the range of 5 to 9 $\text{mgDOC}\cdot\text{L}^{-1}$. This range was maintained throughout the rest of the experimental period. SMP levels of the permeate was maintained at a range of 2 to 5 $\text{mgDOC}\cdot\text{L}^{-1}$. Figure 4.18 shows the percentage of SMP that was retained by the membrane using Equation (4.16). It can be concluded that the membrane was able to retain about an average of 50% of the SMP in the supernatant throughout the 300 days of operation.

Figure 4.19. DOC retention by membranes in submerged MBR system
(Initial DOC retained=50%; HRT=8hr; SRT=200d)

Although there were some reports about the inhibition of the accumulated metabolic products (Zhang and Yamamoto, 1996; Huang *et al.*, 2000), the results with the submerged MBR system in Figure 4.19 shows little accumulation of SMP and those that accumulated in MBR were not inhibitory to the metabolic activity of the activated as effluent quality was still maintained at good levels throughout 300 days of operation. This can be easily explained by the fact that a 200 day SRT had produced acclimated organisms that could degrade the accumulated SMP. The accumulated SMP was degraded into lower molecular weight compounds which can then easily degraded. This had led to the lack of SMP built-up in the MBR system. Similar results were reported in other studies (Gaudy, 1985; Rittmann *et al.*, 1987; Huang *et al.*, 2000). All the results put together, the experiment submerged MBR processes, despite the long SRT of 200 days, could still produced better effluent than the conventional biological treatment process in terms of organic removal.

4.3.3 Nutrients Removal

Figure 4.20 shows the concentration of total nitrogen in the submerged MBR system. Reading was only collected after day 32 after the MBR obtained a more steady-state

operation. TN in the influent wastewater was $10 \text{ mg}\cdot\text{L}^{-1}$ and the eventual TN value in the permeate fell to as low as $0.2 \text{ mg}\cdot\text{L}^{-1}$. This would translate to a 98% removal efficiency of TN. Many researchers also achieved successful high nitrogen removal with MBR systems as reviewed in Section 2.3.3.

Figure 4.20. Variation of TN in submerged MBR system
(Influent $\text{TN}=10\text{mg}\cdot\text{L}^{-1}$; $\text{HRT}=8\text{hr}$; $\text{SRT}=200\text{days}$)

The reason for the initial low removal efficiency could be due one or more to the following reasons: (1) slow growth of the nitrifying bacteria, (2) lack of denitrification in the anoxic section due to initial inappropriate conditions and (3) lack of ammonification bacteria to break down the organic nitrogen to simpler nitrogen forms for assimilation by nitrifying bacteria.

4.3.4 High Performance of Total Nitrogen Removal

TN comprises of organic nitrogen, ammonia, nitrite and nitrate. The organic fraction consists of a complex mixture of compounds including amino acids, amino sugars and

proteins (polymers of amino acids). The compounds that comprise the organic fraction can be soluble or particulate. The nitrogen in these compounds is readily converted to ammonium through the action of microorganism in the aquatic or soil environment (Metcalf & Eddy, 2003). This is known as ammonification.

Ammonification is a step of the biodegradation of nitrogen containing nucleotides and amino acids. In general, ammonification occurs during decomposition of animal and plant tissue and animal fecal matter.

Many organic polymers, particularly proteins and nucleic acids, are composed of repeating units connected by bonds that can be broken down by hydrolysis. Hydrolysis reaction is responsible for the solubilization of cellular components released as a result of cell lysis, preventing build-up in the system. Secondly, it also degrades the particulate organic material in the reactor.

Ammonium in turn undergoes nitrification process whereby ammonium is oxidized to nitrites, then nitrates, in the presence of oxygen (aerobic condition). This is achieved by a group of autotrophic bacteria, mainly from the genera of *Nitrosomonas* and *Nitrobacter*. Following are the reaction equations (Crites & Tchobanoglous, 1998),

Denitrification involves the microbial reduction of nitrate to nitrite and ultimately nitrite to nitrogen gas under anaerobic condition. Distinct from nitrification, a relatively broad range of bacteria can accomplish denitrification. Genera of these heterotrophic bacteria known to contain denitrifying bacteria include *Pseudomonas*, *Micrococcus*, *Archromabacter*, *Thiobacillus* and *Bacillus* (Sørensen and Jørgensen, 1993). Using methanol as an electron donor and neglecting synthesis, denitrification can be represented as a two step process shown below (Sørensen and Jørgensen, 1993).

