# PHENOL REMOVAL USING CERAMIC MEMBRANE BIOREACTOR

LEONG MUI LAN

MASTER OF SCIENCE

FACULTY OF ENGINEERING AND SCIENCE UNIVERSITI TUNKU ABDUL RAHMAN OCTOBER 2011

### ABSTRACT

# PHENOL REMOVAL USING CERAMIC MEMBRANE BIOREACTOR

### Leong Mui Lan

This research aimed to evaluate the performance of ceramic membrane bioreactor (MBR) in the treatment of phenol containing wastewater. The effects of increasing phenol concentrations on the sludge characteristic and flux performance were investigated. Sludge morphology changed from predominantly normal floc, to Zoogloeal floc and then co-existence of Zoogloeal floc and weak microfloc when activated sludge was exposed to synthetic wastewater without phenol, with 200 mg/L phenol and then with increasing phenol to 600 mg/L. Predominance of bulking floc at 400 mg/L of phenol gave poor sludge settleability, while predominance of dispersed growth of pin-point floc at 600 mg/L of phenol deteriorated the quality of effluent with discharged suspended sludge. Removal of chemical oxygen demand (COD) and phenol in submerged membrane bioreactor (sMBR) up to 85 % and 90 %, respectively, were achieved even though at high concentration of 600 mg/L phenol. On top of that, the transition of normal floc to bulking floc and then microfloc changed the nature of fouled layer from porous cake layer

to non-porous "gel" like fouled layer and then pore clogging fouled layer, respectively. Besides, permeability of the membrane declined with operating time. When the sMBR was operated at higher suction pressure, the membrane fouled at higher rate with higher percentage of relative flux compared to low suction pressure. In mitigating membrane fouling, intermittent bubbling and suction was able to recover the relative flux up to 90 % for sMBR operated at high suction pressure without phenol. Inversely, the flux recovery was found to be higher at low suction pressure if toxic phenol was present in wastewater. Lastly, utilisation of low cost ceramic membrane is practical as it is robust to backwashing.

### ACKNOWLEDGEMENT

Firstly, I would like to express my gratitude to my supervisor, Dr. Lee Khia Min, for all she has done for me. I deeply appreciate her efforts in helping and guiding me. Her invaluable guidance, constructive suggestions and constant encouragement throughout the study period have greatly motivated me along the process to produce this report. I would also like to express my deepest gratitude to Dr. Lai Soon Onn and Dr. Ooi Boon Seng, for their continuous and valuable advice, comments and suggestions throughout the research work.

I would like to give special thanks to Universiti Tunku Abdul Rahman for awarding me research fund during my Master's program at Faculty of Engineering and Science.

I am very grateful to laboratory officers and other doctoral and master students for their valuable advice and suggestions throughout the study. A special note of appreciation is also addressed to all my friends for the inspiration and encouragement.

Lastly, thanks for my family for always supporting me and encouraging me throughout my master's study. Their unconditional love, support and encouragement have made completion of my research and study possible.

### **APPROVAL SHEET**

This dissertation/thesis entitled "**PHENOL REMOVAL USING CERAMIC MEMBRANE BIOREACTOR**" was prepared by LEONG MUI LAN and submitted as partial fulfillment of the requirements for the degree of Master of Science at Universiti Tunku Abdul Rahman.

Approved by:

(Dr. Lee Khia Min) Date:..... Supervisor Department of Civil Engineering Faculty of Engineering and Science Universiti Tunku Abdul Rahman

(Dr. Lai Soon Onn) Date:..... Co-supervisor Department of Chemical Engineering Faculty of Engineering and Science Universiti Tunku Abdul Rahman

## FACULTY OF ENGINEERING AND SCIENCE

## UNIVERSITI TUNKU ABDUL RAHMAN

Date: \_\_\_\_\_

# SUBMISSION OF FINAL YEAR PROJECT/ DISSERTATION/THESIS

It is hereby certified that <u>Leong Mui Lan</u> (ID No: <u>08UEM06880</u>) has completed this final year project/ dissertation/ thesis\* entitled "<u>Phenol Removal Using</u> <u>Ceramic Membrane Bioreactor</u>" under the supervision of <u>Dr. Lee Khia Min</u> (Supervisor) from the Department of Civil Engineering, Faculty of Engineering and Science, and <u>Dr. Lai Soon Onn</u> (Co-Supervisor)\* from the Department of Chemical Engineering, Faculty of Engineering and Science.

I understand that University will upload softcopy of my final year project / dissertation/ thesis\* in pdf format into UTAR Institutional Repository, which may be made accessible to UTAR community and public.

Yours truly,

(Leong Mui Lan)

\*Delete whichever not applicable

## DECLARATION

I hereby declare that the dissertation is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UTAR or other institutions.

Name \_\_\_\_\_

Date \_\_\_\_\_

# TABLE OF CONTENTS

# Page

ABSTRACT	ii
ACKNOWLEDGEMENTS	iv
APPROVAL SHEET	v
SUBMISSION OF THESIS SHEET	vi
DECLARATION	vii
TABLE OF CONTENTS	viii
LIST OF TABLES	X
LIST OF FIGURES	xi
LIST OF ABBREVIATIONS/NOTATION/GLOSSARY OF TERMS	XV

# CHAPTER

1.0	INTRODUCTION		
	1.1	Industrial Wastewater	1
		1.1.1 Phenol in Industrial Wastewater	2
	1.2	Overview of Membrane Technology	4
	1.3	Membrane Bioreactor	6

2.0	LITE	ERATUR	<b>REVIEW</b>	9
	2.1	Pheno	l Removal	9
		2.1.1	Activated Sludge Process	15
	2.2	Memb	rane Bioreactor Technology	18
	2.3	Advan	tages and Disadvantages of Submerged	20
		Memb	rane Bioreactor	
	2.4	Subme	erged Membrane Bioreactor Operations	22
	2.5	Factor	s Affecting Membrane Fouling	25
		2.5.1	Biofouling	26
		2.5.2	Organic Fouling	28
		2.5.3	Inorganic Fouling	29
	2.6	Mitiga	tion of Membrane Fouling	31
		2.6.1	Role of Membrane Materials in Preventing	
			Fouling	32
		2.6.2	Hydrodynamic Controls in Mitigating Membrane	
			Fouling	34
			2.6.2.1 Role of Flux	34
			2.6.2.2 Role of Aeration	35
		2.6.3	Biological Controls in Mitigating Membrane	
			Fouling	37
		2.6.4	Chemical Controls in Mitigating Membrane	
			Fouling	40
	2.7	Memb	rane Cleaning	42
	2.8	Proble	m Statements	44

2.9	Objectives

<ul> <li>3.1 Preliminary Studies</li> <li>3.1.1 Specific Oxygen Uptake Rate (SOUR)</li> <li>3.1.2 Phenol Volatilisation Test</li> <li>3.2 Acclimatisation of Activated Sludge towards Phenol</li> </ul>	48 48 50 51 54 56 57
<ul> <li>3.1.1 Specific Oxygen Uptake Rate (SOUR)</li> <li>3.1.2 Phenol Volatilisation Test</li> <li>3.2 Acclimatisation of Activated Sludge towards Phenol</li> </ul>	48 50 51 54 56 57
<ul><li>3.1.2 Phenol Volatilisation Test</li><li>3.2 Acclimatisation of Activated Sludge towards Phenol</li></ul>	50 51 54 56 57
3.2 Acclimatisation of Activated Sludge towards Phenol	51 54 56 57
-	54 56 57
3.3 Sludge Characteristics Study	56 57
3.4 Submerged Membrane Bioreactor (sMBR) Set-up	57
3.4.1 Membrane Characteristics	
3.4.2 Submerged Membrane Bioreactor (sMBR)	
Operation	59
3.5 Flux Characteristics Study	60
3.6 Membrane Scouring and Cleaning	61
3.7 Effluent Analytical Methods	63
4 Results and Discussion	64
4.1 Preliminary Studies	64
4.1.1 Specific Oxygen Uptake Rate (SOUR)	64
4.1.2 Phenol Volatilisation	67
4.2 Acclimatisation of Activated Sludge towards Phenol	68
4.2.1 Daily Effluent Analysis for COD and	
Phenol Removal	69
4.2.2 Profile Study for COD and Phenol Removal	71
4.3 Sludge Characteristics at Varying Influent Phenol	
Concentrations	76
4.3.1 Particle Size Distribution and	
Sludge Morphology Observations	77
4.3.2 Mean Floc Size	84
4.3.3 Sludge Settleabilities and Sludge Concentrations	86
4.4 Membrane Bioreactor	91
4.4.1 Membrane Permeability	92
4.4.2 Flux Characteristics at Varying Suction Pressures	93
4.4.3 Effluent Characteristics	103
4.4.3.1 Synthetic Wastewater Containing Base-mix	
(Without Phenol)	103
4.4.3.2 Synthetic Wastewater with Varying Phenol	
Concentrations	104
4.5 Effect of Sludge Characteristics on Membrane	
Permeabilities	106
4.6 Mitigation of Membrane Fouling	111

5	Conclusions	121
Refe	erences	125
Appendices		141

# LIST OF TABLES

Table		Page
3.1	Feeding composition of synthetic wastewater for batch	53
	reactor during acclimatisation	
4.1	Indication of SOUR values on system condition	66
4.2	Mean floc diameters at varying feed compositions	84
4.3	The effect of increasing phenol concentration in synthetic	98
	wastewater on the fouling rate for sMBR operated at	
	varying suction pressures	
4.4	COD and phenol concentrations of sMBR fed with	103
	synthetic wastewater containing base-mix and increasing	
	phenol concentration at low and high suction pressures	
4.5	The effect of feeding composition on the mean floc size	107
	and the membrane permeability	

# LIST OF FIGURES

Figure		Page
1.1	Molecule structure of phenol	3
1.2	Filtration spectrum	5
1.3	(A) submerged and (B) external configurations of MBR	6
2.1	Phenol degradation	14
2.2	Flux and TMP relationship to determine the critical flux	25
3.1	Illustration for the specific oxygen uptake rate (SOUR) study	49
3.2	Illustration for the phenol air stripping test	50
3.3	Schematic illustration of batch operation during acclimatisation	53
3.4	Illustration for sludge characteristics study	55
3.5	Experimental set-up of MBR	57
3.6	Type of membrane used in MBR operation	58
3.7	SEM result for ceramic filter	58
3.8	Schematic illustration of MBR operation	60
4.1	Specific Oxygen Uptake Rate (SOUR) of activated sludge	65
	at varying phenol concentrations	
4.2	Volatilisation test of phenol at varying phenol concentrations	67
	under sustain aeration	
4.3	Effluent COD and effluent phenol in SBR fed with synthetic	69
	wastewater containing phenol at increasing concentration	

- 4.4 Profiles of (A) phenol, (B) COD and (C) DO in SBR fed with 71 synthetic wastewater containing 200, 400 and 600 mg/L influent phenol concentrations
- 4.5 Sludge size distribution when activated sludge acclimatised to 78 synthetic wastewater containing base-mix, and increasing phenol concentrations
- 4.6 Relative frequency histogram for floc equivalent diameter when 79 activated sludge acclimatised to synthetic wastewater containing (A) Base-mix (B) 100 mg/L (C) 200 mg/L (D) 300 mg/L (E) 400 mg/L and (F) 600 mg/L influent phenol concentration
- 4.7 Microscopic observation (10 X magnification) of the activated 80 sludge acclimatised to synthetic wastewater in the reactor containing: (A) base-mix (B) 100 mg/L (C) 200 mg/L (D) 300 mg/L (E) 400 mg/L (F) 600 mg/L influent phenol concentration
- 4.8 Sludge settleability and sludge concentration of activated 86 sludge acclimatised to synthetic wastewater containing basemix and with increasing phenol concentrations
- 4.9 Effluent suspended solids of activated sludge acclimatised to 87 synthetic wastewater containing base-mix and with increasing phenol concentrations

xii

- 4.10 Membrane permeability of the ceramic membrane in pure water 92 and mixed liquor at varying suction pressures
- 4.11 Relative flux of the ceramic membrane with respect to the 95 operation time at varying suction pressures in sMBR fed with synthetic wastewater containing: (A) base-mix (B) 200 mg/L
  (C) 400 mg/L (D) 600 mg/L influent phenol concentrations
- 4.12 Illustrations of the fouled membranes operated at (A) -7.5 kPa 101 and (B) -30 kPa
- 4.13 Comparison of relative flux at varying bubbling modes for 112
   sMBR fed with synthetic wastewater containing base- mix
   operated at (A) -7.5 and (B) -30 kPa
- 4.14 Comparison of relative flux at varying bubbling modes for 113
  sMBR fed with synthetic wastewater containing 200 mg/L
  influent phenol concentration operated at (A) -7.5 and (B) -30
  kPa
- 4.15 Comparison of relative flux at varying bubbling modes for 114 sMBR fed with synthetic wastewater containing 400 mg/L influent phenol concentration operated at (A) -7.5 and (B) -30 kPa

- 4.16 Comparison of relative flux at varying bubbling modes for 115
  sMBR fed with synthetic wastewater containing 600 mg/L
  influent phenol concentration operated at (A) -7.5 and (B) -30
  kPa
- 4.17 Illustrations for the intermittent scouring effect along 119 membrane surface operated at (A) -7.5 kPa and (B) -30 kPa

# LIST OF ABBREVIATIONS

cBOD	Carbonaceous biochemical oxygen demand
COD	Chemical oxygen demand
DO	Dissolved oxygen
DOE	Department of Environment
EPS	Extracellular polymeric substances
F: M	Food to microorganism ratio
HRT	Hydraulic retention time
J/Jo	Relative flux
MBR	Membrane bioreactor
MLSS	Mixed liquor suspended solids
MLVSS	Mixed liquor volatile suspended solids
PAC	Powdered activated carbon
PAN	Polyacrylonitrile
PE	Polyethylene
PES	Polyethersulfone
PVDF	Polyvinylidene fluoride
SBR	Sequencing batch reactor
sMBR	Submerged membrane bioreactor
SMP	Soluble microbial products
SOUR	Specific oxygen uptake rate
SRT	Sludge retention time
SVI	Sludge volume index

TMP	Transmembrane pressure
TOC	Total organic compound
TTF	Time to filter

### **CHAPTER 1**

### INTRODUCTION

Water is vital for the existence of living organisms. However, rapid population growth and economic development in most of the countries have resulted in limited availability of fresh water resources including Malaysia. It was reported that about 98 percent of Malaysia fresh water supply comes from surface water with minimal treatment from household and industrial discharges (Asia-Pacific Economic Cooperation, 2009). Therefore, the issue of raw surface water contamination and effluent qualities due to the excessive pollution from household and industrial development has become a worldwide concern (Smith *et al.*, 2005 and Philips *et al.*, 2003).

### **1.1 Industrial wastewater**

The composition of wastewater varies widely depending on the sources. In general, wastewater may contain water, pathogen, organic and inorganic particles, macro-solids, gases, emulsion and toxins. Wastewater comprises of liquid wastes that are discharged from several sources especially domestic and industrial sources. It is characterised in terms of physical, chemical and biological compositions. Chemical compositions such as contents of organic, inorganic and gases are the main consideration to generate clean surface water. These chemical wastes can adversely affect the quality of water and encompass a wide range of potential contaminants and concentrations. For biological composition, the elimination of pathogen is crucial in wastewater treatment as this may cause the spread of disease. Thus, the discharge from industrial wastewater is of important to increase the usability of water for ordinary purpose or into certain extent to prevent the occurrence of hazard to public health via chemical poisoning or pathogen infection.

### **1.1.1** Phenol in Industrial Wastewater

Toxic organic constituent is not a naturally occurring substance in an aquatic ecosystem. When these wastes enter the stream, they will stimulate adverse effect towards the aquatic life. The major contributors to toxic pollution are herbicides and pesticides from agriculture and industrial compounds.

Phenol and its degradation by-products in the environment are toxic aquatic pollutants. Phenol is a potential and known human carcinogen, and is closely related to human health concerned, even at low concentration.

Phenol is a molecule which contains hydroxyl group attached to the benzene ring structure (Figure 1.1). Phenol is slightly acidic as the molecule has weak tendency to lose  $H^+$  ion from the hydroxyl group to form highly water-soluble phenoxide anion  $C_6H_5O^-$ . Since phenol is relatively soluble and stable in water, its degradation to reach safety levels of 0.1 to 1 mg/L is hard (L'Amoura *et al.*, 2008).

However, phenol readily degrades in water surface due to the exposure to sunlight, but this degradation takes longer time in deep soil and groundwater (Bhatti *et al.*, 2002).



Figure 1.1: Molecule Structure of Phenol

Phenol is commonly found in industrial compound in environmental matrices. It is widely used in various kinds of industries such as petroleum refineries, gas and coke oven industries, pharmaceuticals, explosive manufacture, phenol-formaldehyde resin manufacture, plastic and varnish industries. Phenol enters the environment during the manufacturing and processing steps. Thus, it is common to discover phenolic pollutants in the raw water of these industries. Phenol concentration ranging from 50 to 2000 mg/L has been reported in many industrial wastes produced in industries and operations (Garcia *et al.*, 1997; Jusoh and Razali, 2008; Kumaran and Paruchuri, 1996).

Proper treatment is required before the wastewater is discharge to external environment since high phenol concentration is toxic to living organisms. The Department of Environment (DOE) Malaysia has limited the phenol concentration at 0.001 and 1 mg/L for industrial wastewater discharge into any inland wastewater depending on the catchment areas (Environmental Quality Act, 1974). There are two common methods used to eliminate the phenol contents in wastewater, i.e., physico-chemical and biological methods. However, most of the physico-chemical methods cause secondary problems in the effluents such as the generation of chlorophenol if chlorination is used in the phenol degradation (Marrot *et al.*, 2006). Besides, the physico-chemical method to degrade phenol usually involves high capital. Thus, the biological method such as activated sludge process has been used extensively in phenol removal to overcome the weakness of secondary pollution and high capital in the physico-chemical method.

### **1.2** Overview of Membrane Technology

Membrane technology has received great attention as an alternative to conventional water treatment. Membrane treatment utilises a semi permeable membrane for the isolation of suspended and dissolved solids in water. There are two general membrane separation processes, i.e., electrical-driven and pressuredriven. In electrical driven membrane process, current is employed to remove ions across the membrane, while purified water is retained in the system. On the other hand, pressure-driven process makes use of hydraulic pressure to drive water flow through the porous membrane. Pressure-driven membrane allows water to flow through the membrane, while inorganic, organic, silica, suspended solids and microorganisms are trapped within the pore of the membrane. Pressure-driven membrane processes include microfiltration, ultrafiltration, nanofiltration and reverse osmosis. Microfiltration and ultrafiltration serve as porous barriers and are often used to remove large organic molecules, colloidal particles and most of the bacteria (Figure1.2). Membranes used in wastewater treatment are typically made of polymeric, ceramic and other metal oxide materials. The selection of the membrane depends on the membrane properties and the application. For example, cellulose polymers are widely used due to its low cost. Polyamide membrane employed in low pressure system is more chemically resistance, has longer lifespan, and is able to remove most of the dissolved salts and organics. Ceramic membrane is one kind of metal oxide membrane and commonly used in industrial processes due to its high temperature resistance (EPRI, 1997).