Nitrogen gas being biologically inert has no significant effect on the environment. Nitrate and nitrite replace oxygen for microbial respiration in this reaction. Therefore, denitrification is commonly occurred in the absence of molecular oxygen, under so called anoxic conditions. Anoxic instead of anaerobic describes the environmental condition involving the absence of oxygen without implying nature of biochemical pathway (Crites & Tchobanoglous, 1998).

Although TN in the influent wastewater was low, in the region of $10 \text{ mg}\cdot\text{L}^{-1}$, the TN in the permeate fell to as low as $0.2 \text{ mg}\cdot\text{L}^{-1}$ after day 100. That would translate to a 98% removal efficiency of TN. TN removal efficiency of the submerged MBR was in the high range to what was reported by Nah *et al.* (2000). Nah and co-workers developed a single tank MBR with intermittent aeration and obtained total nitrogen removal of more than 80%. The reason for the experiment submerged MBR's higher removal efficiency could be due to dedicated tanks for nitrification and denitrification as which Côté *et al.* (1997)

and Ghyoot and Verstraete (2000) applied to their experiments too. Ammonia nitrogen, nitrite and nitrate tests were also conducted on the samples but the results were consistently low even at the start of operation and therefore were questionable. The reason could be due to the nature of the industrial wastewater used which contains mainly organic nitrogen. Therefore, TN values were used as a better gauge to evaluate the nitrogen removal of the system.

The advantage of the 3-stages of the submerged MBR setup was not only to allow for nitrification but also denitrification for total nitrogen removal. Nitrogen in nitrate and nitrite stage present in water has proved to be more lethal in many areas. One example is that nitrate causes *methemoglobinemia* in infants with serious and occasionally fatal effects. The complete retention of microorganisms by the membrane in MBR system also encouraged the growth of specialized nitrifying bacteria, *Nitrosomonas* and *Nitrobacter* in the aerobic COD-tank and MBR-tank and also denitrification bacteria which require anoxic environment. The denitrification bacteria were retained in the N-tank where DO levels were kept below $0.5 \text{ mg}\cdot\text{L}^{-1}$.

Several methods including physical, chemical and biological methods are used in environmental engineering to remove the nitrogen from wastewater. Normally, physical and chemical methods are seldom employed due to the high cost of treatment, especially at small plants. Biological methods being relatively cheaper and very stable are conventionally employed in wastewater treatment. The submerged MBR in this study shows enormous potential as total nitrogen were consistently removed at high efficiency. However, further research work would need to be done to evaluate the economic aspect of using MBR system for complete nitrogen removal.

4.3.5 Other Permeate Quality

One of the 3 major effluents parameters is the TSS (Federal Register, 1988). However, the TSS test is somewhat arbitrary and would depend on the pore size of the filter paper used for the test. Moreover, suspended solids in effluents are usually low or non detectable (N.D.) and measurements of SS become erroneous. Therefore, in cases where

suspended solids concentrations are low, turbidity and colour can be very useful parameters. Colour and turbidity are also important aesthetic standard parameters for drinking waters.

4.3.5.1 Suspended Solids Removal

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 (N.D.) as compared to $200 \text{ mg}\cdot\text{L}^{-1}$ in the influent wastewater using a $1.2\mu\text{m}$ pore size filter (membrane pore size is at $0.9 \mu\text{m}$) as with all the SS tests. However, these N.D values were due to be the precision of the instruments used for the SS test rather than reflect the true value. Therefore, the turbidity and colour tests were conducted for higher degree of accuracy.

4.3.5.2 Turbidity Removal

Turbidity is a test used to indicate the quality of natural water or discharges with respect to colloidal and residual suspended matter. It is a measure of the light-transmitting properties of water as a result of the scattering and absorption of light by suspended solids. A rough relationship exists between suspended solids concentrations and turbidity. Raleigh's law describes scattering of white light by suspended particles,

$$I_s \propto \frac{V^2}{\lambda^4} n \quad (4.24)$$

where I_s = intensity of the scattered light

V = volume of particles

n = number of particles

λ = wavelength of light

From equation (4.24), it is observed that size and concentration of particles influence the measurement of turbidity. Normally, wastewater will contain many different sized particles at different concentrations. Therefore, the relation between suspended solids concentration and turbidity can be highly variable even for different samples from the same source. However, particularly in cases where suspended solids concentrations are low, turbidity can be a very useful parameter. Turbidity readings are usually used for process control and there is also on-line turbidity meters used to monitor the performance of microfiltration units.

*Figure 4.21. Turbidity of permeate samples
(MBR system; HRT=8hr; SRT=200d)*

Turbidity readings were taken from permeate samples throughout the experimental run. From Figure 4.21, the turbidity values varied from 0.123 to 0.136 NTU. These values were half of the PUB (Public Utilities Board, Singapore) tapwater's average turbidity value of 0.29 NTU shown in Figure 4.22. Other turbidity values of clean water sources are also shown. Ultrapure water and distilled water had average turbidity values of 0.077 and 0.089 NTU respectively. In surface water filtration for the treatment of drinking water, turbidity in the filtered water must consistently be equal or less than 0.3 NTU

(Viessman and Hammer, 2005). The permeate samples turbidity readings did meet this standard and proved its high quality.

Figure 4.22. Turbidity comparison chart

4.3.5.3 Colour Removal

Colour is imparted to water by dissolved constituents that absorbed white light and emit light at specific wavelengths. Colour of water is also influenced by its turbidity. Humic acid and fulvic acid imparts colour to natural waters. Colour is a misnomer when measurements are made in the UV range and absorbance should be the right term to use. Table 4.1 shows an overview of the general absorbance of most effluent waters from biological wastewater treatment.

Table 4.1. Colour₂₅₄ of some wastewater types (Metcalf and Eddy, 2003)

Wastewater types	Absorbance at 254nm (absorbance unit·cm ⁻¹)
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

Colour₂₅₄ absorbance readings were taken from permeate samples throughout the experimental run. The absorbance reading for the permeate (membrane filtered effluent) varied from 0.0912 to 0.0962 a.u.·cm⁻¹ shown in Figure 4.23 which was better than the microfiltration effluent (0.15-0.3) as indicated in Table 4.1.

Figure 4.23. Colour₂₅₄ of permeate samples
(MBR system; HRT=8hr; SRT=200d)

CHAPTER 5 MEMBRANE PERFORMANCE AND MEMBRANE FOULING PHENOMENON

5.1 MEMBRANE OPERATIONAL PARAMETER AND MEMBRANE CLEANING

5.1.1 Transmembrane Pressure

*Figure 5.1. Variation of TMP in submerged MBR system
(MBR system; HRT=8hr; SRT=200d)*

The transmembrane pressure throughout the operation time of 300 days is recorded and shown in Figure 5.1. It also indicates the type of cleaning employed on the membrane after the onset of substantial fouling. “M” and “C” would represent that mechanical cleaning and chemical cleaning, respectively that was carried out to restore TMP. 10 washings were carried out on the membrane throughout the 300 operational days. The first washing was carried out at -10 kPa as a running-in for the membranes. Subsequently, the membranes were allowed to reach a maximum TMP of -30 kPa and then -60 kPa before membrane washing was conducted. This to study the fouling trend which will be discussed in later chapters.

5.1.2 Membrane Cleaning and TMP Recovery

One of the key advantages of ceramic membrane over polymeric membrane is the ability to withstand repetitious cleaning. The same ceramic membranes were used throughout the operation days of the MBR. The first two and fifth cleanings were done mechanically which meant the membranes were jet-washed with tapwater and then washed with a soft sponge until the surfaces were visually clean. This was to remove the thick brown layer that was observed on the membranes when they were first taken out of the reactor.