Figure 1.2: Filtration Spectrum (EPRI Community Environmental Center, 1997)

### **1.3** Membrane Bioreactor

Membrane bioreactor (MBR) is a biological wastewater treatment technology coupled with membrane filtration technology. It involves the combination of membrane filtration and activated sludge processes for wastewater treatment. The coupling of activated sludge process with membrane filtration technology has gained popularity as advanced wastewater treatment alternative to conventional activated sludge process due to several advantages such as small footprint, high mixed liquor suspended solids (MLSS) operation, and thus produces good quality effluent (Sun *et al.*, 2006; Rosenberger *et al.*, 2002; Muller *et al.*, 1995; Ueda *et al.*, 1999). In general, MBRs are classified into two types, i.e., submerged MBR (sMBR) and external MBR (Figure 1.3).



Figure 1.3: Submerged (a) and External (b) Configurations of MBR

The sMBR is more popular as compared to the external MBR due to its simplicity of the design and lower energy consumption. In the sMBR, the membrane module is immersed into the bioreactor to act as solid-liquid separator. sMBR is able to produce high quality effluent (Judd, 2008). Bubbles are introduced in the submerged MBR to suspend the activated sludge and maintain oxygen concentration for the biodegradation process. Moreover, bubble aeration in the sMBR consumes only low energy to limit the deposition of foulants on the membrane surface. To achieve the same purpose, external MBR requires the need of high rate recirculation pumps (Judd, 2005).

The major obstacle for the sMBR remains to excessive membrane fouling. The occurrence of fouling is very complicated and often involves many aspects like physical, chemical and biological properties. Factors that influence the membrane fouling are the nature of the feed, membrane properties, biomass characteristics and hydrodynamic environment experienced by the membrane (Le-Clech *et al.*, 2006). The loss of membrane permeability due to fouling requires frequent cleaning of membrane, which further reduces membrane lifespan and lastly increases the operating and maintenance costs (Sablani *et al.*, 2001).

The challenge of the application of MBR is on how to control the membrane fouling during its operation. Overall, there are five common fouling prevention and control strategies: influent pre-treatment, membrane characteristics, hydrodynamic control of operation, chemical addition control, and biological control (Le-Clech *et al.*, 2006; Meng *et al.*, 2006; Meng *et al.*, 2007; Nywening and Zhou, 2008; Ying and Ping, 2006).

Influent pretreatment such as the usage of bar screening can prevent potential foulants from interrupting the filtration process. The effect of membrane characteristics such as pore size distribution has been extensively studied since 1990s. It was found that narrow pore size distribution is able to minimise fouling both in MBR and conventional membrane separation processes (Meng *et al.*, 2009). In view of the membrane properties which are usually determined by manufacturer, the filtration efficacy can be prolonged through the control of the biomass characteristics and hydrodynamic operation. Operating condition and feedwater characteristics indirectly affect the fouling behavior through the modification of sludge characteristics. Thus, the control of sludge retention time (SRT), hydraulic retention time (HRT), aeration intensity and permeate flux have been widely studied to minimise the occurrence of fouling (Chae *et al.*, 2006, Guo *et al.*, 2008; Zhang *et al.*, 2006).

### **CHAPTER 2**

### LITERATURE REVIEW

### 2.1 Phenol Removal

Phenol is one of the most common organic pollutants in water stream. It is known as potential human carcinogen, and is closely related to human health concerned, even at low concentration. According to Jordan et al. (2002), the production rate of phenol is estimated to be about 6 million ton per year, with increasing production globally. Phenol is manufactured through several processes such as Hock process (three-step cumen synthesis and oxidation processes), reaction of benzensulfonate with caustic soda, sodium benzensulfonate alkaline fusion or oxidation of toluene via benzoic acid (Jordan et al., 2002; Schmidt, 2005; Franck and Stadelhofer, 1989; Wittcoff and Reuben, 1996; Weissermel et al., 1997). Phenol has a wide range of applications such as disinfectant, preparation of medicine, peptizing agent, extracting solvent, production of phenolic resins (35 % of phenol applications), monomer for epoxy resins (28 % of phenol applications) and monomer for nylon-6 (16 % of phenol applications) (Guido et al., 2008). Therefore, phenol containing wastewater must not be discarded into open water body without treatment due to its toxic nature.

In recent review, phenol is usually separated from water stream through separation processes such as steam distillation, extraction, adsorption, membrane pervaporation and membrane based solvent extraction. Besides, phenol may also be abated in water solution through oxidation and biofiltration (Guido *et al.*, 2008). However, physical and chemical removal of phenol may generate secondary by-products that will eventually enter the environment as toxic aquatic pollutants.

Physical-chemical method such as ozonisation, adsorption, reverse osmosis, electrolytic oxidation,  $H_2O_2$ , and photocatalysis, are commonly used in treating phenol containing wastewater. The reason of chemical processes using oxidising agents is to effectively reduce the content of phenolic compounds in the wastewater. During the oxidation process, oxidising agents transform these toxic substances to less harmful elements which are safe to be discharged to the environment.

Ozone is one of the strongest oxidants technically applied because it is readily available, water-soluble and generally leaves to less-toxic substance. Ozone is a powerful oxidising agent and can effectively transform phenolic compounds to the products that are less fouling potential than the parent compounds. Ozone molecules can react with electron-rich sites of the organic molecules, or by indirect pathway whereby the hydroxyl radicals resulting from the reaction of ozone act as the oxidants for the next chain reactions. In the process, ozone molecules attack the nucleophilic sites and unsaturated bonds of the phenol to give intermediates such as hydroquinone, benzoquinone and catechol, while oxalic acid becomes the main product (Gimeno *et al*, 2005).

Photocatalysis is the acceleration of a photoreaction in the presence of a catalyst. This greatly enhances the oxidation of phenol by UV irradiation. Electron-hole pairs created by the catalyst will generate free radicals to undergo secondary oxidation or reduction reaction. Oxidation of phenol or other organic contaminants can be done by coating titanium dioxide nanoparticles onto magnetic particles, while agitating and exposing the contaminants to UV light. Titanium dioxide photocatalysis has been greatly investigated for its application in the removal of pollutant such as phenol due to its low cost, non-toxic, and resistant to photo-corrosion with high oxidation strength (Thompson and Yates, 2006).

Adsorptive process with the use of activated carbon as an adsorbent is widely applied in the removal of contaminants in liquid streams or wastewater (Radovic *et al.*, 2000). Adsorptive process involves a series of activities such as saturation, adsorption, desorption and regeneration. Two general types of activated carbon such as granular activated carbon and activated carbon fiber are used to remove organic pollutant such as phenol. Adsorption of phenolic waste on the activated carbon is greatly influenced by the carbon pore size distribution and the property of the phenol as an adsorbate. Phenolic compounds undergo oligomerisation on the activated carbon surface when oxygen is present in the test environment and appreciable increases in the adsorptive capacity. Laszlo et al. (2003) proposed the interactions between carbon surface and phenol in three stages: (i) electron donor-acceptor interactions between aromatic phenolic ring and the basic surface oxygen (carbonyl group); (ii) dispersion among the aromatic phenolic ring and the pi electrons of the carbon structure; (iii) electrostatic attraction and repulsion in the presence of ions. Regeneration efficiency of the activated carbon has been a major concern in the activated carbon usage. Some of the phenols and its derivatives may adsorb on carbon irreversibly, where the irreversibly adsorbed phenol cannot be desorbed in water or by heating process (Terzyk, 2007). This leads to the difficulty in the regeneration of adsorbent such as activated carbon despite various methods such as thermal regeneration (using steam, hot water or heated nitrogen and microwave heating technology) and chemical regeneration (using pH-swing or solvent extraction) were studied and developed (Ama et al., 2004; Bercic et al., 1996).

The use of chemicals such as hydrogen peroxide alone or hydrogen peroxide coupling with iron (II) salt (Fenton reaction) are the common noncatalytic and homogeneous catalytic destructions of phenol through oxidation. Hydrogen peroxide ( $H_2O_2$ ) has high oxygen content, low cost, and it acts as a strong oxidant in both acidic and basic solutions. Iron (II) salt in Fenton reaction can increase the reactivity of hydrogen peroxide to produce high fluxes of hydroxyl radicals which can oxidize phenol and other organic compounds in solution (Neyens and Baeyens, 2003). Besides hydrogen peroxide, Throop (1975, 1977) had reported alternative oxidation procedures for the elimination of phenol through oxidation by chlorine, chlorine dioxide and potassium permanganate. Unfortunately, these methods are not adopted due to the formation of secondary chlorinated organic compounds and the dispersion of manganese compounds. Furthermore, the costs of these chemicals are expensive and the pHs of the reactions need to be controlled precisely.

In biological treatment process, the microorganisms degrade phenol into other non-toxic chemical compounds. Aerobic biodegradation of phenol is common and occurs through the main intermediate, which is catechol derivatives; followed by its cleavage via ortho- and meta-oxidation (Figure 2.1). Extradiol opening of the catechol derivatives contributes to the formation of acetaldehyde and pyruvate, while intradiol opening of the catechol derivatives form succinate and pyruvate as final products (Barrios-Martinez *et al.*, 2006). All these products are eventually being as carbon sources through the metabolism of microorganism.



Figure 2.1: Phenol Degradation (Barrios-Martinez et al., 2006)

### 2.1.1 Activated Sludge Process

Activated sludge is a natural microbial consortium consisting of microorganisms, non-living organic materials, and inorganic compounds. Activated sludge process is defined as a system where the biological flocs are continuously circulated to contact with each other, while oxidise the organic contents in the presence of oxygen (Lawrence *et al.*, 2009). Types of microorganisms used in the biodegradation of wastewater are selected based on the tolerance of biomass to toxic compounds, and the variable environment which achieve desirable treatment. In the past, most of the researches conducted involved single microbial species which may limit in field applications as variety of contaminants are present in the waste (Guido, 2008).

Two common phenol degrading bacteria are *Rhodococci* and *Pseudomonades*. Biological treatment of the phenolic compounds is not easy because at either low concentration (lower than 200 mg/L), or at sufficiently high phenol concentration, the growth rate of the microorganisms can be inhibited, which further retarded the metabolic capability of microorganisms using phenol as a substrate for their growth (Marrot *et al.*, 2006). The presence of toxicants such as phenol can result in the deflocculation, which causes settling problems in the sedimentation tank. Thus, to achieve satisfactory phenol removal efficiency, phenol concentration needs to be maintained below the threshold limits and acclimatisation of the microorganisms to the toxic wastewater is a must.

15

Acclimatised activated sludge degrades phenolic compounds more efficiently than the pure strains by one or more than two orders of magnitude faster (Lawrence *et al.*, 2009).

Marrot *et al.* (2006) reported that mixed cultures showed better quality for phenol degradation than the pure culture. The contact of co-aggregative cell (floc formation) in the mixed culture enables the mutualistic relationship for biofilm growth and enhances the overall development of the microbial community in the system. Long Jiang et al. (2006) had proven the advanced performance of mix culture in degrading phenol containing waste compared to pure strain. The coaggregation of two bacterial strains (Propioniferax-like PG-01 and Comamonas sp. PG-08) degraded phenol at an initial phenol concentration of 250 mg/L was found to be faster than each strain did separately. Besides, Saravanan et al. (2008) also investigated the biodegradation of phenol by mixed microbial culture in treating synthetic waste containing phenol. Mixed microbial culture, isolated from the sewage treatment plant was selected to study in batch shake flask using synthetic phenol in the concentration range of 100 to 500 mg/L. It was found that increasing phenol concentration from 100 to 500 mg/L increased the lag phase from 0 to 66 hours and prolonged the biodegradation process from 84 to 354 hours. They concluded that the biodegradation rate of phenol decreased with increasing initial phenol concentration.

Other than microbial community, the floc structures also play an important role in determining the phenol degradation efficacy. In general, floc structure is classified into three groups (ideal normal, bulking and pinpoint floc) based on the balance between floc-forming and filamentous bacteria (Gray, 1990). Normal floc showed a good balance between floc-forming and filamentous bacteria with bigger floc size of more than 100  $\mu$ m, with sludge volume index (SVI) of about 70 mL/g. On the other hand, proliferation of filamentous bacteria was observed in bulking sludge with floc size more than 100 µm but at high SVI value. Conditions such as dissolved oxygen (DO), low pH, increasing sulphides concentration, and nutrient deficiency will stimulate the growth of filamentous species (Gerardi, 2002). Despite filamentous microorganism gives settleability problem, it can still be used in wastewater treatment. The other kind of floc, pinpoint floc consists of floc-forming bacteria without a filament backbone and usually less than 50 µm in diameter (Richard et al., 2003). Dispersed growth or pin-point floc occurs very often in industrial wastewater due to the high organic loading. The existence of pin-point floc gives low SVI with turbid effluent which further deteriorates the treatment efficiency.

In recent years, a combination of the membrane filtration process and the biodegradation process in the biological system, called membrane bioreactor (MBR), has been employed to treat toxic waste such as phenol. Barrios-Martinez *et al.* (2006) and Marrot *et al.* (2006) studied the feasibility of MBR system to treat high phenol content in synthetic wastewater. Phenol was used as the limiting

substrate in their studies. The performance of the MBR was evaluated through the membrane performance and the biodegradation of phenol. It was found that the acclimatised activated sludge was able to completely remove the phenol as high as 50 g/day and achieved the steady state in just a few hours. They concluded that acclimatisation was important to support the microorganism to ensure that they had the necessary enzymatic material to degrade phenol and to reveal a new population which was adapted to phenol and able to consume phenol as substrate.

### 2.2 Membrane Bioreactor (MBR) Technology

Membrane technology has gained great interest in the past few years and has wide applications in the treatment of wastewater and water reclamation. Membrane bioreactor (MBR) is named after the two major processes in the reactor, which are biological wastewater treatment process coupled with membrane filtration technology. The activated sludge process is employed for the biological waste degradation, while the treated effluent is subjected to membrane separation. Due to the more stringent in effluent discharge standards in most of the countries, the MBR technology has become an attractive alternative to conventional activated sludge systems, which is possible to be used for expansion and upgrading of the existing systems (Ahn *et al.*, 1999). There are two common configurations of MBR, i.e., external MBR and submerged MBR. The membrane can be either fixed externally to the reactor and operated under pressure, or submerged in the reactor and operated under vacuum.

For external MBR, cross-flow membranes are used and the membrane module is located apart from the activated sludge reactor. This can ideally control the fouling by reducing the deposition of foulants on the membrane surface (Chang *et al.*, 2002). However, the external MBR usually consumes more energy and requires larger footprint. Furthermore, the tubular membrane used in the cross flow MBR has lower packing density and is more expensive (Rosenberger *et al.*, 2002). Owing to this, mixed liquor is pumped into the tubular membrane module to obtain the required high shear stresses to reach high permeate flux values (Lacoste *et al.*, 1993). Consequently, high circulation velocity is always needed in the tubular membrane that contributes eventually to high head loss and high energy consumption (Krauth and Staab, 1993).

On the contrary, low cost capillary and hollow fibre membranes are common in most submerged MBR. This kind of membranes has higher packing density and can be operated at lower transmembrane pressure (TMP). As a result, the operation flux can be reduced and energy consumption is less. Furthermore, the coarse bubbles generated from the aeration in the reactor are utilised to maintain sufficient oxygen for the microorganism metabolism, and create shear stress to suppress the deposition of foulants on the membrane surface. This eliminates the requirement of high rate circulation pump as in external MBR (Judd, 2004). Besides, submerged MBR has lower tendency towards fouling, and contributing to less cleaning and replacement of membrane (Cote and Thompson, 2000; Gander *et al.*, 2000). In view of the low energy consumption, together with less fouling tendency of the membrane, submerged MBR is more popular in the application in domestic and industrial wastewater treatment.

### 2.3 Advantages and Disadvantages of Submerged MBR

MBR technology is actively used for municipal and wastewater treatments as this system can produce excellent effluent quality for water reuse or recycling (Liao *et al.*, 2006; Meng *et al.*, 2009; Judd, 2006; Yang *et al.*, 2006). High quality effluent is usually accomplished by the membrane filtration with suitable pore size, resulting in low turbidity, suspended solids and biochemical oxygen demand with bacteria free effluent.

Submerged MBR (sMBR) is well-known for its compact and small footprint build-up. The introduction of MBR has eliminated the need for secondary clarifier, and thus minimised the problems associated with sludge settling (Defrance *et al.*, 2000; Rosenberger *et al.*, 2002; Ueda and Hata, 1999). Besides, the membrane module immersing in the reactor can retain the biomass. As the MBR is able to retain the biomass completely in the reactor, it can be operated at high biomass concentration with low food to microorganism (F: M)
ratio. This minimises the sludge production in the MBR as the biomass is mostly lost through endogenous degradation (Sun *et al*, 2006). When the excess sludge production is minimised, the organic removal efficiency increases accordingly to give effluent with low COD strength.

Fluctuation of the organic loading to the reactor is common and this inconsistency in loading always affects the biological treatment efficiency. Fortunately, this shock loading seldom happens in MBR as high MLSS in MBR is able to cope with the shock loading with slight adjustment on the F: M ratio. Therefore, the introduction of toxicant, such as phenol, can be degraded more effectively in the MBR.

Due to the above mentioned advantages, MBR has gained high attention in water and wastewater treatment. The superior performance of the MBR has attracted increasing number of researchers to further improve its treatment efficacy. However, the membrane fouling and cost of membrane remain the major obstacles for wide application of this technology.

Membrane fouling is associated with the deposition of foulants on the membrane surface which further reduces the operational flux. This leads to high energy consumption and chemical requirement to clean the membrane and recover the ideal flux. Besides, membrane life-span may be shortened as irreversible fouling due to the pore blocking is hardly removed by physical or chemical cleanings. For the last few years, even though the fouling factors in the MBR such as sludge characteristics, operational parameters, membrane materials and feedwater characteristics were considerably reviewed, the information of the complex nature of foulants and activated sludge properties on fouling are still the driving force for researcher to find out the effective approaches to solve the current problems (Chang *et al.*, 2002; Le-Clech *et al.*, 2006; Meng *et al.*, 2009).

# 2.4 Submerged Membrane Bioreactor Operations

MBR has been receiving great attention in past few years, even though the fouling nature is not yet fully understood. It is important to note that with proper operation of the system, better control of membrane fouling can be achieved. According to Meng *et al.* (2009), operating conditions such as sludge retention time (SRT), hydraulic retention time (HRT), aeration and permeate flux were the key determinants to prolong the optimal operation of the MBR.