After the membranes were re-installed in the reactor, the operation was restarted. However, the suction pressure could not be restored to its initial suction pressure of -1 kPa. Moreover, the suction pressure also increased rapidly and more so after the second mechanical cleaning.

On the third, fourth, sixth and subsequent cleanings, chemical cleaning was done after mechanical washing. The membranes were immersed in 0.5% sodium hypochlorite solution (NaOCl) for an hour with slight agitation, followed by rinsing with tapwater and finally soaking in distilled water with slight agitation for an hour to remove the sodium hypochlorite. The suction pressure was restored to its original initial value of -1 kPa and clearly also maintained a longer period of lower suction pressures.

This clearly proves the presence of a type of fouling of the membrane which could not be removed by mechanical cleaning. However, more tests including morphology of the used membrane surface must be conducted to prove the presence and the nature of this type of fouling. Results of these tests will be discussed in the following chapters.

5.1.3 Membrane Cleaning Effect on Transmembrane Pressure

Table 5.1 breakdowns the days when membrane cleaning was carried out and also the type of membrane cleaning used. It also indicates the operational TMP values before and after the membrane cleanings. The original startup operational TMP for a new membrane was -1 kPa. The first two membrane cleanings done mechanically on day 11 and day 25 could not restore the TMP to the initial startup TMP. This was probably due to

incomplete removal of deposited foulants on the membrane. However, chemical cleanings used on day 34 and day 56 manages to restore the TMP to -1 kPa, stating a more thorough removal of deposited foulants. Mechanical cleaning done again on day 99, like the previous mechanical cleaning done can only restore the TMP to -3 kPa. This proves that the TMP can only restore to its startup values by chemical cleaning. Chemical cleanings performed for the rest of the experimental period on day 120, 163, 204, 246 and 282, all restored the startup TMP of -1kPa.

Table 5.1. TMP before and after membrane cleaning

Day	type of cleaning	pressure before cleaning (-kPa)	pressure after cleaning (-kPa)
11	mechanical	10	2
25	mechanical	30	3
34	chemical	30	1
57	chemical	30	1
99	mechanical	60	3
120	chemical	60	1
163	chemical	60	1
204	chemical	60	1
246	chemical	60	1
282	chemical	60	1

Table 5.2 exhibits the average TMP incremental rate throughout experimental period. This test was divided into three parts with different TMP limit as -10, -30 and -60 kPa. Initially, the TMP incremental rate was $0.82 \text{ kPa}\cdot\text{d}^{-1}$ as the TMP value increased from -1 to -10 kPa within 11 days. Consequently, the membrane undergone mechanical cleaning, and then the TMP value was restored to -2kPa. However, the mechanical cleaning did not completely remove the foulant from the membrane, as the rate of TMP incremental was

increased to $1.14 \text{ kPa}\cdot\text{d}^{-1}$ compared with the previous TMP incremental rate (0.82 kPa). The same phenomena happen to the -30 kPa TMP limit when mechanical cleaning was applied. This observable fact is probably due the reason that mechanical cleaning could only remove the slime layer at membrane surface. On the other hands, chemical cleaning was able to remove more foulant compared with mechanical cleaning as the TMP incremental rate was lower ($1.26 \text{ kPa}\cdot\text{d}^{-1}$) compared with mechanical cleaning ($3 \text{ kPa}\cdot\text{d}^{-1}$). The results illustrate that chemical cleaning is more effective to remove the foulants. However, the pore fouling could not be completely removed by chemical cleaning as the TMP incremental rate after chemical cleaning was increasing. TMP increased from $1.37 \text{ kPa}\cdot\text{d}^{-1}$ in the period of day 120 to day 163 to 1.71 kPa in the period of day 279 to day 300 with 4 more chemical washings in between these two periods.