Proper controls of SRT and HRT are important to ensure optimisation of the MBR operation (Barker and Stuckey, 1999; Grelier *et al.*, 2006). Based on several studies, it was concluded that the reduction of SRT and HRT might increase the transmembrane pressure (TMP), which increased the fouling of MBR and contributed to poor performance of MBR (Ahmed *et al.*, 2007; Meng, *et al.*, 2007; Ng *et al.*, 2006; Zhang *et al.*, 2006b). This is because when HRT and SRT decreased, the concentration of the soluble microbial products (SMP) and bound extracellular polymeric substances (EPS) in sludge floc were increased (Cho et al., 2005; Liang et al., 2007). Bound EPS is referred to as proteins, polysaccharides, nucleic acids, lipids, humic acids and other constituents found at or outside the cell surface. The major role of these bound EPS is to keep the floc in threedimensional matrix, but also the contributor to membrane fouling (Meng et al., 2009). On the contrary, SMP is a pool of organic compounds released into solution as a result of substrate metabolism and biomass decay. Both SMP and bound EPS are directly related to the growth and substrate utilisation. Therefore, increase of organic loading might stimulate high production of EPS and SMP, leading to high sludge viscosity, rise of TMP and eventually fouling potential (Laspidou and Rittmann, 2002). Ahmed et al. (2007) reported that prolonged SRT provided better membrane permeation. Their study found that increase of SRT from 20 to 100 days decreased the potential of membrane fouling. Therefore, it is important to control the HRT and SRT at optimal level, in order to control the bound EPS and SMP concentrations, and thus limiting the membrane fouling.

Aeration in MBR is very crucial. Besides providing oxygen to biomass to attain required dissolved oxygen (DO) concentration, aeration is also used to suspend the biomass in the reactor. More importantly, aeration is capable of mitigating the fouling. According to Wicaksana *et al.* (2006), aeration could mitigate membrane fouling by inducing hydraulic shear on membrane surface and causing lateral movement for membrane hollow fibres. Regulation of aeration is important in determining the floc structure and membrane filtration in the MBR. In addition, the impact of aeration intensity on optimal operation of MBR is very complex. High aeration certainly can reduce the attachment of foulants on membrane surface, but it will also lead to floc breakage. Once the floc breakage occurs, colloids and solutes will become the major foulants (Fan and Zhou, 2007).

In the MBR operation, permeate flux is another critical parameter to control the transfer of treated effluent and suspended or dissolved solids, while affecting the deposition of cake layer on the membrane surface. Generally, fouling is increased with increasing operational flux as foulants may transfer at a higher rate towards the membrane surface. However, Nagoka and Nemoto (2005) discovered that when operational flux was increased below the critical flux, the decreasing of loading rate or increasing shear force was able to reduce the fouling potential. Critical flux is defined as maximum permeate flux where stable flux can be maintained for certain period of time without an increase in TMP (Defrance and Jaffrin, 1999). Below the critical flux, TMP increases linearly with permeate flux (Figure 2.2). However, when exceeding the critical flux, the linear relationship of TMP and flux is no longer existed (Bacchin *et al.*, 2006).



Figure 2.2: Flux and TMP Relationship to Determine the Critical Flux

# 2.5 Factors Affecting Membrane Fouling

Membrane fouling remains the major obstacle for wide application of MBR technology. Lee *et al.* (2001) proposed that the membrane fouling process in the MBR can be attributed to pore blocking and cake layer deposition. In the application of MBR, membrane fouling occurs in the following sequences (Meng *et al.*, 2009):

- (1) Adsorption of solutes or colloids within or on membrane surface
- (2) Attachment of sludge flocs on membrane surface
- (3) Formation of cake layer on membrane surface
- (4) Detachment of foulants by shear stress
- (5) Spatial and temporary changes of foulant compositions, such as bacteria community and components, in long-term operation.

Membrane fouling is a time-controlled process. It may be reversible or irreversible depending on the interactions between foulants and membrane materials (Wiesner and Aptel, 1996). Reversible or removable fouling is caused by loosely attached foulant layer on the membrane surface, which can be easily removed by physical cleaning. However, for irreversible fouling, it is always induced by pore blocking which is hardly removed by any approach even with chemical cleaning. The concept of removable and irremovable fouling is based on the nature of fouling such as biofouling, organic fouling and inorganic fouling (Meng *et al.*, 2009). In general, membrane fouling is often associated with phenomena such as concentration polarization, adsorption, scaling, pore clogging, cake formation and biofouling. There is synergistic interaction between organic fouling and inorganic fouling due to the formation of complexes during the treatment process (Kabsch-Korbutowicz, 1992).

### **2.5.1 Biofouling**

Biofouling is always associated with the biological activities in the system. It is defined as the deposition and the growth of bacteria cells or flocs along the membrane surface, especially when the MBR is operated at low pressure (Pang *et al.*, 2005). Biofouling is initiated with the deposition of cells on the membrane surface, followed by the growth of cells and the formation of cake layer. Sludge characteristics such as particle size, settleability, mixed liquor suspended solids (MLSS), extracellular polymeric substance (EPS) and soluble microbial product (SMP) are commonly related to the occurrence of biofouling. The size of the activated sludge or its components such as SMP and EPS strongly affects the membrane fouling. If the size of the sludge or their components is comparable or smaller than the membrane pore size, adsorption and pore blocking may occur. Inversely, cake layer may deposit on the membrane surface.

Some researchers suggested that MLSS was the main factor that contributing to membrane fouling. High MLSS concentration is often found to increase the fouling potential (Chang *et al.*, 2001; Magara and Itoh, 1991). In contrast, in certain condition, high MLSS concentration can mitigate the fouling (Lee *et al.*, 2001), or even has small or no impact on fouling (Fan and Zhou, 2007; Hong *et al.*, 2002; Le-Clech *et al.*, 2003; Rosenberger *et al.*, 2002). Both Hong *et al.* (2002) and Le-Clech *et al.* (2003) found that there was no correlation between MLSS concentration and the critical flux when the MBR was operated between 2 and 8 g/L.

EPS are biopolymer substances that are identified to be one of the most significant contributors to biofilm formation on the membrane surface (Hong *et al.*, 2002). EPS concentration is closely related to the sludge settleability, which may affect membrane fouling (Meng *et al.*, 2006). It was found to have ability to form gel layer, which further enhanced microbial attachment and organic adsorption and eventually deteriorated the fouling (Judd, 2004; Laspidou and Rittmann, 2002). In addition, SMP has been recognized to be a one of the

significant foulants in MBR (Rosenberger *et al.*, 2006). Besides, Iritani *et al.* (2007) discovered that the relative contribution of SMP towards membrane fouling was approximately 100 %. Furthermore, Lyko *et al.* (2008) suggested that SMP components might form complex with metal cations, and accumulate on the membrane surface or penetrate into the pores depending on the back transport mechanisms such as inertial lift, shear-induced diffusion and Brownian diffusion (Meng *et al.*, 2009). If the SMP passed through the membrane pore, post treatment was needed to eliminate these contaminants. Otherwise, SMP concentration could be controlled through operation parameters such as SRT and HRT as discussed in Section 2.4.

## **2.5.2 Organic Fouling**

Organic fouling is always referred to the deposition of biopolymer such as proteins and polysaccharides on the membrane surface (Zhou *et al.*, 2007). Usually, proteins or polysaccharides are easily deposited onto membrane due to the permeate flow, but is difficult to back transport. Most of the literatures indicated that organic fouling is mostly originated from SMP or EPS of the activated sludge. Metzger and colleagues (2007) conducted a study to investigate the spatial distribution of foulants on membrane surface. The inner layer was discovered to predominate with high concentration of bound proteins as compared to upper layer (consisting of sludge flocs) and intermediate layer (consisting of bacteria aggregates and SMP). However, the second intermediate layer was found to contain high concentration of polysaccharides. Besides, Teychence et al. (2008) found that polypeptides in the deposition compounds contributed to membrane fouling based on the results of HP-SEC and fluorescence analyses. Furthermore, Rosenberger et al. (2006) suggested that high polysaccharide concentrations with molecular weight larger than 120 kDa in sludge supernatant contributed to high fouling rates.

## **2.5.3 Inorganic Fouling**

Even though biofouling and organic fouling are the main focus for the past few years, some recent findings suggested that inorganic fouling might also contribute to significant fouling problem. Kang *et al.* (2002) and Ognier *et al.* (2002) proposed that inorganic membrane material such as ceramic experienced more serious inorganic fouling due to the precipitation of calcium carbonate and alkalinity of the sludge present in wastewater. You *et al.* (2006) pointed out that inorganic fouling was irreversible due to the cohesive properties between the inorganic foulants and the membranes. Besides, Wang *et al.* (2008) revealed that the coupling of organic and inorganic foulants enhanced the cake layer formation.

Scaling or inorganic fouling is formed through two general ways, chemical precipitation (due to the presence of cations and anions in MBR) or bioprecipitation (due to ionisable groups in biopolymer). Concentration polarisation contributes to chemical precipitation of inorganic salts such as iron, carbonate or phosphate, on the membrane surface. Chemical precipitation usually occurs when the concentration of inorganic anions or cations have exceeded the saturation concentration as a result of concentration polarisation. You *et al.* (2005) found that aeration and carbon dioxide from the metabolism of microorganism could affect the potential of membrane scaling due to the saturation of carbonate salts. However, it is possible to pre-treat the wastewater with chemicals such as EDTA, where it could remove the hardness of wastewater, and reduce the occurrence of inorganic fouling (Al-Amoudi and Lovitt, 2007). Biological precipitation occurs primarily due to the presence of ionisable groups such as acidic functional group (R-COOH) from the biopolymers. Costa *et al.* (2006) proposed that when the R-COOH functional group interacted with the metal ions in wastewater, it would form a dense gel layer which increased the rate of flux declination. The metal ions could be neutralised and formed complex with the organic foulants depositing on the membrane surface when the ions moved along with the treated water.

In summary, the basic factors that influence the membrane fouling are membrane properties, hydrodynamic environment experienced by the membrane and feedwater characteristics. In addition, feedwater characteristics and hydrodynamic conditions are able to modify the sludge properties and the membrane fouling behavior. For example, the introduction of toxic influent may affect the activity and biological performance in the treatment plant by changing the dominance of sessile species (Brindle and Stephenson, 1996; Meng *et al*, 2009; Papadimitriou *et al.*, 2007; Rosenberger *et al.*, 2005). Membrane fouling occurs more readily on hydrophobic membrane than on hydrophilic membrane due to the hydrophobic interaction between the foulants and membrane Thus, many attentions have been attributed to modify the membrane from hydrophobic to hydrophilic in order to reduce the fouling (Yu *et al.*, 2005b). Also, the physiochemical characteristics and physiology of activated sludge such as shape, size, porosity, extracellular polymeric substances (EPS), soluble microbial products (SMP), carbohydrates and polysaccharides were found to be the key factors determining the membrane fouling (Chang *et al.*, 2002; Lee *et al.*, 2003; Li *et al.*, 2005a; Li *et al.*, 2005b; Van Dijk and Roneken, 1997; Yu *et al.*, 2005). In order to optimise the performance of MBR, control strategies to operate the system should be implemented accordingly by adopting the favorable conditions to mitigate the membrane fouling.

# 2.6 Mitigation of Membrane Fouling

Based on the literature, the factors affecting membrane fouling are mainly membrane materials, biomass characteristics, feedwater characteristics and operating conditions (Le-Clech *et al.*, 2006). The severity of fouling is directly determined by the sludge characteristics and hydrodynamic conditions, while operating conditions and feedwater have indirect influence on it through modifying the sludge characteristics (Meng *et al.*, 2009). Therefore, the common strategies to mitigate the membrane fouling are classified as hydraulic, chemical and biological controls. Most of the studies suggested that membrane fouling can be controlled by reducing flux, increasing membrane aeration and physical or chemical cleaning of membrane (Chang and Judd, 2002; Judd, 2005; Chang and Lee, 1998)

### 2.6.1 Role of Membrane Materials in Preventing Fouling

In the submerged MBR, the membrane module is immersed in the reactor to retain the biomass during separation, and hence produce satisfactory effluent quality. Membrane is only used as a filter in the MBR to produce effluent that meets the standard criteria required. Therefore, it is feasible to substitute the commercial high cost membrane with a cheaper and porous membrane. In order to minimise the occurrence of membrane fouling, membrane material remains the major consideration in the set-up of the MBR (Meng et al., 2009). Membrane used for treatment must possess high chemical and thermal resistance with advanced mechanical strength, which is compatible to be used in wastewater treatment. In addition, membrane fouling occurs more readily on hydrophobic membrane than on hydrophilic membrane due to the hydrophobic interaction between the foulants and membrane (Yu et al., 2005a; Yu et al., 2005b). Hydrophilic membrane can prevent the hydrophobic interaction between the foulants and membrane, and hence reduce the deposition of foulants on the membrane surface.

Besides, Manem and Sanderson (1996) suggested the membrane used for filtering biological suspensions should be neutral or negatively charged to minimise the floc adsorption. Zhang *et al.* (2008) studied the fouling resistance of three polymeric membranes for ultrafiltration. They discovered that the affinity capability between polyacrylonitrile (PAN) with EPS was the lowest as compared to polyvinylidene fluoride (PVDF) and polyethersulfone (PES). Besides, Yamato *et al.* (2006) suggested that PVDF membrane could prevent the irremovable fouling more effectively as compared to polyethylene (PE) membrane. Other than polymeric membrane, inorganic membrane such as stainless steel membrane, are commonly used in special applications such as high temperature wastewater treatment (Meng *et al.*, 2009). Zhang *et al.* (2005, 2006c) found that stainless steel membrane could be an alternative membrane for the treatment of high temperature wastewater as it could achieve higher permeate flux.

Due to the impact of membrane materials on the fouling resistance, great attention has been focused to modify the membrane properties such as pore size distribution and hydrophobicity. For example, Yu *et al.* (2005a, 2005b, 2008) had developed plasma treatment on the membrane surface to improve the anti-fouling property of PE hollow fiber microporous membranes. The fouling potential of NH<sub>3</sub> and CO<sub>2</sub> plasma treated membranes were found to be lower than those unmodified membrane with shallow modification depth. However, this plasma modification is hardly to be extended on large scale due to the complicated surface chemical reaction which is difficult to understand in detail. To overcome the weakness of plasma treatment, Yu *et al.* (2007) further investigated the membrane surface modification using graft polymerization method coupled with UV radiation. The photo-chemical modified membrane showed better filtration ability as the hydrophilicity of the membrane was greatly increased. Even though the membrane fouling resistance can be increased by surface modification, development of low-cost and anti-fouling membrane is still the major concern in order to widely apply the membrane technology in municipal and industrial wastewater treatment.

#### 2.6.2 Hydrodynamic Controls in Mitigating Membrane Fouling

Hydrodynamic control of the membrane filtration process includes reducing flux, increasing membrane aeration and intermittent permeation (Chang and Judd, 2002; Judd, 2005; Chang and Lee, 1998)

### 2.6.2.1 Role of Flux

Low pressure operation of MBR with low initial flux is able to decelerate the deterioration of membrane fouling (Field *et al.*, 1995). On the other hand, high membrane flux was found to increase the attachment of particles or molecules onto the membrane and overwhelming the back transportation rate. When the membrane flux is high, the large particles or molecules with high back transportation rate are pulled towards the membranes and cause fouling (Kimura et al., 2008). Nagoka and Nemoto (2005) revealed that when operational flux increased below the critical flux, fouling potential could be reduced. When the submerged MBR is operated at low suction pressure, the foulants are transported at a lower rate towards membrane surface. Thus, this can greatly reduce the fouling rate due to slow cake formation. Nonetheless, low pressure membrane usually has high fouling potential due to the biological floc, EPS, and biocolloids if the MBR is not operated in the crossflow mode with imposition of shear stress at the membrane surface. Commonly, low pressure MBR is either used in processing high solids content feed where air bubbling is used to control fouling, or, used in low solids content feed where regular backwash is employed to remove deposition (Fane *et al.*, 2005). Therefore, in order to operate the MBR in low pressure or low flux, it is important to couple with hydrodynamic control such as backwash and increase shear stress, to optimise the membrane operation with least energy.

#### 2.6.2.2 Role of Aeration

Other than permeate flux, another common effective way to control membrane fouling is through the shear-stress generated from aeration and intermittent permeation (relaxation). In recent years, air-sparging has gained attention to enhance the hydrodynamic conditions and efficient use of aeration in the MBR (Delgado *et al.*, 2008). Aeration is a significant factor to determine the MBR's performance by providing the oxygen for biodegradation while

suppressing the build up of cake layer on the membrane surface. Air bubbles is utilised to generate localized cross-flow conditions along the membrane surface and thus reducing the deposition of cake layer on the membrane (Bouhabila *et al.*, 1998; Ueda *et al.*, 1997; Ivanovic and Leiknes, 2008). However, the relationship between aeration intensity and MBR performance was complicated and not well developed. Also, there was no direct relationship between the fouling resistance and the aeration intensity (Han *et al.*, 2005). Although high aeration can reduce the attachment of sludge layer on the membrane surface, it also leads to the floc breakage (Gui *et al.*, 2002). Colloids and solutes arise from the damaged sludge may become the other major foulants at high aeration intensity which cannot be reduced by shear stress (Fan and Zhou, 2007). Besides, Shane Trussell *et al.* (2007) found that increasing the coarse bubble aeration intensity could increase the MLSS concentration before a decline of 10 % in membrane permeability.

To overcome the weakness of aeration strength on membrane fouling, intermittent aeration has been developed to allow the restructuring of activated sludge and to mitigate the membrane fouling effectively. Furthermore, aeration is a very cost-consuming parameter in the operation of MBR due to the energy consumption. Approximately 80 % of the total energy cost in a submerged MBR is contributed by aeration. Thus, proper management of aeration seems to be important in order to mitigate the fouling and operation cost of MBR simultaneously (Gander *et al.*, 2000b; Owen *et al.*, 1995; Van Kaam *et al.*, 2008). Other than aeration mode (continuous or intermittent), the air-sparging technology

has also been studied to enhance the flux in submerged MBR. Chang and Judd (2002) found that air-lift module was able to increase the permeate flux by 43 % when coarse bubble was introduced. The air-jet module experienced pore clogging due to the deposition of biosolids inside the lumen during the operational period. However, if the pore clogging could be prevented by periodic backwash, the air-jet sparging could produce 20 % higher fluxes than air lift module. In brief, aeration intensity, aeration mode and air-sparging technology are the effective approaches to mitigate membrane fouling in the MBR. Therefore, thorough investigation on the interactions among these three approaches might be helpful to improve the fouling resistance.

#### 2.6.3 Biological Controls in Mitigating Membrane Fouling

Based on the recent reviews, the physiochemical characteristics and physiology of sludge floc such as shape, size and porosity were found to be the key factors determining the membrane fouling. Meng *et al.* (2009) reviewed that operating parameters such as SRT, HRT, dissolved oxygen (DO) and food-to-microorganism ratio (F: M) could modify the sludge characteristics. Thus, biological control of such parameters (HRT, SRT, sludge concentration or MLSS, F: M ratio) would modify floc structures and effectively mitigate the fouling (Chang *et al.*, 2002; Lee *et al.*, 2003; Li *et al.*, 2005; Van Dijk and Roneken, 1997; Yu *et al.*, 2006). Increase in the MLSS could reduce the HRT at a given time, resulting in more compact treatment process and reducing sludge production.

However, there was a conflict of interest, i.e., the increase in MLSS declined the membrane's permeability due to the accumulation of foulants on the membrane surface (Shane Trussell *et al.*, 2007).

An interesting finding revealed that special structure of the sludge floc could reduce membrane fouling by forming porous cake layer on the membrane surface which might be removed by air scouring. The flocs were overlapped and left some holes among the deposited cake layer. The formation of porous cake layer could alleviate membrane fouling by preventing the SMP from directly attaching on the membrane (Yu et al., 2006). Besides, sludge particle size was found to influence filtration characteristics in the MBR. The sludge particle size is strongly affected by hydrodynamic controls of the operation such as aeration intensity and HRT. If the biological flocs are comparable, or smaller than the membrane pores, adsorption and pore blocking may occur, contributing to irreversible fouling. On the other hand, if the flocs are larger than the membrane pores, cake layer may form on the membrane surface (Bai and Leow, 2002; Lim and Bai, 2003). In addiction, large floc particles were found to increase the membrane permeability in the presence of low SMP by serving as "second membrane". This "second membrane" blocks the SMP from directly contacting with the membrane module (Yu et al., 2006). Weak floc and small particles like organic solutes and colloids existing in the turbulent environment may lead to floc breakage and cause dense cake layer formed on the membrane surface. In order to minimise the potential of floc breakage, aeration intensity and feedwater characteristics should be monitored closely.

On the other hand, microbial cell length and sludge bulking conditions were also related to cake compressibility constant and membrane fouling (Choi *et al.*, 2002; McCarthy *et al.*, 1998). Bulking bacteria was one of the problems in the operation of submerged MBR. The existence of filamentous bulking bacteria was observed with increasing sludge volume index (SVI). The excessive growth of filamentous bacteria was found to enhance the deposition of foulants on the membrane surface due to the sudden increase of bound EPS. As a consequence, the sludge viscosity and the hydrophobicity were enhanced, which increased the fouling rate and shortened the stable filtration period (Sun *et al.*, 2007). In order to limit the fouling due to sludge bulking, preventive action such as proper control of food-to-mass ration (F:M), low mean cell residence time (MCRT), short hydraulic retention time (HRT), nutrient efficiency and reduction of readily degradable carbonaceous biochemical oxygen demand (cBOD) should be adopted (Gerardi, 2002).

### 2.6.4 Chemical Controls in Mitigate Membrane Fouling

Mitigation of membrane fouling by means of chemical approach is always associated with the addition of coagulant and adsorbent. Powdered activated carbon (PAC) is a common adsorbent used in the MBR to uptake soluble organic and to enhance the flocculation ability. The effectiveness of PAC in controlling the membrane fouling has been studied by researchers. Introduction of PAC not only reduces the biopolymers in sludge suspension, but also provides a solid support for the biomass growth and reduces the floc disintegration (Ying and Ping, 2006; Ng *et al.*, 2006). Furthermore, PAC is also able to uptake the EPS content in the reactor at an optimum dosage of 1.2 g/L (Li *et al.*, 2005). It was found that the irremovable fouling resistance was reduced when the EPS content was minimised upon the addition of PAC. Although PAC addition could increase the performance of MBR, it would still reduce the flux due to the increasing of sludge viscosity, if the addition of PAC is beyond the optimal level (Akram and Stuckey, 2008).

Coagulants such as alum and zeolite are also used to enhance the membrane filtration by improving the floc structure and strength, besides removing SMP (Lee *et al.*, 2001). Addition of 1 g/L of zeolite could encourage the attach growth of microorganisms and enhance the membrane permeability. Holbrook *et al.* (2004) revealed that addition of alum could decrease the SMP content by 25 % and improved the membrane hydraulic performance. Both the studies of Lee *et al.* (2001) and Holbrook *et al.* (2004) proved that there were no

optimal coagulant concentrations to reduce the membrane fouling. However, addition of alum could increase the particle size distribution and subsequently lowered the specific resistance and improved permeability.

Other than alum and zeolite, addition of calcium, ferric chloride and chitosan can also reduce the SMP concentration, which will further lower the hydrophobicity, induce flocculation, reduce floc breakage and reduce pore blocking possibility (Ji *et al.*, 2008; Song *et al.*, 2008; Zhang *et al.*, 2008). Fan and Zhou (2007) compared the effectiveness of ferric chloride, alum and organic polymer in reducing the colloidal total organic compound (TOC) and time to filter (TTF) in the MBR. Organic polymer was found to be able to increase the MLSS particle size effectively and was more efficient in improving TTF, but had little impact on sludge filterability. All these studies indicated that the addition of coagulants and adsorbents into biomass suspension could eliminate organic solutes and colloids, which further achieve the objective of controlling membrane fouling.

# 2.7 Membrane Cleaning

Membrane cleaning is the final resolution for removing the foulants, which is usually classified into physical or chemical cleaning. Physical cleaning is associated with membrane permeation and membrane backwash. Backwash is referred as the back transport of foulants back to the biomass suspension. Usually, backwash frequency, duration and intensity are the key parameters in the design of backwashing. Several factors that determine the frequency and duration of backwash are type of membrane, sludge retention time, aeration mechanism and aeration rate (Le-Clech *et al.*, 2006). Yigit *et al.* (2009) discovered that longer backwash duration with less frequency could recover the flux more effectively than frequent backwashing.

Besides backwashing, membrane relaxation could significantly improve membrane filtration. When the membrane operation is temporarily discontinued, back transport of foulants is enhanced as the reversible attached foulants can diffuse away from the membrane due to the concentration gradient and shear stress (Le-Clech *et* al., 2006; Hong *et al.*, 2002).

Even though periodic backwashing and membrane relaxation can recover the membrane permeability, the effectiveness may decrease with operation time with the accumulation of irreversible foulants on membrane surface (Le-Clech *et* al., 2006). Therefore, chemical cleaning can be adopted as maintenance and recovery cleanings. Usually, the chemical reagents used for backwashing or soak cleaning are sodium hypochlorite (NaOCl), sodium hydroxide (NaOH) and hydrogen peroxide ( $H_2O_2$ ). If backwashing is performed, high concentration of NaOCl or citric acid will be used. The concentrated chemical solution is allowed to stay in the membrane for a certain duration, and backwash is initiated for few times depending on the degree of fouling. In soak cleaning, membrane is immersed into separate tank filled with chemical overnight with specific frequency (depending on the application and the nature of foulant).

In summary, membrane selection, mixed liquor characteristics, sludge properties and membrane cleaning methods are important in alleviating membrane fouling. Hydrophilic membrane is always the primary choice for the application of submerged MBR to avoid the hydrophobic interaction between the foulants and the membrane. Besides, hydrodynamic conditions in the MBR can be achieved by regulating the aeration mode and aeration intensity. Next, incorporation of chemicals such as adsorbents or coagulants can enhance the membrane permeability through the removal of organic colloids and solutes, while encouraging the attach growth of sludge. Lastly, the sludge properties can be modified by regulating the feeding compositions and operating conditions as this could also prevent undesired fouling.

# 2.8 **Problem Statements**

In Europe and Asia, MBR researches and applications are focused more on municipal wastewater treatment with large flow and low organic strength. Although MBR has been widely installed all around the world, most of the public sewage treatment plants in Malaysia are still using mechanical plants such as sequencing batch reactor and trickling filter. Investment and operation cost of the MBR are too expensive for developing countries like Malaysia. Especially the costly commercial membrane has restricted wide application of MBR. In addition, membrane fouling is the major drawback for MBR. Consequently, frequent membrane cleaning and replacement are required in the MBR operation, which increase the operating costs. Many anti-fouling strategies have been proposed for the MBR process. Among these reviewed strategies, replacement of the commercial membrane with cheaper filters should be the most feasible one. These alternative filters with appropriate pore size and resistance to chemical and temperature should be considered as they could achieve comparable effectiveness as in the use of costly commercial membrane.

Besides, according to the literature review, the relationship between the activated sludge and the membrane filtration has been greatly evaluated. The focus was especially on membrane fouling. Most of the researches mainly investigated the technical control on membrane fouling by regulating the operation conditions such as aeration and backwash. Despite of this, the

progression in the prevention of fouling is relatively slow. Moreover, the influence of toxicants such as phenol in the feeding compositions towards the sludge characteristics and membrane fouling is not widely studied. Since the major foulant is biomass, it is important to determine the nature of sludge at different feeding compositions and various operation modes. In view of this, the morphology and the particles size of the activated sludge can play an influential role on determining the flux performance. Therefore, characteristics of sludge would be essential to understand the fouling nature in the MBR and the modification of sludge morphology can enhance the performance of submerged MBR. Unfortunately, the relationship between the sludge characteristics and membrane fouling is complicated and is not extensively explored. As activated sludge is evolved from microorganisms, it is feasible to change their properties by regulating the feeding compositions and the operating conditions in the treatment system. By minimising the occurrence of fouling-induced floc in biomass, membrane fouling rate can be reduced to satisfactory level (Masse *et al.*, 2006).

MBR primarily uses chemicals and energy to control fouling. For example, intermittent permeation, membrane backwashing and the addition of cleaning agents are the mostly used applications. Effectiveness of various bubbling modes for fouling mitigation in the MBR is influenced by the operating conditions. Thus, proper management of aeration seems to be important in order to mitigate the fouling and reduce operation cost of MBR simultaneously. To overcome the weakness of aeration strength on membrane fouling, intermittent aeration is developed to allow the restructure of activated sludge and mitigate the membrane fouling effectively. Furthermore, aeration is the most cost-consuming parameter in the operation of MBR due to the energy consumption. Approximately 80 percent of total energy cost in a submerged MBR is contributed by aeration. About twothirds of energy used in municipal MBRs is needed to generate crossflow from air sparging to control fouling (Gui *et al.*, 2002; Fan and Zhou, 2007). However, there is no clear relationship on the aeration intensity and membrane fouling resistance. Therefore, the mode of aeration has become a key factor to mitigate the fouling with minimal energy consumption.

# 2.9 Objective

Membrane bioreactor is commonly used nowadays to treat wastewater for reuse purpose. In this project, removal of phenol was evaluated in membrane bioreactor operated with continuous aeration. The aim of this research was to evaluate the performance of combined biological treatment and membrane filtration to give final effluent quality that meets the local discharge standards. The main objectives of this study were:

- (1) To evaluate the performance of ceramic membrane bioreactor (MBR) in the treatment of phenol containing wastewater.
- (2) To investigate the effect of increasing phenol concentrations on the sludge characteristics and its impact towards membrane fouling.
- (3) To study the filtration performance of MBR at varying suction pressures.
- (4) To investigate the effect of various bubbling modes in mitigating membrane fouling in the MBR process.

### Chapter 3

## **Materials and Methodology**

# **3.1 Preliminary Studies**

Preliminary studies, such as to investigate the impact of phenol toxicity on biodegradation via specific oxygen uptake rate (SOUR), the potential of phenol removal by stripping process via volatilisation test, and acclimatisation of activated sludge with increasing phenol concentrations using batch study were conducted.

### **3.1.1** Specific Oxygen Uptake Rate (SOUR)

The SOUR test was employed to study the toxicity effect of phenol on activated sludge (Lee, 2001). It was run by measuring the uptake of dissolved oxygen at varying initial phenol concentrations. Mixed liquor was collected during the React mode and the uptake of the dissolved oxygen was observed and recorded as the decrease of dissolved oxygen in the mixed liquor, indicated by the Dissolved Oxygen meter (YSI 52) at appropriate time interval.

50 mL of mixed liquor from the reactor was used as seed in 300 mL BOD bottle (Figure 3.1). 250 mL of the synthetic influent with varying phenol

concentrations (ranged from 0 to 2000 mg/L) was subjected into the BOD bottle. The pre-calibrated DO probe was immediately inserted into the bottle and the DO readings were recorded at every ten seconds until the DO dropped to 1.0 mg/L. Linear plots of the change of recorded DO against time with  $R^2$ >0.99 were constructed for every phenol concentration. The SOUR was interpreted as the milligram of oxygen consumed per gram of mixed liquor volatile suspended solids (MLVSS) per hour or it could be calculated from the slope of the plot of oxygen uptake data against time per gram of MLVSS (Equation 3.1).



Figure 3.1: Illustration for the Specific Oxygen Uptake Rate (SOUR) Study

## **3.1.2** Phenol Volatilisation Test

Volatilisation test was performed as pre-experimental test to determine the potential of phenol loss under aerated condition (Yoong *et al.*, 2000). Therefore, in the test, any loss of phenol would be caused by air stripping from aeration. The test was carried out in a 4 L batch reactor with phenol substrate at low (~100 mg/L), medium (~500 mg/L) and high concentrations (~700 mg/L) as shown in Figure 3.2. Aeration and mixing were provided using air stone and air pump. 20 mL of the sample was collected from each reactor at the beginning of the test and then every one hour for analysis. The total duration of the test was eight hours. The phenol concentration and COD of the phenol substrates collected at every one hour interval were used to investigate whether there was any loss of phenol by volatilisation. COD test was analysed following APHA 5220-C Closed Reflux & Titrimetric Method (APHA, 1998), while the phenol balance of the solution was tested using UV-Vis spectrophotometer between the wavelength of 190 and 400 nm (lambda max at 269 nm) (Singer and Yen, 1980).



Figure 3.2: Illustration for the Phenol Air Stripping Test

### **3.2 Acclimatisation of Activated Sludge towards Phenol**

Acclimatisation of activated sludge formed by microbial consortium is important as it enhances the interaction between all the species present in flocs, while possess enzymatic material required for the phenol degradation and reveals the new population which is adopted to the toxic agent and is able to consume it as a substrate (Barrios-Martinez *et al.*, 2006; Marrot *et al.*, 2006). Batch operation was adopted for the acclimatisation of activated sludge towards increasing phenol concentration (0 to 600 mg/L). The acclimatisation was carried out in a single tank reactor with dimension of 35 cm (H) × 15 cm (W) × 40 cm (L). The working volume of the reactor was 18 L. Initially, activated sludge was cultured for two months in a batch study with synthetic wastewater containing base-mix (Table 3.1) as a carbon source. At the end of the culturing stage and there after, phenol was introduced to replace the base-mix as a carbon source.

The sequencing batch reactor (SBR) was operated two cycles per day with Fill, React, Settle, Draw and Idle periods with the ratio of 2:8:1:0.5:0.5 for a cycle time of 12 h. Synthetic wastewater containing phenol was fed to the reactor during the Fill mode with a flow rate of 58 mL/min. Phenol was biodegraded in the aerated mixed liquor during the 8 h React mode. Later the treated effluent was discharged (Draw mode) after the mixed liquor was allowed to settle for an hour. Aeration was provided throughout the Fill and React modes. Therefore, the biodegradation of phenol had already begun at the beginning of the Fill mode (Figure 3.3).

When the activated sludge was adapted to synthetic wastewater containing phenol with increasing concentration of phenol from 0 to 600 mg/L, the extent of sludge acclimatisation together with its performance in degrading phenol were monitored through daily effluent analysis (Chemical Oxygen Demand-COD and phenol concentration), sludge characteristics (sludge concentration and settleability) and profile study.

Profile study was conducted based on the degradation of phenol by analysing the COD and phenol concentration in the mixed liquor along the Fill and React modes at different phenol concentrations. The mixed liquor was collected during Fill and React modes, filtered and the filtrate was analysed for COD and phenol concentrations. Besides, the utilisation of dissolved oxygen (DO) by microorganism to degrade phenol in the reactor was also monitored during the Fill and React modes.

Composition	Concentration (mg/L)
Bactopeptone	188
Sucrose	563
Ammonium chloride	172
Magnesium sulphate	49
Dipotassium hydrogen phosphate	250
Iron (III) chloride	11.3
Sodium bicarbonate	14.7

 Table 3.1: Feeding Composition of Synthetic Wastewater for Batch Reactor

 During Acclimatisation



Figure 3.3: Schematic Illustration of Batch Operation during Acclimatisation

# 3.3 Sludge Characteristics Study

The change in the sludge characteristic was evaluated to investigate the impact of varying phenol concentrations in synthetic wastewater on the activated sludge. This change was closely monitored at every phenol concentration during and after the acclimatisation of activated sludge to that particular phenol concentration. Characteristics of the sludge were assessed through mixed liquor suspended solids (MLSS), sludge volume index (SVI), sludge morphological observation and sludge particle size distribution.

The MLSS and SVI were studied based on APHA 2540-D Total Suspended Solids Dried at 103-105 °C and APHA 2710-D The Determination of Sludge Volume Index, respectively (APHA, 1998). The MLSS indicates the concentration of suspended solids in the mixed liquor sample, whereas, the SVI is used to monitor the settling characteristics of the activated sludge and other biological suspensions. The activated sludge was also characterised in terms of particle size distribution by Particle Size Analyser (CILAS 1180 Liquid) and morphology observation by light microscope. Well-mixed activated sludge was collected from the reactor for morphological and particle size distribution study. A drop of sludge was deposited on the slide and covered with a covered slip. Image of the sludge was observed under bright field light microscope with magnification of 10 X. The microscope was attached to the Nikon digital camera and three pictures were captured at every four corners and the centre of the slide. A total of 60 pictures were captured from four slides (for each phenol concentration studied) and 600 flocs were selected for particle size distribution study. The images were calibrated using micrometer slides and further interpreted by Image J software (Figure 3.4). The floc size distribution was determined statistically using Microsoft Excel and illustrated in histogram and particle distribution function (linear scale).



Observation through Microscope

Data Interpretation by Image J software

Figure 3.4: Illustration for Sludge Characteristics Study

### 3.4 Submerged Membrane Bioreactor (sMBR) Set-up

When the sludge was acclimatised to the desired phenol concentration, it was then subjected to the sMBR operation. During the sMBR operation, the extent of the membrane fouling or flux performance was evaluated at various suction pressures. In addition, the fouling characteristic of the membrane was also studied under the influence of various phenol concentrations and was explained and related to sludge characteristics at different phenol loadings. Lastly, various modes of aeration were performed to investigate the mitigation of membrane fouling.

The sMBR was equipped with an aerated bioreactor, membrane unit and suction line consisting of vacuum pump, vials and sample collection flask (Figure 3.4). Ceramic membrane module (commercially available in hypermarket) was used in the experiment. Parallel water filtering assembly was attached to the diaphragm vacuum pump (GAST model: DOA-P504-BN) to create transmembrane pressure for the hollow membrane module.


Figure 3.5: Experimental Set-up of MBR

# **3.4.1 Membrane Characteristics**

A low-cost commercial household hollow ceramic membrane module was employed in this study (Figure 3.6). Based on the scanning electron microscopy (SEM) study, the membrane was made from diatomaceous earth which is hydrophilic in nature (Figure 3.7). The immersed membrane module has an active membrane area of 0.038 m<sup>2</sup> with nominal pore size of 0.5  $\mu$ m.