Table 5.2. Membrane fouling rate

day		initial TMP (-kPa)	final TMP (-kPa)	average fouling rate ($-\text{kPa}\cdot\text{d}^{-1}$)	remarks
from	to				
0	11	1	10	0.82	
11	18	2	10	1.14	mechanical cleaning
11	25	2	30	2.00	mechanical cleaning
25	34	3	30	3.00	mechanical cleaning
34	57	1	30	1.26	chemical cleaning
57	99	1	60	1.40	chemical cleaning
99	120	3	60	2.71	mechanical cleaning
120	163	1	60	1.37	chemical cleaning
163	204	1	60	1.44	chemical cleaning
204	242	1	60	1.55	chemical cleaning
242	279	1	60	1.59	chemical cleaning
279	300	1	37	1.71	chemical cleaning

5.2 BIOMASS FOULING BEHAVIOUR ON MEMBRANE SURFACE IN THE SUBMERGED MBR SYSTEM

MBR is currently one of the most prevailing advanced wastewater treatment technologies. It is devised to overcome the difficulty of separating suspended matter from reacted effluent by gravitational settling in conventional activated sludge processes. This is achieved through a membrane filtration unit permitting the enhanced and consistent extraction of clean water (Bai and Leow, 2002). Despite the many advantages of MBR, the cost of MBR has so far inhibited their widespread inauguration. Owen *et al.* (1995) reported that the most significant factors influencing the overall cost were the power requirements, membrane costs, membrane replacement frequency. Davies *et al.* (1998) also estimated that membrane modules accounted for 85% of the capital cost and membrane replacement accounted for 40% to 75% of the running cost of the MBR. This first factor was overcome with the emergence of submerged MBRs which have lower power consumption (Ueda *et al.*, 1996; Dijk and Roncken, 1997; Gander *et al.*, 2000). With the cost of membranes only a tenth of what it was ten years ago, the remaining factor would be the membrane replacement frequency and that would depend greatly on membrane fouling.

Membrane fouling phenomena presents important limitations on the technology applied. The immediate effect of fouling is to cause a reduction in permeate flux, whilst the long term effect may lead to irreversible fouling from microbial action on the membrane material and the reduction of membrane lifetime. Fouling causes an increase in filtration resistance and it may be expressed by the following equation in accordance to Darcy's law,

$$R = \frac{\Delta p}{\eta J} \quad (5.1)$$

whereby, in a fixed flux system, J , the change in resistance, R is signified by an change in pressure, Δp , assuming a fixed viscosity, η is maintained. In membrane filtration, Δp is often represented as change in TMP.

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 occluded. Inorganic and organic fouling usually respectively refers to scalants and macromolecular species (Judd, 2004). Organic fouling, also characterized as biofouling is the major problem arising from biofilm formation in the pores or on the surface of the membrane (Ridgeway and Flemming, 1996).

Biofouling may be initiated with the deposition of individual bacteria cells on the membrane surface and the cells subsequently multiply and form a biofilm. Biofilm requires very little nutrient to remain viable, hence they readily form on the membrane surface, where membranes are in contact with biomass concentrations generally in the region of 8 to 18 g/l (Judd, 2004). The presence of biofouling could destroy membrane structural integrity and leads to system failure, causing irreversible membrane damage and increasing the operational and maintenance costs (Lim and Bai, 2003). Conversely, the biofilms are thought to provide some protection to the membrane since such films are more selective (i.e. more highly-rejecting) than the membrane itself (Judd, 2004). To sum-up all the different fouling mechanisms, the total filtration resistance, R_t can be expressed as,

$$R_t = R_m + R_p + R_c \quad (5.2)$$

whereby, R_m being the intrinsic membrane resistance this is characteristic to the selected membrane used and therefore leaves the pore resistance, R_p and biofilm or cake resistance, R_c which are variables. From various literature, R_p was claimed as the predominant resistance in membrane fouling (Bouhabila *et al.*, 2001), while others claimed R_c to be (Chang and Lee, 1998; Kim *et al.*, 1998; Lee *et al.*, 2000).