Figure 3.6: Type of Membrane Used in MBR Operation



Figure 3.7 SEM Result for Ceramic Filter

#### 3.4.2 Submerged Membrane Bioreactor (sMBR) Operation

The schematic diagram for the experimental set-up is illustrated in Figure 3.8. The bioreactor was made of glass with a working volume of 22 L to ensure the membrane module was fully immersed in the bioreactor. A commercial household dead-end hollow ceramic membrane module was immersed in the bioreactor for membrane separation.

During the operation, the bioreactor was continuously fed with synthetic wastewater with the composition shown in Table 3.1. Timer and peristaltic pump were used to control this continuous feeding process from feeding tank to bioreactor. Aeration was supplied by air pump connected to air-stone to suspend the biomass and provide oxygen to the microorganism. Besides, membrane scouring was achieved with air pump where air bubbles were distributed through the aeration ring located at the bottom of the membrane. The influent flow rate was set based on the permeate flux, which should maintain constant working volume in the bioreactor. Permeate was collected from sample collecting flask using a diaphragm vacuum pump attached to suction line. The suction pressure was applied within the range of -7.5 to -30 kPa for each bubbling mode (without bubbling, continuous bubbling and intermittent bubbling).



Figure 3.8: Schematic Illustration of MBR Operation

## **3.5 Flux Characteristics Study**

The suction pressure was applied by diaphragm vacuum pump in a range of -5 to -30 kPa for every feeding composition (base-mix without phenol, 200, 400 and 600 mg/L phenol concentrations) to evaluate the impact of feeding composition on the floc and flux characteristics. Flow rate of the permeate (Equation 3.2) was determined by measuring the volume of permeate collected over specific time (fixed at one minute in this study). Permeate flux could be defined as the ratio of flow to membrane surface area. The permeate flux (Equation 3.3) was calculated by measuring the volume of permeate over time and expressed in term of relative flux, J/Jo (%) (Equation 3.4). The flux was determined at every two minutes until steady-state flux was observed for all the studies. Fouling rate was determined by obtaining the gradient from flux declination plot and expressed in term of  $(J/J_0) / min$  (Equation 3.5).

Flow Rate = Volume of permeate collected (L) / Time (Hour) (Equation 
$$3.2$$
)

Relative Flux = Flux at specific time (J) / Initial flux (J<sub>0</sub>) X 100 % (Equation 3.4)

Fouling Rate = Slope of the plot of relative flux against time

#### 3.6 Membrane Scouring and Cleaning

The principle limitation of the MBR process lies in the membrane fouling due to the deposition of fouled layer on the membrane surface. Various methods have been adopted to suppress the deposition of fouled layer on the membrane surface. Most of which is to increase the shear stress along the membrane surface through the bubbles generated from aeration. This study was aimed to investigate the effect of various aeration modes, namely, without bubbling, with intermittent bubbling or with continuous bubbling on the fouling characteristic in the sMBR. For intermittent bubbling mode, intermittent bubbling and pausing of suction (relaxation) were applied to the membrane for a duration of one minute once the relative flux (J/Jo) was declined to lower than 70 % from the initial flux (Jo). For continuous bubbling mode, the shear stress was continuously introduced to prevent the deposition of fouled layer on the membrane surface.

Chemical cleaning and backwashing were employed to recover the membrane permeability after each operation. Chemical cleaning of the membrane module was performed by sonic cleaning in 1% sodium hydroxide solution for 20 minutes. Then, backwashing was performed on the membrane by reversed suction after each experiment.

The membrane permeability was determined using pure water before and after the cleaning processes. A new membrane was used if the recovery of the membrane permeability was less than 90 %. Membrane permeability indicates how much energy is required to make permeate or the degree of fouling (You *et al.*, 2006). Permeability is the ratio of flux to transmembrane pressure (Equation 3.6).

Permeability = Flux / TMP (Equation 3.6)  
= Flow / Membrane Area. TMP  
(Expressed in LMH / kPa Or L / 
$$m^2$$
. hour. kPa)

## **3.7 Effluent Analytical Methods**

Organic waste degradation was determined by subjecting the permeate collected from the MBR operation to chemical oxygen demand (COD) test and total suspended solids (TSS) according to APHA 5220-C Closed Reflux & Titrimetric Method and APHA 2540-D Total Suspended Solids Dried at 103-105 °C, respectively (APHA, 1998). Mixed liquor suspended solids (MLSS) and sludge volume index (SVI) were measured based on APHA 2540-D Total Suspended Solids Dried at 103-105 °C and APHA 2710-D The Determination of Sludge Volume Index, respectively (APHA, 1998). Phenol concentration was determined by UV–Vis spectrophotometer between a wavelength range of 190 and 400 nm with maximum absorption at 269 nm (Singer and Yen, 1980).

### Chapter 4

#### **Results and Discussion**

### 4.1 **Preliminary Studies**

#### 4.1.1 Specific Oxygen Uptake Rate (SOUR)

Based on APHA standard methods (2710 A, 2710 B), SOUR test is known as the oxygen consumption or respiration rate (APHA, 1998). This parameter is defined as milligram of oxygen consumed per gram of mixed liquor volatile suspended solids (MLVSS) per hour. SOUR measures influent organic load and its biodegradability. Besides, this test also provides an indication of the presence of toxic or inhibitory wastes, degree of stability and the condition of a sample, and calculation of oxygen demand rates at various points in the aeration basin (APHA, 1998). As dissolved oxygen uptake and aerobic microbial respiration in the system are closely linked, it was observed that the SOUR values were particularly corresponded to the changes in microbial activity. Therefore, to determine the tolerance of activated sludge towards phenol, the toxicity of phenol on activated sludge was investigated at phenol concentration ranging from 100 to 2000 mg/L. Figure 4.1 shows the SOUR decreased as phenol concentration increased.



Figure 4.1: Specific Oxygen Uptake Rate (SOUR) of Activated Sludge at Varying Phenol Concentrations

From the study, a decrease in SOUR indicated that the toxicity of phenol had retarded the bioactivity of the activated sludge. According to the literature, SOUR values may provide a helpful guideline to indicate the condition of the treatment plant as summarised in Table 4.1 (APHA, 1998).

SOUR Values	Indication	
>20	Not enough solids for the BOD loading	
12 - 20	Good BOD removal and a sludge that settles well in the final	
	clarifier.	
<12	Too many solids or there has been a toxic occurrence.	

Table 4.1: Indication of SOUR Values on System Condition

The plot of SOUR gave a good indication of the biological activity in the reactor in the absence of phenol. In the absence of phenol (base-mix with 0 mg/L phenol), the SOUR of the activated sludge was about 14 mg  $O_2$ / (g MLVSS.h) (Figure 4.1). According to Table 4.1, this SOUR value indicated the activated sludge usually performed well by giving high COD removal and good sludge settleablity (discussed in Sections 4.2.1 and 4.3.3). As the phenol concentration increased from 50 to 2000 mg/L, SOUR values decreased accordingly from 13 to 6 mg  $O_2$ / (g MLVSS.h). The decrease of SOUR indicated low microbial activity due to the retardation of increasing phenol toxicity towards the bioactivity of the sludge. The acclimatisation of activated sludge to the increasing phenol concentration inhibits the growth of the activated sludge. The toxicity effect of phenol on the activated sludge bioactivity was further shown in the COD and phenol removals in batch study at increasing phenol concentrations (Section 4.2).

## 4.1.2 Phenol Volatilisation

Based on the phenol volatilisation tests in Figure 4.2, it was observed that the phenol concentration remained relatively constant during the whole duration of the test. There was no phenol loss under aerated condition for low, medium and high phenol concentrations.



Figure 4.2: Volatilisation Test of Phenol at Varying Phenol Concentrations under Sustain Aeration.

This result showed that when phenol was subjected into the reactor, it was fully biodegraded by the activated sludge instead of evaporation or air-stripping process. Therefore, the loss of phenol due to volatilisation during the experiments could be neglected.

### 4.2 Acclimatisation of Activated Sludge towards Phenol

Sequencing batch reactor (SBR) was employed to acclimatise the activated sludge to increasing phenol concentrations. Acclimatisation was carried out in batch study to support the activated sludge to produce the enzymatic material needed to degrade phenol and to reveal new population which can adapt to phenol and which is able to consume phenol as carbon source (Marrot *et al.*, 2006). The length of the acclimatisation period varies enormously depending on the concentration of phenol and the bioactivity of the activated sludge. Linkfield *et al.* (1989) also found that the period of acclimatisation might be long in anaerobic environments. Thus, the activated sludge was acclimatised in an aerobic condition throughout the present study.

The extent of the activated sludge in acclimatising the phenol was evaluated through daily effluent chemical oxygen demand (COD) and effluent phenol removal efficiency, together with the profiles of phenol, COD and dissolved oxygen (DO) in the reactor.

### 4.2.1 Daily Effluent Analysis for COD and Phenol Removal

Variation of effluent COD at different influent phenol concentrations (100 to 600 mg/L) is illustrated in Figure 4.3.



Figure 4.3: Effluent COD and Effluent Phenol in SBR Fed with Synthetic Wastewater Containing phenol at Increasing Concentration.

Throughout the study, the activated sludge exhibited good phenol removal efficiency with no phenol detected in the effluent up to 400 mg/L of influent phenol concentration. This indicated that phenol was completely degraded for influent phenol concentrations up to 400 mg/L. In addition, the COD present in

the effluent was always below 100 mg/L which meets the industrial wastewater discharged requirement by local government (DOE, 1974; Jusoh and Razali, 2008). Uygur and Kargi (2004) discovered that no inhibition on COD removal by activated sludge if the initial phenol concentrations are regulated below 400 mg/L. Thus, it can be assumed that the COD present in the effluent was largely caused by effluent suspended solids that discharged from the reactor.

However, accumulation of phenol was observed when the activated sludge was subjected to 600 mg/L of influent phenol concentration. The effluent COD and phenol concentrations fluctuated between 50 to 450 mg/L and 0 to 100 mg/L, respectively. These effluent quality levels did not comply to the Malaysia Department of Environment (DOE) discharge requirement where the effluent discharge into inland waters for the purpose of human consumption shall contain COD less than 100 mg/L and phenol concentration less than 1 mg/L. The ability of activated sludge acclimatised to 600 mg/L of influent phenol concentration declined drastically, probably attributed by the phenol toxicity which retarded the activity of activated sludge towards biodegradation. As observed in Figure 4.1, the retardation of phenol toxicity towards activated sludge biodegradation was shown in very low SOUR.

#### 4.2.2 Profile Study for COD and Phenol Removal

The biodegradation of phenol in the sequencing batch reactor (SBR) was also evaluated by analysing chemical oxygen demand (COD) and phenol concentration in the mixed liquor during the Fill and React modes. Besides, the dissolved oxygen (DO) level in the reactor during the biodegradation of phenol was also monitored. Figures 4.4 (a) to 4.4 (c) show the phenol, COD and DO profiles, respectively, at different influent phenol concentrations.





Figure 4.4: Profiles of (a) Phenol, (b) COD and (c) DO in SBR Fed with Synthetic Wastewater Containing Base-mix, 200, 400 and 600 mg/L Influent Phenol Concentrations



Figure 4.4: Profiles of (a) Phenol, (b) COD and (c) DO in SBR Fed with Synthetic Wastewater Containing Base-mix, 200, 400 and 600 mg/L Influent Phenol Concentrations

Introduction of phenol into the SBR up to 200 mg/L was immediately degraded with small accumulation of about 10 mg/L of phenol (Figure 4.4 (a)) in mixed liquor during the Fill mode. This corresponded to an accumulation of 80 mg/L of COD (Figure 4.4 (b)). Besides, the profiles study showed that degradation of COD and phenol had reached steady-state where the concentration of COD and phenol became constant at below 100 and 1 mg/L, respectively, within the Fill mode. This meant that phenol was very quickly degraded before the end of the Fill mode and the removal efficiency of phenol nearly 100% could be achieved within the Fill mode when only low influent phenol concentration was introduced into the SBR. This result was further supported by the DO profiles in Figure 4.4 (c). Low DO values during the Fill mode indicated that the activated sludge utilised most of the dissolved oxygen to degrade the accumulated phenol in the reactor. Once the phenol in the bioreactor was almost degraded, and activated sludge required less DO, the DO in the reactor increased to about 5 mg O<sub>2</sub>/L.

When the SBR was subjected to the introduction of higher influent phenol concentration of 400 mg/L, accumulation of both COD and phenol became more significant. The added phenol was not quickly assimilated by activated sludge in the SBR but slowly accumulated to a maximum of 85 mg/L phenol (Figure 4.4 (a)) which corresponded to 250 mg/L COD (Figure 4.4 (b)) during the Fill mode. This accumulation showed that the bioactivity of the activated sludge was retarded and thus biodegradation rate of the substrate dropped. It took about another 20 minutes after the Fill mode in order for both COD and phenol in mixed

liquor to achieve steady-state. As in the case of 200 mg/L phenol, the DO level in the reactor dropped to minimum during the Fill mode when oxygen was required for biodegradation. The DO level increased slowly and maintained at around 6 mg  $O_2/L$  (Figure 4.4 (c)) once the steady-state was achieved.

Inhibition of activated sludge towards biodegradation of phenol has actually been proven in the SOUR study (Figure 4.1). In addition, removal efficiency of phenol in the SBR declined with increasing influent phenol concentration. However, with the sufficiently long React mode, the accumulated phenol in the SBR would eventually be assimilated with high removal efficiency. This finding was in agreement with Uygur and Kargi (2004) study, where the phenol was almost completely degraded up to 400 mg/L.

However, when influent phenol concentrations increased further to 600 mg/L, accumulation of phenol and COD up to 200 and 1000 mg/L, respectively, was observed at the end of Fill mode (Figures 4.4 (a) and (b)). Moreover, the biodegradation rate of phenol was very much lower at 600 mg/L influent phenol concentration as compared to 400 mg/L influent phenol concentration. This showed that the bioactivity of the activated sludge was badly inhibited and it took up the whole eight hours React mode to biodegrade this accumulated substrate. In spite of this, there was still about 100 mg/L phenol corresponding to 600 mg/L COD left in the effluent at the end of React mode. In this instance, the activated sludges in the reactor were still tried hard to degrade the substrate and this kept

the DO level in the reactor very low, about 2 mg  $O_2/L$  (Figure 4.4 (c)) throughout both the Fill and React modes. This suggested that the bioactivity of activated sludge was strongly affected by the toxicity of phenol as proven in the SOUR study (Figure 4.1). Removal efficiency of phenol at this 600 mg/L influent phenol concentration was deteriorated due to the retardation of activated sludge bioactivity at high phenol concentration. It can be concluded that activated sludge could not acclimatise to high phenol concentration very well. At this stage, the activated sludge performed very poorly by giving very high COD (as detected in effluent of Figure 4.3) and turbid effluent due to poor sludge settleability even at long React mode of operation.

In summary, at lower phenol concentration of 200 mg/L, activated sludge can adapt to this level of phenol concentration very well with high substrate removal efficiency. At higher phenol concentration of 400 mg/L, the phenol toxicity exerted to activated sludge increased and the extent of acclimatisation dropped. However, good removal efficiency could still be sustained by providing long React time. Further increasing the phenol concentration to 600 mg/L would definitely increase the toxic level towards activated sludge. Owing to this, inhibition took place and bioactivity of the activated sludge declined. The activated sludge was not well acclimatised at this phenol level and eventually removal efficiency of the substrate was deteriorated.

## 4.3 Sludge Characteristics at Varying Influent Phenol Concentrations

The change of wastewater nature has striking effect on the characteristics of activated sludge in the biological suspensions (Le-Clech et al., 2003). Floc structure is one of the most frequent monitored parameters as flocs are the functional and operative units in the bioreactor, with varying texture and sizes influenced by the environmental conditions (Arregui et al., 2010). The treatment effectiveness and the effluent clarification are relied on the floc dimensions, structure, aggregation and filamentous aspect, which are the crucial parameters in wastewater treatment process to optimise the plant performance (Sezgin et al., 1978). Therefore, characteristics of activated sludge were taken into consideration during the study of the impact of varying influent phenol concentrations on the phenol removal efficiency and fouling propensity in the sMBR. The fouling effects of the synthetic influent are generally attributed to such properties as wastewater composition, types and characteristics of contaminants, organic loading, temperature, and pH (Geng and Hall, 2006). In the case of using phenol as feed, the resulting retardation and disintegration of activated sludge into smaller floc generally leads to higher fouling rate due to irreversible pore blocking (Wisniewski and Grasmick, 1998). Therefore, it is important to monitor the sludge characteristics for every concentration of influent phenol to verify the feasibility of activated sludge for phenol removal efficiency and to assess the filterability of sMBR for attaining high quality effluent.

The effect of increasing influent phenol concentration on the sludge characteristics was investigated through the observation of the sludge's particle size distribution, sludge morphology, mean floc size, sludge settleabilities and sludge concentrations.

## 4.3.1 Particle Size Distributions and Sludge Morphology Studies

Figures 4.5 and 4.6 illustrate the sludge size distribution and relative frequency histogram for floc equivalent diameter at varying feeding compositions throughout the study. The floc structures throughout the study at varying feeding compositions are illustrated in Figure 4.7.



Normalized number of particles per class width, f(Dp,j)

Figure 4.5: Sludge Size Distribution When Activated Sludge Acclimatised to Synthetic Wastewater Containing Base-mix and Increasing Phenol Concentrations.



Figure 4.6: Relative Frequency Histogram for Floc Equivalent Diameter when Activated Sludge Acclimatised to Synthetic Wastewater Containing
(a) Base-mix; (b) 100 mg/L; (c) 200 mg/L; (d) 300 mg/L; (e) 400 mg/L and (f) 600 mg/L Influent Phenol Concentration



Figure 4.7: Microscopic Observation (10 X magnification) of the Activated
Sludge Acclimatised to Synthetic Wastewater in the Reactor
Containing: (a) Base-mix; (b) 100 mg/L; (c) 200 mg/L; (d) 300
mg/L; (e) 400 mg/L and (f) 600 mg/L Influent Phenol Concentration

When the activated sludge was exposed to synthetic wastewater containing only base-mix (without phenol), the equivalent diameter of this acclimatised activated sludge was mainly distributed between 0 and 100  $\mu$ m and appeared most frequently around 50  $\mu$ m (Figures 4.5 and 4.6(a)). According to Amaral and Ferreira (2005), particle size within 10 to 100  $\mu$ m was classified as normal floc. This normal floc with irregular shapes and without undesired filamentous growth was observed in the activated sludge which was acclimatised to the synthetic wastewater without phenol (Figure 4.7(a)).

On the other hand, when the activated sludge was acclimatised to synthetic wastewater with increasing phenol concentration to 300 mg/L, the sludge equivalent diameters were concentrated at around 0 to 200 µm (Figures 4.6 (b) to (d)) with the minimal occurrence of Zoogloeal floc (Figures 4.7 (b) to (d)). The Zoogloeal growth was indicated by the dendrite projections from the floc aggregates. Gerardi (2002) had suggested several conditions associated with the Zoogloeal growth which included high or low food-to-mass ratio (F: M), high mean cell residence time (MCRT), long hydraulic retention time (HRT), nutrient deficiency and the presence of readily degradable carbonaceous biochemical oxygen demand (cBOD). The occurrence of Zoogloeal growth in this study was possibly caused by the high F: M ratio as the influent phenol loading was increased from 100 to 300 mg/L, while the mixed liquor suspended solids (MLSS) which corresponded to sludge concentrations were decreased gradually (Section 4.3.3).

The sludge size ranges of both activated sludge exposed to base-mix and 200 mg/L influent phenol concentration feeding compositions were found to be smaller than those of the flocs in conventional activated sludge process which usually range from 70 to 300  $\mu$ m (Zhang *et al.*, 1997). The smaller size of flocs in both of these feeding compositions had provided an advantageous condition for the mass transfer of carbon and oxygen. This enhanced the organic removal in the MBR as the smaller sludge more readily adapt to the changes in feed water quality as discussed in Section 4.4.3 (Huang *et al.*, 2001). The sludge fed with sucrose and 200 mg/L phenol did not encounter bulking problem throughout the operation, which was indicated by the low SVI values (Figure 4.8 in Section 4.3.3).

There was a drastic change in the floc size distribution and floc morphology when the activated sludge acclimatised to 400 and 600 mg/L of phenols. The floc size distributed with bimodal curves from 0.1 to 600  $\mu$ m and 9 to 1300  $\mu$ m, respectively, at 400 and 600 mg/L influent phenol concentrations. This disclosed a fact that two populations of flocs were dominated in the activated sludge, a microfloc with size less than 10  $\mu$ m and macrofloc with size more than 100  $\mu$ m, which was attributed to broad distributions of sludge size at both 400 and 600 mg/L influent phenol concentration. The co-existence of both types of flocs was examined under the microscope (Figures 4.7 (e) to (f)). Zoogloeal floc and weak microfloc were observed in activated sludge which was fed with 400 and 600 mg/L of phenol. As referred to Figure 4.5, bimodal distribution of the sludge size that acclimatised to 400 mg/L phenol was skew to right, leading to more Zoogloeal or bulking floc than the weak microfloc. The occurrence of Zoogloeal floc was mainly due to high food-to-microorganism (F:M) ratio in the reactor as the influent phenol loading was increased from 200 to 400 mg/L, while the mixed liquor suspended solids which corresponded to sludge concentrations were decreased gradually (Section 4.3.3) (Gerardi, 2002). These bulking flocs would eventually cause settling problem and give high sludge volume index (SVI).

Once the influent phenol concentration increased to 600 mg/L, the coexistence of weak microfloc and Zoogloeal floc was also observed (Figure 4.7), with sludge size distributing from 9 to 1300 µm, but was skew more to smaller floc size (Figure 4.5). This meant that at 600 mg/L of influent phenol concentration, weak microfloc was predominate than Zoogloeal floc. Phenol inhibited the microbial activity and flocculation of the sludge (Uygur and Kargi, 2004; Yu and Gu, 1996). At relatively high 600 mg/L phenol concentration, phenol toxicity inhibited the floc from aggregation which led to dispersed growth with pin-point floc that resulted in low SVI with turbid effluent (Gray, 1990), which further deteriorated the removal efficiency (Figure 4.3). The decrease of the bioactivity at increasing phenol concentrations was evidenced in the SOUR study (Figure 4.1). The bioactivity dropped approximately 30% when the phenol concentration increased to 400 mg/L. This SOUR was further declined to more than 60 % after the activated sludge was exposed to 2000 mg/L phenol (Figure 4.1). Thus, the influence of the increasing phenol concentration in the synthetic wastewater on the sludge morphology was proven.

#### 4.3.2 Mean Floc Size

Table 4.2 revealed the mean floc size in the activated sludge that acclimatised to base-mix and increasing phenol concentration throughout the operation.

 Table 4.2:
 Mean Floc Diameters at Varying Feed Compositions

Feed	Mean Floc Diameter (µm)
Base-mix	41
200 mg/L Phenol	44
400 mg/L Phenol	160
600 mg/L Phenol	167

As elaborated earlier (Section 4.3.1), the sludge exhibited irregular shape and loosely aggregated in structure when it was fed with base-mix only. On the other hand, minimal occurrence of Zoogloeal floc with dendrite projections from the floc aggregates was observed when activated sludge acclimatised to 200 mg/L of phenol. The occurrence of these flocs was noted by having mean floc size of 41 and 44  $\mu$ m, respectively, as base-mix and 200 mg/L phenol were fed as influents.

There was a drastic increased in the mean floc sizes when the activated sludge was acclimatised to 400 and 600 mg/L of phenols, which were 160 and  $167 \mu m$ , respectively. This was due to the co-existence of Zoogloeal floc and weak microfloc (Figures 4.5 and 4.7) in the activated sludge. The occurrence of Zoogloeal floc was identified by dendrite projections and was mainly due to high food-to-microorganism (F: M) ratio in the reactor. The changed of the sludge morphology from predominantly normal floc to Zoogloeal floc and then the coexistence of Zoogloeal and microfloc when the activated sludge was exposed to the synthetic wastewater without phenol, with increasing phenol to 200 mg/L, and then to 600 mg/L, respectively, would further influence the sludge settleability. According to Gray (1990), normal floc showed a good balance of floc-forming and filamentous bacteria with bigger floc size of more than 100  $\mu$ m, with sludge volume index (SVI) of about 70 mL/g. On the other hand, proliferation of filamentous bacteria was observed in bulking sludge with floc size more than 100 µm, but at high SVI value. As discussed later in Section 4.3.3, the sludge settleability measured in terms of SVI was actually shown to be affected by the change of sludge's morphology.

### 4.3.3 Sludge Settleabilities and Sludge Concentrations

Figure 4.8 presents the sludge concentrations measured as mixed liquor suspended solids (MLSS), and sludge settleability measured as sludge volume index (SVI), while Figure 4.9 exhibits the effluent suspended solids when the activated sludge was acclimatised to synthetic wastewater at different influent phenol concentrations.



Figure 4.8: Sludge Settleability and Sludge Concentration of Activated Sludge Acclimatised to Synthetic Wastewater Containing Base-mix and with Increasing Phenol Concentrations



Figure 4.9: Effluent Suspended Solids of Activated Sludge Acclimatised to Synthetic Wastewater Containing Base-mix and with Increasing Phenol Concentrations

The SVI is primarily used to evaluate the mixed liquor thickening characteristics besides settleability (Metcalf and Eddy, 2003). The SVI could have close relation to extracellular polymeric substances (EPS), which act as bridge for binding cells and other particulate materials together. The settleability and compactness of the activated sludge are directly related to floc structure (Pujols and Canlers, 1992). Hence, the floc structure is the key factors in determining the sludge compactness and settleability, which further affecting the biological removal efficiency. Bulking floc and floc disintegration are the two most common factors leading to the sludge settling problems (Comas *et al.*, 2003). As discussed earlier, microscopic observations (Figure 4.7) performed on the mixed liquor

samples exhibited the alterations in sludge morphology which further influenced the sludge settling characteristics (Figure 4.8).

When feeding composition consisted of base-mix or low influent phenol concentration of 200 mg/L, the activated sludge posed good settleability and compactness with SVI scattered below 50 mL/g (Figure 4.8). The sludge also grew from 3 to 12 g/L when the feeding composition was base-mix. As phenol was introduced into the reactor, the sludge concentration dropped gradually and scattered around 8 to 10 g/L. The decrease in the MLSS might be due to the sudden toxicity effect exerted to activated sludge when 200 mg/L of phenol was introduced. Once the activated sludge adapted to phenol, the sludge's growth balanced up the loss and maintained at quite high MLSS (about 10 g/L). Owing to this sufficient amount of sludge, the phenol could be assimilated efficiently and resulted in high removal efficiency (Figure 4.3).

As shown in Figure 4.8, it was noted that increasing influent phenol concentration up to 400 mg/L increased the SVI. The SVI increased gradually beyond 50 mL/g when activated sludge was acclimatised to 400 mg/L phenol. Based on the morphology observations and particle size distributions studies, low SVI for the activated sludge that was acclimatised to the synthetic wastewater containing phenol concentration below 400 mg/L was basically due to the predominant of normal floc with minimal Zoogloeal floc that gave good compactness. Dendrite projection from the Zoogloeal floc enhanced the sludge settleability by bridging up the floc, and therefore produced clear effluent without suspended sludge (Figure 4.9). However, poorer settleability was observed at the latter stage of the acclimatisation of activated sludge to 400 mg/L influent phenol concentration with a SVI of around 120 mL/g. When the settleability of the sludge was deteriorated, the sludge concentration also declined accordingly to 4 g/L (Figure 4.8) due to the retardation of sludge's growth and sludge loss to the discharged effluent.

Suspended solids in the effluent after the mixed liquor had settled for 30 minutes also indicated the floc structure in the sludge suspension (Chang et al., 1999). At the latter stage of the acclimatisation of activated sludge to 400 mg/L phenol, owing to the toxicity of phenol at this phenol concentration, some of the floc were inactivated and disintegrated to weak microflocs which were quite close to dispersed or pin-point floc (Uygur and Kargi, 2004; Yu, 1994). In addition, bulking floc was more predominate than this microfloc as shown in sludge size distribution (Figure 4.5). This bulking floc contributed to poor compactness of sludge blanket during settling, resulting in the increase of SVI beyond 50 mL/g (Figure 4.8), while the dispersed growth led to discharged suspended sludge in the effluent (Figure 4.9). Similar finding was also reported by Uygur and Kargi (2004) where the SVI was found to increase drastically when the phenol concentration was higher than 400 mg/L due to the inactivation and disintegration of the organisms. However, Yu and Gu (1996) discovered that at low influent phenol concentration of less than 400 mg/L, growth of filamentous bacteria was

stimulated and reduced the sludge settleability. As influent phenol concentration increased to more than 800 mg/L, the accumulated phenol exerted inhibitory effect to microorganisms and stimulated the growth of dispersed bacteria which caused turbid effluent (Yu and Gu, 1996).

The turbidity in effluent of activated sludge which was acclimatised to 400 and 600 mg/L phenol (Figure 4.9) revealed the presence of microfloc and bulking floc simultaneously. Due to the retardation of sludge's growth by high phenol toxicity, the MLSS also decreased gradually from 8 g/L at the beginning of 400 mg/L influent phenol operation to around 5 to 6 mg/L at the end of 600 mg/L influent phenol operation (Figure 4.8). According to Laspidou and Rittmann (2002), increase of organic loading might stimulate high production of EPS, leading to high sludge viscosity. Therefore, increasing phenol concentration to 600 mg/L would encourage the sludge disintegration and the release of EPS from the sludge deflocculation. This increased the binding of sludge floc, which caused the occurrence of macrofloc and microfloc at this influent phenol concentration.

In summary, the introduction of increasing phenol concentration and thus its toxicity is important in influencing the sludge characteristics. For influent phenol concentration less than 400 mg/L, normal floc with minimal Zoogloeal floc in the activated sludge enhanced the sludge settleability with a very clear effluent. On the other hand, co-existence of Zoogloeal floc and microfloc was observed in the activated sludge that was acclimatised to relatively high phenol concentration of 400 and 600 mg/L. Predominance of bulking floc at 400 mg/L showed high SVI and exhibited poor sludge settleability, while predominance of dispersed growth of pin-point floc at 600 mg/L deteriorated the quality of effluent with discharged suspended sludge.

### **4.4 Membrane Bioreactor**

Increasing phenol concentration in wastewater increased the toxic level that was exerted to the activated sludge. High concentration of phenol or its toxicity will disintegrate the sludge and lead to dispersed growth that eventually deteriorates the quality of treated effluent with discharged suspended sludge. In order to provide higher quality effluent and to overcome this kind of settleability problem, submerged membrane bioreactor (sMBR) was used in which solid-liquid separation was achieved by means of membrane filtration instead of conventional process of settling and drawing. Also, with the development of less expensive ceramic membrane, sMBR process will play an important role in wastewater treatment in future. However, the main disadvantage of MBR process is the occurrence of membrane fouling. Thus, better understanding of the influence of influent loading on fouling and developing control strategies will further facilitate the wide application of this technology. In this study, the extent of the membrane fouling or flux performance was evaluated at various suction pressures. In addition, the fouling characteristic of the membrane was also studied under the influence of various phenol concentrations, and was explained and related to

sludge characteristic at different phenol loadings. Besides, treated effluent in sMBR was monitored to analyse its treatment efficiency and to assess the performance of the sMBR system. Lastly, improvements on the sMBR's filterability performance was achieved by evaluating various bubbling modes (non-bubbling, continuous bubbling and intermittent bubbling) on the fouling rate.

#### **4.4.1 Membrane Permeability**

The effect of suction pressures on the permeate flux and the membrane permeability is presented in Figure 4.10.



Figure 4.10: Membrane Permeability of the Ceramic Membrane in Pure Water And Mixed Liquor at Varying Suction Pressures
Owing to the fouling effect, the permeability of the membrane in pure water was higher ( $35.164 \text{ L/m}^2.\text{h.kPa}$ ) compared to the permeabilities in the mixed liquor of MBR ( $22.687 \text{ L/m}^2.\text{h.kPa}$ ). The presence of suspended solids in the wastewater caused the clogging and deposition of flocs on the membrane surface which further deteriorated the membrane permeability.

### 4.4.2 Flux Characteristics at Varying Suction Pressures

In general, the deposition of foulants on the membrane is proportional to the permeate flow or the operation flux. In order to understand how the suction pressure affects the flux declination, the permeate flux was monitored at varying feeding compositions during the operation of submerged membrane bioreactor (sMBR). In this study, the suction pressure was regulated by diaphragm vacuum pump in a range of -7.5 to -30 kPa for every feeding composition (base-mix without phenol, 200, 400 and 600 ppm phenol concentrations). Flow rate of the permeate was determined by measuring the volume of permeate collected over specific time (fixed at one minute in this study). The extent of fouling in sMBR system was assessed quantitatively through the variation of the relative flux (J/Jo) with time. The relative flux (J/Jo) is expected to decrease with time due to fouling phenomenon. In general, the permeate flux decreased with time at three different suction pressures of -7.5, -15 and -30 kPa at varying influent phenol concentrations as shown in Figures 4.11 (a) to 4.11 (d).



Figure 4.11: Relative Flux of the Ceramic Membrane with Respect to the Operation Time at Varying Suction Pressures in sMBR Fed with Synthetic Wastewater Containing (a) Base-mix, (b) 200 mg/L, (c) 400 mg/L, (d) 600 mg/L of Influent Phenol Concentration



Figure 4.11: Relative Flux of the Ceramic Membrane with Respect to the Operation Time at Varying Suction Pressures in sMBR Fed with Synthetic Wastewater Containing (a) Base-mix, (b) 200 mg/L, (c) 400 mg/L, (d) 600 mg/L of Influent Phenol Concentration

The decrease of the permeate flux over time was mainly due to the continuous operation of suction filtration that induced the deposition of foulant on the membrane surface and reduced the flow of permeate through the membrane. In addition, initial sharp decline in the relative flux was observed at the first five minutes operation time for the sMBR operated with pressures of -15 and -30 kPa at all the feeding compositions (Figures 4.11 (a) to (d)).

Table 4.3 shows the declining rate of the permeate flux increased with increasing suction pressure. A sudden increase in fouling rate was observed when the suction pressure was increased from -7.5 to -15 kPa, and the fouling rate became relatively stable at -30 kPa with slight decrease for sMBR fed with synthetic wastewater containing phenol. The increase of fouling rate was mainly caused by the pore clogging and the formation of compact cake layer on the membrane surface at high suction pressure. The compact cake layer served as a barrier for the flow of liquid through membrane at high suction pressure.

Table 4.3: The Effect of Increasing Phenol Concentration in SyntheticWastewater on the Fouling Rate for sMBR Operated at Varying<br/>Suction Pressures.

Synthetic Wastewater containing	Fouling Rate for MBR Operated at Varying Suction Pressures (% relative flux/min)			
	-7.5 kPa	-15 kPa	-30 kPa	
Base-mix	0.5	6.8	8.0	
200 mg/L Phenol	0.8	7.9	7.4	
400 mg/L Phenol	3.2	7.4	6.3	
600 mg/L Phenol	1.5	3.2	2.2	

In the sMBR fed with synthetic wastewater containing base-mix and 200 mg/L influent phenol concentration (Figures 4.11 (a) and (b)), the membrane fouled at a higher rate at higher suction pressure of -15 and -30 kPa as compared to those operated at low suction pressure (-7.5 kPa). Besides, rapid declination of the permeate flux was also observed which was caused by high initial operating flux at high suction pressure. Hong *et al.* (2002) proposed that the thickness of fouled layer was directly related to foulant flux entering the cake layer which was the function of foulant concentration and permeate flow. The transportation and the compression of fouling components onto the membrane layer were enhanced at high suction pressure (Bilad *et al.*, 2011). Thus, the sMBR operated at high suction pressure might transfer the foulant at a higher rate towards the deposited cake layer, resulting in a sharp declination in relative flux. This can be seen in Table 4.3 where the fouling rate increased from 0.5 and 0.8 % relative flux/min at

suction pressure of -7.5 kPa to 6.8 and 7.9 % relative flux/ min at suction pressure of -15 kPa for sMBR fed with synthetic wastewater containing base-mix and 200 mg/L phenol, respectively.

Furthermore, particle size distribution study (Figure 4.5) showed that the size of the bioflocs fell within the range of 0.1 to 100  $\mu$ m with an average floc size of 41 and 44  $\mu$ m for the sMBR fed with synthetic wastewater containing base-mix and 200 mg/L influent phenol, respectively. According to the floc size distribution (Figure 4.5), normal floc with minimal Zoogloeal floc were predominated in the activated sludge fed with synthetic wastewater containing base-mix and 200 mg/L phenol. Sludge size of this kind of flocs was greater compared to the pore size of the membrane. Therefore, it was only loosely aggregated with the formation of cake layer. The permeate could still pass through the porous cake layer attached loosely on membrane surface and could be easily removed by the liquid flow or the shear-stress from aeration.

Nonetheless, for sMBR fed with synthetic wastewater containing 400 and 600 mg/L phenol, the membranes fouled faster, 3.2 and 1.5 % relative flux/ min, respectively, at -7.5 kPa, as compared to the sMBR used to treat 200 mg/L influent phenol. These were mainly due to the presence of two distinctive floc sizes (Figures 4.5 and 4.6), i.e., Zoogloeal floc (which corresponded to increasing EPS and lipids concentration in the mixed liquor) and microfloc (which might induce serious pore blocking and irreversible fouling). At 400 mg/L phenol,

Zoogloeal or bulking floc was predominated compared to microfloc. According to Laspidou and Rittmann (2002), increase of organic loading might stimulate high production of extracellular polymeric substance (EPS) and soluble microbial products (SMP), which lead to high sludge viscosity, rise of transmembrane pressure (TMP) and eventually fouling potential. On the other hand, when phenol concentration increased to 600 mg/L, weak microfloc was dominated due to the floc disintegration. These small flocs could easily clog the membrane pore which was hardly removed by the shear stress generated from liquid flow.