5.2.1 Microfiltration Membrane with Ultrafiltration Quality

From Figure 4.14, the COD values of the permeate remained consistently low at less than $20 \text{ mg}\cdot\text{L}^{-1}$ after an initial startup period and fell to less than $10 \text{ mg}\cdot\text{L}^{-1}$ after 100 days of operation. That would correspond to a high COD removal efficiency of more than 99%. Graphical evidence of TOC removal as elucidated in Figure 4.16 also shows similar results to COD removal. TOC was reduced from an influent wastewater of $334 \text{ mg}\cdot\text{L}^{-1}$ to $3 \text{ mg}\cdot\text{L}^{-1}$ in the permeate which also correspond to a high removal efficiency of more than 99%. The turbidity of the permeate was also compared to other clean water sources as shown in Figure 4.22. Turbidity measured in NTU, of the permeate was consistently at a range of 0.123 to 0.136 NTU, which is even better than local tapwater (0.28 NTU) used for comparison. However, this high quality of treatment is non-typical for the MF membrane with a pore size of $0.9\mu\text{m}$.

5.2.2 Fouling Phenomenon

As filtration proceeds, membrane becomes covered with fouling deposits and the process of this deposition as membrane fouling. Fouling is mostly caused by the deposition of colloidal matters inside the membrane porous structure and the formation of a biofouling layer on the membrane surface. Judd (2004) reported that almost half of all fouling deposits in membrane systems comprise a biofouling layer. Existing technologies can delay biofouling layer formation, but cannot prevent it. Therefore, the mechanisms of biofouling layer formation are studied to improve the understanding of fouling phenomena.

During initial stages of membrane fouling, suspended microbial cells are transported with the fluid flow to solid surfaces (membrane pores and surface), where they may be absorbed. These absorbed cells grow, replicate and excrete extracellular polymer substances (EPS) which binds the cells together. The aggregates of cells, EPS and other particulate matter accumulated at the membrane surface are termed biofilms (Characklis & Marshall, 1990). It have been suggested by most biofilm researchers that biofilms are composed of micro-colonies of microbial aggregates EPS and other particulate matter (Wolfaardt *et al.*, 1994; Bishop & Rittmann, 1995; Costerton *et al.*, 1995). This forms the

basis of the sturdy base fouling layer. After the onset of the biofilms on the membrane surfaces, most foulants which are much larger the membrane pore size (10-50 μ m) (Defrance *et al.*, 2000; Huang *et al.*, 2001) and are thus too big to enter the biofilm will form a fouling “cake layer”.

From Section 5.1.3, it can be clearly deduced that chemical cleaning is needed to restore the transmembrane pressure back to the original TMP value. This can be explain by the fact that mechanical cleaning can only remove the cake layer but only partially remove the biofilm layer. This further reinforced the presence of a sturdy base fouling layer (biofilm layer) and a more volatile surface fouling layer (cake layer). Lewandowski and Beyenal (2004) also reported the presence of a base film and a surface film.

5.2.3 Effects of Biofouling on Membrane Performance

A look at the SEM captures of the membrane surface depicted in Figure 5.2 shows tiny pores on the “base layer” of sizes smaller than the actual membrane pore sizes. This can explain the phemonemon of the MBR system achieving COD/TOC removal efficiency of more than 99%, which is a result of a “UF” biofilm layer. These tiny pores were exposed by “cracks” occurring on the surface layer as shown in Figure 5.3. It can be deducted that uplift arising from the air bubble rising along the membrane surface helps to induce shear stress which constantly “opened up” the cake layer.

Figure 5.2. SEM photo of (left) clean MF membrane surface; (right) same MF membrane with UF-size “pores”

Figure 5.3. SEM photo of (left) clean MF membrane surface; (right) cake layer formation on same MF membrane

To further investigate and proved this phenomenon, COD/TOC tests were conducted on the activated sludge of the MBR system on day 76 when performance was the best. The tests were to try to determine the effective pore size of the MF membrane after a period of usage. The activated sludge withdrawn from the system was filtered through different filters with decreasing pore sizes and results of the COD/TOC of the filtrates were shown in Figure 5.4.

Figure 5.4. COD/TOC results of activated sludge from submerged MBR after filtering through different filter sizes membranes

The following modeling equations were obtained from Figure 5.4 can be used determine the effective membrane pore size after the onset of fouling.

$$\text{pore size} = e^{\left[\frac{(COD-21.5)}{2.9} \right]} \quad (5.3)$$

$$\text{pore size} = e^{\left[\frac{(TOC-3.54)}{0.305} \right]} \quad (5.4)$$

The pore size was determined to be $0.0024\mu\text{m}$ and $0.0022\mu\text{m}$ correlating from a permeate COD value of $4\text{ mg}\cdot\text{L}^{-1}$ and TOC value of $1.667\text{ mg}\cdot\text{L}^{-1}$ on day 76 respectively. Therefore, the effective membrane pore size can be averaged at $0.0023\mu\text{m}$, which is at the high side of UF range.

5.3 BIOFOULING STRUCTURE AND BIOMEMBRANE LAYER

5.3.1 Proposed Biofouling Structure

Note: M – Mechanical cleaning, C – Chemical cleaning

Figure 5.5. Variation of TMP in submerged MBR system
(MBR system; HRT=8hr; SRT=200d)

From the characteristic first 100 day TMP chart in Figure 5.5, there exists a recurring trend as illustrated in Figure 5.6. As explained earlier in this paper, external membrane fouling consists of a biofilm layer and a cake layer but an internal fouling mechanism also existed. Chang et al. (2001) reported this as deposition within the pores of the membrane or simply pore plugging/ fouling. Tracey and Davies (1994) in their experimental works with protein filtration also tried to distinguished between internal (pore blockage or pore constriction) and external (cake formation) fouling.

Figure 5.6. Observed membrane fouling trend

The initial increase in the TMP was a result of the formation of a biofilm layer, a transparent and sticky layer, largely composed of EPS. Subsequent exponential increase in the TMP was caused by the formation of a volatile cake layer which will stabilize at a certain threshold thickness controlled by aeration intensity provided in the system. The ultimate TMP increase would be attributed to the pore plugging and could only be removed by chemical washing. In conclusion, the total TMP of the system can be proposed as:

$$TMP_{total} = TMP_{membrane} + TMP_{biofilm} + TMP_{cake} + TMP_{pore} \quad (5.5)$$

whereby, the total increase in TMP can be expressed as the sum of the increase in TMP of the membrane, biofilm layer, cake layer and pore plugging. By substitution into Equation (5.1 and (5.2),

$$R_t = R_m + R_p + R_c + R_b \quad (5.6)$$

We can conclude that the the total resistance should consists of an additional parameter R_b , biofilm resistance. Based on all the results, the following biofouling structure shown in Figure 5.7 is proposed.

Figure 5.7. Proposed biofouling structure formation on membrane surface

5.3.2 Biomembrane Layer

A comparison before and after chemical cleaning of the membrane were made on the permeate quality. As shown in Figure 5.8, the removal of the biofilm layer greatly reduces permeate quality. When chemical washing was conducted on day 57, the COD and TOC values an hour after the membranes were put back to service were higher than the COD and TOC value of the supernatant (passing 0.45 μ m filter). The reason was that when the more selective biofilm layer was removed, the effective pore size of the ceramic membranes was of 0.9 μ m, hence the higher COD and TOC values than the supernatant.

Figure 5.8. Comparisons of results before and after chemical cleaning of membrane

We can term this biofilm layer which acts as a membrane or rather as a “biomembrane”. The biomembrane is a formation of a dynamic membrane layer that has a higher rejection rate than the membrane itself. The ceramic membrane had served as a supporting structure to that layer of “biomembrane” that has higher selectivity. This is analogous to the morphology of a hollow fibre (HF) asymmetric UF membrane as shown in Figure 5.9. The HF membrane comprises a very thin skin layer on a highly porous thick substructure. The thin skin acts as the selective membrane and the more porous sub-layer acts as a support for the thin, fragile skin and has little effect on the separation characteristics.