Apart from the observation mentioned earlier, that is membrane fouled faster at higher suction pressure, the relative flux was also found to be lower at - 7.5 kPa than at -15 and -30 kPa, especially for sMBR fed with synthetic wastewater containing base-mix and 200 mg/L influent phenol concentration (Figures 4.11 (a) and (b)). This can be explained by the thickness and compactness of fouled layer on the membrane surface. At low suction pressure of -7.5 kPa, the membrane experienced lower compression force leading to the formation of thick and loose fouled layer along the membrane surface (Figure 4.12 (a)). The loosely packed and thick fouled layer might trap the air within the overlapped floc particles in fouled layer. Overtime, thicker and thicker fouled layer was formed gradually and more air was trapped. This hindered the flow of permeate through the membrane and eventually the relative flux was lowered. In contrast, at high suction pressure of -15 and -30 kPa, due to the high transportation rate of foulant to membrane and high compression force

experienced by the membrane, thin and compact fouled layer was formed very quickly (Figure 4.12 (b)). This thin and compact fouled layer was still able to facilitate the filtration of permeate, thus higher relative flux can be maintained (up to 80 % relative flux at suction pressure of -30 kPa, Figures 4.11 (a) and (b)). Nonetheless, at high suction pressure, the membrane fouled extremely fast with 8.0 and 6.8 % relative flux/ min (Table 4.3) for sMBR fed with synthetic wastewater containing base-mix and 200 mg/L phenol, respectively.





Figure 4.12 (a)

Figure 4.12 (b)



(b) -30 kPa

Figure 4.11 (d) shows an exceptional flux characteristic where the lowest relative flux of 20 % was obtained at the highest suction pressure of -30 kPa. As explained earlier, thin and compact fouled layer was favored at high suction pressure without air trapping within the overlapped floc particles. This allowed the continuous filtration of the permeate through the membrane. However, at increasing phenol loading to 600 mg/L, the sludge characteristics study showed that the floc was disintegrated. The blockage of membrane pores by these disintegrated flocs was hardly to be removed by the shear stress from liquid circulation and eventually led to irreversible fouling.

In summary, when the sMBR was operated at higher suction pressure, foulants were transported to the membrane surface at a faster rate. Thin, compact and without air trapping fouled layer was formed very quickly on the membrane surface owing to the high compression force experienced by the membrane. Therefore, fouling rate increased with suction pressure with higher percentage of relative flux. In contrast, thick and loosely fouled layers were formed gradually at lower suction pressure. The membrane fouled slower with lower percentage of relative flux as the trapped air within the overlapped flocs in fouled layer hindered the flow of permeate through the membrane.

# 4.4.3 Effluent Characteristics

The effluent quality of the sMBR at varying feeding compositions is summarised in Table 4.4 to evaluate the performance of sMBR in removing phenol.

Table 4.4: COD and Phenol Removals of sMBR Fed with Synthetic Wastewater Containing Base-mix and Increasing Phenol Concentration at Low and High Suction Pressures

	Feeding	Base-mix	200 mg/L	400 mg/L	600 mg/L
Suction	1		Influent	Influent	Influent
Pressu	e		Phenol	Phenol	Phenol
			000/	000/	0.50/
	COD	94%	89%	88%	85%
-7.5	Removal				
kPa	Phenol	-	92%	92%	90%
	Removal				
	COD	90%	70%	84%	35%
-30	Removal				
kPa	Phenol	-	80%	89%	65%
	Removal				

#### **4.4.3.1** Synthetic wastewater containing base-mix (without phenol)

The sMBR showed good performance in removing organic constituents contributed from base-mix (sucrose and peptone) in the influent wastewater. In the sMBR, COD in the permeate was solely contributed by the remaining soluble organic constituents as suspended solids were completely retained by membrane filtration. Cote *et al.* (1998) and Gander *et al.* (2000a) reported that membrane in the MBR was able to improve the COD removal by 30% as the membrane completely retained the suspended COD and high molecular weight organic compounds. Through the permeate analysis, it was discovered that biological removal efficiency dropped with increased suction pressures. The COD removals in the sMBR fed with base-mix were the highest, 94 % and 90 %, respectively, when the sMBR was operated at -7.5 and -30 kPa of suction pressures. At higher suction pressure, influent and permeate flow rate had to be increased accordingly to maintain the constant working volume in the experimental reactor. Sun *et al.* (2006) reported that microorganism in the reactor required sufficient time to completely oxidise the organic constituents to carbon dioxide and water, while synthesis the remaining into new cellular materials. This explained at high suction pressure, hydraulic retention time was reduced and led to incomplete degradation of COD in the mixed liquor, resulting in higher COD in permeate.

#### 4.4.3.2 Synthetic wastewater with varying phenol concentrations

The concentration of phenol in the industrial wastewater usually ranged between 100 and 1000 mg/L (Al- Malack, 2007). In Section 4.3, the characteristic of the sludge was proven to be affected by increasing phenol loading from 0 to 600 mg/L, where the sludge's morphology shifted from predominantly normal floc to Zoogloeal floc and then co-existence of Zoogloeal floc together with disintegrated floc. The shift of the sludge morphology would actually influence the phenol removal efficiency as can be seen in Table 4.4.

The performance of the submerged MBR (sMBR) in removing organic constituents declined as the activated exposed to phenol containing wastewater. As observed in Table 4.4, the COD and phenol removals in the sMBR dropped slightly to 89 % and 92 %, 88 % and 92 %, 85 % and 90 %, respectively, when the sMBR was operated at -7.5 kPa with influent phenol concentrations of 200, 400 and 600 mg/L. When the sMBR was operated at -30 kPa for the same phenol concentrations influent, the COD and phenol removals were further reduced to 70 % and 80 %, 84 % and 89 %, 35 % and 65 %, respectively.

These observations revealed that longer degradation period was required for higher concentration of phenol in influent. In the operation of the sMBR, hydraulic retention time (HRT) of the reactor solely depends on the suction pressure of membrane filtration. Thus, the higher the suction pressure, the shorter the HRT in order to maintain the constant working volume in the reactor. This means that the shorter the contact time between microorganism and phenol in the sMBR. Even though the sludge has already acclimatised to that particular phenol concentrations at each run, there was still accumulation and incomplete removal of phenol in the mixed liquor and permeate. This was due to the increasing toxic effect exerted to microorganism by increasing phenol loading. Uygur *et al.* (2004) discovered that as the phenol concentration was more than 400 mg/L, the activated sludge might be inhibited from COD and nutrients removal (Uygur and Kargi, 2004). The inhibitory effect of phenol towards the sludge activity was further supported by SOUR in Section 4.1.1 (Figure 4.1). However, the sMBR was also proven to show the feasibility in producing clear effluent using acclimatised sludge (Barrios-Martinez *et al.*, 2006). Very clear effluent was observed and none of the discharged suspended sludge was detected in the collected permeate throughout the sMBR operation at different phenol loadings or at different suction pressures.

# 4.5 Effect of Sludge Characteristics on Membrane Permeabilities

According to Farquharson (2007), fouling potential would increase with decreasing particle size. However, Meng *et al.* (2006) reported that fouling rates had a negative correlation with mean particle size for particles falling in certain ranges. Therefore, particle size distribution is one of the important factors affecting fouling other than mean floc size. Table 4.5 outlines the impact of feeding composition on the mean floc size and membrane permeability.

Feeding Composition	Mean Floc Size (µm)	Membrane Permeability (L/m <sup>2</sup> .h.kPa)
Control	-	40.6
Base-mix	41	27.4
200 mg/L Phenol	44	22.7
400 mg/L Phenol	160	10.1
600 mg/L Phenol	167	12.4

Table 4.5: The Effect of Feeding Composition on the Mean Floc Size and the Membrane Permeability

Permeability of the membrane declined from 27.4 to 12.4 L/m<sup>2</sup>.h.kPa when the sMBR was fed with synthetic wastewater containing base-mix and then with increasing phenol concentration. As explained in Section 4.3, the characteristic of the sludge was strongly influenced by different phenol loadings. This included the sludge size distribution (Figure 4.5) and sludge's morphology (Figure 4.7). The change in membrane permeabilities for each type of influent clearly depicted the influence of phenol concentration on the sludge's size and their structure, which further affected the filtration performance in the sMBR.

Membrane permeabilities for the operation of sMBR fed with synthetic wastewater containing only base-mix and 200 mg/L phenol were found to be quite similar, which were 27.4 and 22.7 L/m<sup>2</sup>.h.kPa (Table 4.5), respectively. This similarity could be explained by particle size distribution and floc's structure. Based on the morphology observations in Figure 4.7, the flocs that were acclimatised to these two synthetic wastewaters (base-mix and 200 mg/L influent

phenol concentration) were dominated with normal floc with minimal Zoogloeal floc without undesired filamentous growth. In addition, the floc size distribution (Figure 4.5) showed that the size of the floc at these feeding concentrations ranged within 0.1 to 100 µm with an average floc size of around 40 µm. Sludge size of this kind of floc was greater than the pore size of the membrane. Therefore, it was only loosely aggregated with the formation of cake layer. As observed in the reduction of relative flux over time in the sMBR (Figures 4.11 (a) and (b)), these weak and less compact flocs deposited as porous cake layer on the membrane surface when suction pressures were applied across the membrane. The cake layers accumulated on the membrane surface were found to have voids within the overlaps of flocs which were proven by Yu et al. (2006) using scanning electron microscope (SEM). With the porous fouled layer, permeate could still pass through the voids between the deposited particles easily even though the cake layer created certain resistance to the permeate flow. Furthermore, the loosely attached porous cake layer on the membrane surface could be easily removed by the flow of liquid or the shear-stress from aeration.

The mean values for the flocs present in both influents (base-mix and 200 mg/L phenol) were found very close to the optimal mean floc size suggested by Sun *et al.* (2006). Sun *et al.* (2006) identified that the optimal floc size with 50  $\mu$ m would enhance the MBR performance by attaining the highest flux rate and reduce the membrane fouling. This finding explained the high membrane permeabilities (Table 4.5) and lower fouling rate (Table 4.3) of the sMBR fed

with synthetic wastewater containing base-mix and 200 mg/L phenol at low suction pressure.

The influence of floc size on the membrane permeability was further evidenced at 400 and 600 mg/L influent phenol concentrations. At 400 and 600 mg/L influent phenol concentrations, the membrane permeabilities were decreased tremendously to 10.1 and 12.4 L/m<sup>2</sup>.h.kPa, respectively. As shown in Figure 4.5, bimodal curves were observed in the sMBR fed with 400 and 600 mg/L phenol concentrations. This indicated two population of flocs were coexisting in the sMBR; a microfloc with size less than 10 µm and macrofloc or Zoogloeal floc with size greater than 100  $\mu$ m. The concurrent presence of these two distinctive flocs is illustrated in Figure 4.7. At 400 mg/L phenol, Zoogloeal or bulking floc was predominated compared to microfloc. According to Laspidou and Rittmann (2002), increase of organic loading might stimulate high production of extracellular polymeric substance (EPS) and soluble microbial products (SMP), which led to high sludge viscosity, rise of transmembrane pressure (TMP) and eventually fouling potential. The bulking floc tends to form non-porous "gel" like fouling layer due to compact floc structure and viscous mixed liquor (Meng et al., 2006; Nakanishi et al., 1987). The "gel layer" easily attached on the membrane surface and blocked the membrane pores, which was hard to be removed by airscouring or liquid flow, and led to lower membrane permeability (Yu et al., 2006).

On the other hand, when phenol concentration increased to 600 mg/L, weak microfloc was dominated due to the floc disintegration. These small flocs can easily clog the membrane's pore. Wisniewski and Grasmick (1998) found that the mixed liquor suspension produced from the floc disintegration consisted of particles having size of around 2  $\mu$ m. Besides, the existence of microfloc in this study was confirmed by high turbidity of the effluent after settlement (Figure 4.9), which corresponding to non-settleable fraction in the mixed liquor. The microfloc with diameter which was comparable or smaller than the membrane pores might be adsorbed on the pore wall, and inducing serious pore blocking. Pore blocking caused irreversible fouling, and the cake layer was strongly attached on the membrane surface which was hardly removed by shear stress generated from liquid flow.

Further explanation of low membrane permeability at high influent phenol concentration can be elaborated with the presence of EPS. The release of EPS from the floc disintegration led to the adherence of floc into large aggregates (Le-Clech *et al.*, 2006). The secretion of EPS around the cell surface and intercellular space served as "glue" to adhere the existing Zoogloeal floc into bulking floc. From microscopic observation, the Zoogloeal floc appeared as compact and regular shape structure with dendrite projections. The SVI for 400 and 600 mg/L influent phenol were very close to 100 mL/g (Figure 4.8), indicating bulking and the formation of poor settleability sludge in sludge suspension. Bulking sludge at high influent phenol concentration fouled the membrane more severely than

normal granular sludge at low influent phenol concentration (Choi *et al.*, 2002; Lim and Bai, 2003; Thompson and Forster, 2003). Moreover, the presence of Zoogloeal floc was corresponding to the increasing EPS and lipids concentration in the mixed liquor. As the EPS and lipid concentrations increased, the viscosity of the sludge in the mixed liquor was enhanced and consequently the porosity and the structure of fouling cake layer were affected (Kim *et al.*, 1998).

## 4.6 Mitigation of Membrane Fouling

Although the MBR process generates acceptable quality effluent during fouling, continuous membrane filtration tends to decrease the membrane permeability due to the deposition of foulants on the membrane. In order to increase the flux or membrane permeability and to maintain the optimal permeate flux in the sMBR, the deposited cake layers need to be removed. Usually, specific cleaning methods such as intermittent aeration and relaxation are carried out to remove the fouled layer on the membrane surface. In this study, mitigation of membrane fouling by scouring effect created from the uplifting air bubbling was investigated.

Figures 4.13 to 4.16 illustrate the effect of various bubbling scenarios on the relative flux at suction pressures of -7.5 and -30 kPa when the sMBR was fed with synthetic wastewater containing base-mix, 200, 400 and 600 mg/L influent phenol concentrations.



Figure 4.13: Comparison of Relative Flux at Varying Bubbling Modes for sMBR Fed with Synthetic Wastewater Containing Base-mix Operated at (a) -7.5 and (b) -30 kPa



Figure 4.14: Comparison of Relative Flux at Varying Bubbling Modes for sMBR Fed with Synthetic Wastewater Containing 200 mg/L Influent Phenol Concentration Operated at (a) -7.5 and (b) -30 kPa



Figure 4.15: Comparison of Relative Flux at Varying Bubbling Modes for sMBR Fed with Synthetic Wastewater Containing 400 mg/L Influent Phenol Concentration Operated at (a) -7.5 and (b) -30 kPa



Figure 4.16: Comparison of Relative Flux at Varying Bubbling Modes for sMBR Fed with Synthetic Wastewater Containing 600 mg/L Influent Phenol Concentration Operated at (a) -7.5 and (b) -30 kPa

In general, the relative fluxes declined with the operation time when the sMBR were operated without bubbling and with continuous bubbling modes. As observed, the performance of the continuous bubbling and suction in mitigating fouling did not exceed that of the non-bubbling mode (Figures 4.13 to 4.16). When the membrane was fouled, the relative flux was maintained at a higher percentage of relative flux with mitigation mode of without bubbling than that with continuous bubbling. There was no flux enhancement in the continuous bubbling operation due to the fluid resistance generated from the uplifting bubbles (Hong *et al.*, 2002). The bubbles that were continuously lifted up from the bottom of membrane served as a barrier for the flow of permeate. This indicated that the effect of continuous scouring on the membrane for mitigation of fouling was not significant.

The sMBR operated with intermittent bubbling and suction showed superior performance in mitigating membrane fouling as the relative flux could be recovered during the relaxation interval. As the air bubbles were lifted up from the aeration ring locating at the bottom of membrane, the deposited cake layer on the membrane surface was removed by the shear stress. This further enhanced during the intermittent membrane relaxation, where the relaxation assisted the air bubbles to diffuse the foulants back to the mixed liquor suspension. Consequently, the deposited cake layer on the membrane surface was loosened and depleted, and eventually the relative flux was recovered to about 70% and 90% at suction pressures of -7.5 and -30 kPa, respectively, for the sMBR fed with synthetic

wastewater containing only base-mix (Figures 4.13 (a) and (b)). For the sMBR fed with synthetic wastewater containing 200 mg/L phenol, the recovery of the relative flux could be achieved up to about 80 % for both suction pressures of -7.5 and -30 kPa (Figure 4.14 (a) and (b)). Similarly to the sMBR with 400 and 600 mg/L phenol, as high as 70 % to 100 % (Figures 4.15 (a) and (b)) and 80 % to 90 % (Figures 4.16 (a) and (b)) of flux recovery were obtained, respectively, at suction pressures of -7.5 and -30 kPa.

Higher flux recovery was observed at -30 kPa as compared to -7.5 kPa for the sMBR fed with base-mix. This might be due to the thickness and compactness of the fouled layer (Figures 4.12). Fouled layer at -7.5 kPa was loosely-packed and thick due to the low compression force (Figure 4.12 a). The thick fouled layer could block the uplifting bubbles to scour the membrane surface. Besides, there were vacant spaces between the overlapping floc particles which could trap the air bubbles within the slimy fouled layer. The trapped air bubbles along the membrane surface acted as an obstacle for the flow of permeate (Figure 4.17). When higher suction pressure was applied to the sMBR, higher compression force led to the formation of thin and compact cake layer (Figure 4.12 (b)). This kind of compact cake layer did not allow the entrapment of air bubbles. Hence, the air bubbling could scour the foulants deposited on the membrane surface more efficiently, and induced higher flux recovery (Figure 4.17 (b)). This implies an important finding that, the flux could be recovered ideally when intermittent bubbling and relaxation was employed in the operation of high suction pressure MBR.

Contrarily, higher flux recovery was observed at lower suction pressure when the sMBR was fed with higher phenol loading. For the sMBR fed with 400 and 600 mg/L influent phenol concentrations (Figures 4.15 and 4.16), flux recovery of up to 100 % and 90 %, respectively, was obtained at lower suction pressure than at higher suction pressure (only 70 % and 80% flux recovery, respectively). This might be due to the appearance of floc in the mixed liquor. At influent phenol concentration of 400 mg/L, bimodal of sludge size distribution was obtained with predominance of bulking floc. The bulking floc tend to form non-porous "gel" like fouling layer due to compact floc structure and viscous mixed liquor (Meng et al., 2006; Nakanishi et al., 1987). The "gel layer" was easily attached on membrane surface and blocked the membrane pores, which was hard to be removed by air-scouring or liquid flow, and led to lower membrane permeability (Yu et al., 2006). On the other hand, when phenol concentration was increased to 600 mg/L, weak microfloc was dominant due to the floc disintegration. Higher influent phenol concentration might induce the floc to disintegrate into smaller floc. These small flocs would easily clog the membrane's pore. On top of the morphology of floc that caused irreversible pore clogging, higher suction pressure of -30 kPa would transport the foulant to the membrane surface faster with greater compression force. Consequently, irreversible thin and compact fouled layers were formed as well as pore clogging. This finding implies

that the mitigation of membrane fouling is not only relied on the mode of bubbling and the suction pressure, instead, the phenol loading that influenced the characteristics of the sludge also played a significant role in improving the flux recovery.