Figure 5.9. SEM photo of a HF asymmetric UF membrane

CHAPTER 6 CONCLUSIONS AND RECOMMENDATIONS

This study has revealed that the implementation of submerged MBR system to replace conventional activated sludge process especially in high strength industrial wastewater treatment to be very promising. From the results obtained, the laboratory scale submerged MBR did produce excellent results and stability in the conversion of high strength industrial wastewater into clean water with the advantage of a very low sludge yield.

The submerged MBR showed exceptionally high performance in COD/TOC/TN removal for a high strength industrial wastewater feed of $1000 \text{ mgCOD}\cdot\text{L}^{-1}$, $334 \text{ mgTOC}\cdot\text{L}^{-1}$ and $10 \text{ mgTN}\cdot\text{L}^{-1}$. During the 300 days of continuous operation, COD values of the permeate fell to less than $10 \text{ mg}\cdot\text{L}^{-1}$ after just 100 days. This would represent an excellent organic reduction of 99%. It was found from the study that the biological process of the MBR was responsible for 90-98% of COD removal while the membrane separation contributed to further 2–10% of COD removal. TOC removal also showed identical high reduction percentage of 99%. Nutrients removal efficiency of the industrial wastewater was also high at 98% TN removal. Experimental results indicated that there were little accumulation of SMP and inorganics and it did not affect the quality of the permeate and the operation of the submerged MBR throughout the 300 days of operation period with an SRT of 200 days.

The turbidity value of the permeate was consistently in the range of 0.123 to 0.136 NTU and colour₂₅₄ absorbance readings varied from 0.0912 to 0.0962 a.u. $\cdot\text{cm}^{-1}$. The turbidity values were better than local tapwater used for comparison. Colour₂₅₄ results were also better than those of typical clean water microfiltration effluent despite being treated wastewater effluent. No SS can be obtained from the permeate as compared to $200 \text{ mg}\cdot\text{L}^{-1}$ in the influent industrial wastewater. This high quality of the permeate presented an exciting opportunity for the permeate to be reuse or recycle instead of discharge into open waters.

The high quality of the permeate was found to be due to the formation of a biomembrane that has a higher rejection rate than the membrane itself. The effective pore size of the biomembrane layer on day 76 was determined to be approximated at $0.0023\mu\text{m}$, which is

at the high side of UF range. The presence of the “biomembrane” resulted from a layer biofilm observed using SEM. The total resistance experienced by the membranes in the submerged MBR was determined to be the sum of resistances by the membrane, pore, cake layer and included a new parameter, the resistance of a biofilm layer. The original ceramic membrane had served as a supporting structure to that layer of “biomembrane” that has higher selectivity. This is analogous to the morphology of a hollow fibre asymmetric UF membrane.

The study also found that sludge generation was very low in the submerged MBR system which was one of the major advantages over CAS process. The sludge yield, Y_G of the MBR system was $0.115 \text{ gVSS} \cdot \text{gCOD}^{-1}$ which was twice less than the lower value reported for CAS system. The treatment and disposal of excess sludge usually represent 50-60% of total wastewater treatment cost for CAS processes. Sludge production in the submerged MBR was consistently low at $0.0016 \text{ kgVSS} \cdot \text{d}^{-1}$ after steady state was achieved. In this study, the decreasing tendency of the sludge yield for increasing sludge concentration was also observed. The energy provided by the substrate is largely used for endogenous respiration and thus net growth is limited, even retarded as time progresses. The submerged MBR also revealed the abundant presence of higher microorganisms like that protozoa and metazoa apart from bacteria flocs which helped to reduce the sludge production of the submerged MBR.

The system was monitored for a long period of 300 days to confirm on these results especially, the stability of the submerged MBR system with a long SRT of 200 days. Although the main objective of this research study was achieved, the author would like to recommend further studies on the submerged MBR which could include the followings,

- HRT and SRT could be varied in future works to determine their effects on the performance of submerged MBR system.
- Other types of membranes in materials or different pore sizes should also be tested to verify the phenomenon observed.

- A larger pilot scale size submerged MBR could be studied to determine the effects of upsizing on the phenomenon observed
- A cost evaluation of a pilot scale size submerged MBR could also be done. This would allow for economic comparisons with other conventional techniques.

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