Figure 4.17: Illustrations for the Intermittent Scouring Effect Along Membrane Surface Operated at (a) -7.5 kPa and (b) -30 kPa

Complete recovery of flux was not achieved by intermittent bubbling and membrane relaxation. This finding was similar to the study reported by Hong *et al.* (1997), where the permeate flux was only partially recovered. Incomplete recovery of permeate flux after relaxation was mainly due to the irreversible fouling. These adsorbed bioflocs on the membrane surface and pores which could not be removed by mechanical scouring, even no suction pressure was applied to the membrane. According to Decarolis *et al.* (2001), pore clogging fouling would only be recovered by chemical cleaning or backwashing. Air backwashing was more superior to the air scouring to maintain the membrane permeability (Chae *et al.*, 2006). Therefore, it is practical if low cost ceramic membrane was used as it is robust to backwashing.

In summary, air scouring generated from the gas bubbles was able to mitigate the fouling as proposed by most of the researchers. Membrane fouling could be effectively mitigated by intermittent air scouring and relaxation. Whilst, there was no significant enhancement of membrane permeability with the application of continuous air scouring as compared to the membrane without scouring effect. However, with the presence of toxic substance, such as phenol in the feeding composition, the change of the sludge's characteristics needed to be considered in the fouling mitigation.

## **CHAPTER 5**

## CONCLUSIONS

Phenol removal by using ceramic submerged membrane bioreactor (sMBR) was successfully evaluated. In the treatment of wastewater containing phenol, the effect of increasing phenol concentration on the characteristics of the sludge and the performance of sMBR were investigated. Fouling characteristics of the membrane at different suction pressures and the mitigation of membrane fouling at various bubbling modes were also successfully evaluated.

The change in the characteristic of the sludge was evaluated to investigate the impact of varying phenol concentrations in synthetic wastewater towards the activated sludge. It was found that the sludge morphology changed from predominantly normal floc to Zoogloeal floc when the activated sludge was exposed to synthetic wastewater without phenol and then with increasing phenol to 400 mg/L. The occurrence of normal floc with minimal Zoogloeal floc in the activated sludge enhanced the sludge settleability with a very clear effluent. At relatively high influent phenol concentration of 400 and 600 mg/L, the coexistence of bulking floc and microfloc was observed through the bimodal sludge size distribution study. Predominance of bulking floc at 400 mg/L gave poor sludge settleability with high SVI values, while predominance of dispersed growth of pin-point floc at 600 mg/L deteriorated the quality of effluent with discharged suspended sludge.

The shift of the morphology of the sludge at different phenol concentration influenced the performance of sMBR in the treatment of phenol containing wastewater. Up to 94 % of COD removal was achieved when sMBR was fed with synthetic wastewater with base-mix (without phenol). Even though when phenol in synthetic wastewater was increased to 600 mg/L, treatment performance of sMBR can still be maintained with COD and phenol removal of 85 % and 90 %, respectively. However, biological removal efficiency declined with increased suction pressures. Hydraulic retention time of the MBR and also the contact time between microorganism and phenol were reduced at high suction pressure. This led to incomplete degradation of COD in the mixed liquor, resulting in lower COD and phenol removals.

The extent of the membrane fouling or flux performance was evaluated at various suction pressures ranging from -7.5 to -30 kPa. It was found that permeability of the membrane in the bioreactor declined with operating time due to the accumulation of foulants on membrane surface. When the sMBR was operated at higher suction pressure, thin and compact fouled layer was formed very quickly on the membrane. Foulants were transported to the membrane surface at a faster rate leading to higher fouling rate. In contrast, the membrane fouled slower with lower percentage of relative flux when the sMBR was

operated at lower suction pressure. Thick and loosely fouled layers were formed gradually, which trapped air within the overlapped flocs in fouled layer that hindered the flow of permeate through the membrane.

Fouling characteristic of the membrane was closely related to the sludge characteristic at different phenol concentrations. For sMBR fed with base-mix and 200 mg/L phenol, the loosely aggregated normal floc and minimal Zoogloeal floc with floc size greater than the pore size of the membrane led to the formation of porous cake layer. This porous cake layer attached loosely on the membrane surface and could be easily removed by the flow of liquid or the shear-stress from aeration. At 400 and 600 mg/L of phenol concentrations, floc disintegration took place, leading to the co-existence of bulking floc and microfloc. The predominance of bulking floc at 400 mg/L of phenol tend to form non-porous "gel" like fouling layer, while the predominance of disintegrated microfloc at 600 mg/L phenol caused irreversible pore blocking in sMBR.

Mitigation of membrane fouling was performed by introducing shear stress along the membrane surface at varying bubbling modes (non-bubbling, continuous bubbling and intermittent bubbling). Intermittent bubbling and suction during the operation of sMBR showed superior performance in recovering the relative flux. Up to 90 % of flux recovery was obtained for sMBR fed with basemix at high suction pressure. Inversely, flux recovery was found to be higher at low suction pressure if toxic phenol was present in wastewater. Therefore, it was concluded that membrane fouling could be effectively mitigated by intermittent air scouring and relaxation. In addition, the change of the sludge's characteristics owing to the presence of toxic substance at high concentration needed to be considered in the fouling mitigation as well besides bubbling modes and suction pressures. Furthermore, incomplete recovery of permeate flux owing to irreversible pore clogging fouling can only be recovered by chemical cleaning or backwashing. Hence, utilisation of low cost ceramic membrane in MBR is practical as it is robust to backwashing.

### LIST OF REFERENCES

- Ahmed, Z., Cho, J., Lim, B. R., Song, K. G. and Ahn, K. H. (2007). Effects of sludge retention time on membrane fouling and microbial community structure in a membrane bioreactor. *Journal of Membrane Science*, 287 (2), 211-218.
- Ahn, K. H., Cha, H. Y. and Song, K. G. (1999). Retrofitting municipal sewage treatment plants using an innovative membrane bioreactor system. *Desalination*, 124 (1-3), 279-286.
- Akram, A. and Stuckey, D. C. (2008). Flux and performance improvement in a submerged anaerobic membrane bioreactor (SAMBR) using powdered activated carbon (PAC). *Process Biochemistry*, 43 (1), 93-102.
- Al-Amoudi, A. and Lovitt, R. W. (2007). Fouling strategies and the cleaning system of NF membranes and factors affecting cleaning efficiency. *Journal of Membrane Science*, 303 (1-2), 4-28.
- Al-Malack, M. H. (2007). Performance of an immersed membrane bioreactor (IMBR), *Desalination*, 214 (1-3), 112-127.
- Ama, C. O., Menendez, J. A., Parra, J. B. and Pis, J. J. (2004). Microwaveinduced regeneration of activated carbon polluted with phenol. A comparison with conventional thermal regeneration. *Carbon*, 42 (2), 1383-1387.
- Amaral, A.L. and Ferreira, E. C. (2005). Activated sludge monitoring of a wastewater treatment plant using image analysis and partial least squares regression. *Abalytuca Chimica Acta*, 544 (1-2), 246–253.
- APHA (1998). Standard Method for the Examination of Water and Wastewater. 20<sup>th</sup> Edition. Washington D.C : APHA.
- Arregui, L., Perez-Uz, B., Salvado, H. and Serrano, S. (2010) Progresses on the knowledge about the ecological function and structure of the protists community in activated sludge wastewater treatment plants. Current Research, Technology and Education Topics in Applied Microbiology And Microbial Biotechnology, A. Mendez-Vilas (Ed.), 972-979.
- Asia-Pacific Economic Cooperation (2009). Malaysia: Water & Wastewater Treatment,URL:http://egs.apec.org/morearticles/155\_malaysia\_water\_a\_w astewater\_treatment. Accessed on 28 May 2010.

- Bacchin, P., Aimar, P. and Field, R. W. (2006). Critical and sustainable fluxes: Theory, experiments and applications. *Journal of Membrane Science*, 281 (1-2), 42-69.
- Bai, R. and Leow, H.F. (2002). Microfiltration of activated sludge wastewater the effect of system operation parameters. Separation and Purification Technology, 29 (1), 189-198.
- Barker, D. J. and Stuckey, D. C. (1999). A review of soluble microbial products (SMP) in wastewater treatment systems. *Water Research*, 33 (14), 3063-3082.
- Barrios-Martinez, A., Barbot, E., Marrot, b., Moulin, P. and Roche, N. (2006).Degradation of synthetic phenol-containing wastewaters by MBR. *Journal of Membrane Science*, 281(1-2), 288-296
- Bercic, G., Pintar, A. and Levec, J. (1996). Desorption of phenol from activated carbon by hot water regeneration. In: Desorption isotherms. *Industrial Engineering Chemical Resource*, 35 (12), 4619-4625.
- Bilad, M. R., Declerck, P., Piasecka, A., Vanysacker, L., Yan, X. and Vankelecom, I. F. J. (2011). Treatment of molasses wastewater in a membrane bioreactor: Influence of membrane pore size. *Separation and Purification Technology*, 78 (2), 105-112.
- Bouhabila, E. H., Ben-Aim, R. and Buisson, H. (1998). Microfiltration of activated sludge using submerged membrane with air bubbling. *Desalination*, 118 (1-3), 315-322.
- Brindle K. and Stephenson T. (1996). The application of membran biological reactors for the treatment of wastewaters. *Biotechnology and Bioengineering*, 49 (6), 601-610.
- Chae, S. R., Ahn, Y. T., Kang, S. T. and Shin, H. S. (2006) Mitigated membrane fouling in a vertical submerged membrane bioreactor (VSMBR). *Journal Membrane Science*, 280 (1-2), 572-581.
- Chang I. S., Lee C. H. and Ahn K. H. (1999). Membrane filtration characteristics in membrane coupled activated sludge system: The effect of the floc structure on membrane fouling. *Separation Science and Technology*, 34 (9), 1743-1750.
- Chang I.S., Clech P.L., Jefferson B. and Judd S. (2002), Membrane fouling in membrane bioreactors for wastewater treatment. *Journal of Environmental Engineering*, 128 (11), 1018-1029.

- Chang, I. S. and Judd, S. J. (2002). Air sparging of a submerged MBR for municipal wastewater treatment. *Process Biochemistry*, 37 (8), 915-920.
- Chang, I. S. and Lee, C. H. (1998) Membrane filtration characteristics in membrane coupled activated sludge system – the effect of physiological states of activated sludge on membrane fouling. *Desalination*, 120 (3), 221-233.
- Chang, I. S., Clech, O. L., Jefferson, B. and Judd, S. (2002). Membrane fouling in membrane bioreactors for wastewater treatment. *Journal of Environmental Engineering*, 128 (11), 1018-1029.
- Chang, I., Bag, S. and Lee, C. (2001). Effects of membrane fouling on solute rejection during membrane filtration of activated sludge. *Process Biochemistry*, 36 (8-9), 855–860.
- Cho, J., Song, K. G., Yun, H., Ahn, K. H., Kim, J. Y. and Chung, T. H. (2005). Quantitative analysis of biological effect on membrane fouling in submerged membrane bioreactor. *Water Science and Technology*, 51 (6-7), 9-18.
- Choi, J. G., Bae, T. H., Kim, J. H., Tak, T. M. and Randall, A. A. (2002). The behavior of membrane fouling initiation on the cross-flow membrane bioreactor system. *Journal of Membrane Science*, 203 (1-2), 103-113.
- Comas, J., Rodriguez-Roda, I., Sanchez-Marre, M., Cortes, U., Freixo, A., Arraez, J.and Poch, M. (2003). A knowledge-based approach to the deflocculation problem: integrating on-line, off-line and heuristic information. *Water Research*, 37 (10), 2377–2387.
- Costa, A. R., de Pinho, M. N. and Elimelech, M. (2006). Mechanisms of colloidal natural organic matter fouling in ultrafiltration. *Journal of Membrane Science*, 281 (1), 716-725.
- Cote, P. and Thompson, D. (2000). Wastewater treatment using membranes: the North American experience. *Water Science and Technology*, 41 (10-11), 209-215.
- Cote, P., Buisson, H. and Praderie, M. (1998). Immersed membrane activated sludge process applied to the treatment of municipal wastewater. *Water Science Technology*, 38 (4-5), 437-442.
- Decarolis, J., Hong, S. And Taylor, J. (2001) Fouling behavior of a pilot scale inside-out hollow fiber UF membrane during dead-end filtration of tertiary wastewater. *Journal Membrane Science*, 191 (14), 165-178.

- Defrance, L. and Jaffrin, M. (1999). Comparison between filtration and fixed transmembrane pressure and fixed permeate flux: Application to a membrane bioreactor used for wastewater treatment. *Journal of Membrane Science*, 152 (2), 203-210.
- Defrance, L., Jaffrin, M. Y., Gupta, B., Paullier, P. and Geaugey, V. (2000). Contribution of various constituents of activated sludge to membrane bioreactor fouling. *Bioresource Technology*, 73 (2), 105-112.
- Delgado, S., Villarroel, R. and Gonzalez, E. (2008). Effect of the shear intensity on fouling in submerged membrane bioreactor for wastewater treatment. *Journal of Membrane Science*, 311 (1-2), 173-181.
- Environmental Quality Act (1974). Environmental Quality (Sewage and Industrial Effluents) Regulations 1979. In: Regulations 8(1), 8(2), 8(3) Parameter Limits of Effluents of Standards A and B. Malaysia: Department of Environment (DOE).
- EPRI Community Environmental Center. (1997).Membrane technologies for water and wastewater treatment. *Industrial and Agricultural Technologies and Services*, Techcommentary, 1-6.
- Fan, F. and Zhou, H. (2007). Interrelated effects of aeration and mixed liquor fractions on membrane fouling for submerged membrane bioreactor processes in wastewater treatment. *Environmental Science and Technology*, 41 (7), 2523-2528.
- Fane, A. G., Yeo, A., Law, A., Parameshwaran, K., Wicaksana, F. and Chen, V. (2005). Low pressure membrane processes ~ doing more with less energy. *Desalination*, 185 (1-3), 159-165.
- Farquhaarson, A. (2007). Dynamics of mixed liquor characteristics and their impacts on fouling in submerged MBRs for wastewater treatment. Thesis for Master of Science, University of Guelph, Canada.
- Field, R.W, Wu, D., Howell, J.A. and Gupta, B.B. (1995) Critical flux concept for microfiltration fouling. *Journal of Membrane Science*, 100 (3), 259-272.
- Franck, H. G. and Stadelhofer, J. W. (1989). Industrial Aromatic Chemistry. In: Phenol. (pp148-157). Berlin: Springer Verlag.
- Gander, M. A., Jefferson, B. and Judd, S. J. (2000a). Membrane bioreactors for use in small wastewater treatment plants: membrane materials and effluent quality. *Water Science and Technology*, 41 (1), 205-211.
- Gander, M., Jefferson, B. and Judd, S. (2000b). Aerobic MBRs for domestic wastewater treatment: a review with cost considerations. *Separation and Purification Technology*, 18 (2), 119-130
- Garcia, I. G., Venceslada, J. L. B., Jimenez Pena, P. R. and Gomez, E. R. (1997).Biodegradation of Phenol Compounds in Vinasse Using Aspergillus Terreus and Geotrichum Candidum. *Water Resource*, 31(8), 2005-2011.
- Geng, Z. and Hall, E.R. (2006). Characterisation of fouled membranes from a membrane enhanced biological phosphorus removal system. *Water Science and Technology*, 54,169-176.
- Gerardi, M. H. (2002) Settleability Problems and Loss of Solids in the Activated Sludge Process, Environmental Protection Magazine Series, Wiley-Interscience, New York.
- Gimeno, O., Carbajo, M., Beltran, F. J. and Rivas, F. J. (2005). Phenol and substituted phenols AOPs remediation. *Journal of Hazardous Materials*, 119 (1-3), 99-108.
- Gray, A. F. (1990). Activated Sludge- Theory and Practice, Oxford University Press (pp.187)
- Grelier, P., Rosenberger, S. and Tazi-Pain, A. (2006). Influence of sludge retention time on membrane bioreactor hydraulic performance. *Desalination*, 192 (1-3), 10-17.
- Gui, P., Huang, X., Chen, Y. and Qian, Y. (2002). Effect of operational parameters on sludge accumulation on membrane surfaces in a submerged membrane bioreactor. *Desalination*, 151, 185.
- Guido, B., Silvia, B., Carlo, R. and Laura, A. (2008). Technologies for the removal of phenol from fluid streets: A short review of recent developments. *Journal of Hazardous Materials*, 160 (2-3), 265-288
- Guo, W.S., Vigneswaran, S., Ngo, H. H., Kandasamy and J. and Yoon, S. (2008).
  The role of a membrane performance enhancer in a membrane bioreactor:
  a comparison with other submerged membrane hybrid systems. *Desalination*, 231 (1-3), 305-313W.
- Han, S. S., Bae, T. H., Jang, G. G. and Tak, T. M. (2005). Influence of sludge retention time on membrane fouling and bioactivities in membrane bioreactor system. *Process Biochemistry*, 40 (7), 2393-2400.

- Holbrook, R.D., Higgins, M.J., Murthy, S.N., Fonseca, A.D., Fleischer, E.J., Daigger, G.T., Grizzard, T.J., Love, N.G. and Novak, J.T. (2004). Effect of alum addition on the performance of submerged membranes for wastewater treatment. *Water Environment Research*, 76 (7), 2699-2702.
- Hong, S. P., Bae, T. H., Tak, T. M., Hong, S. and Randall, A. (2002) Fouling control in activated sludge submerged hollow fibre membrane bioreactor. *Desalination*, 143 (3), 219-228.
- Hong, S., Faibish, R. and Elimelech, M. (1997) Kinetics of permeate flux decline in crossflow membrane filtration of colloidal suspensions. *Journal of Colloid and Interface Science*, 196 (2), 267-277.
- Hu, A. Y. and Stuckey, D. C. (2007). Activated carbon addition to a submerged anaerobic membrane bioreactor: effect on performance, transmembrane pressure, and flux. *Journal of Environmental Engineering*, ASCE 133 (1), 73-80.
- Huang X., Gui P., Qing Y. (2001). Effect of sludge retention time on microbial behaviours in a submerged membrane bioreactor. *Process Biochemistry*, 36 (10), 1001-1006.
- Iritani, E., Katagiri, N., Sengoku, T., Yoo, K. M., Kawasaki, K. and Matsuda, A. (2007). Flux decline behaviors in dead-end microfiltration of activated sludge and its supernatant. *Journal of Membrane Science*, 300 (1-2), 36-44.
- Ivanovic, I. and Leiknes, T. (2008). Impact of aeration rates on particle colloidal fraction in the biofilm membrane bioreactor (BF-MBR). *Desalination*, 231 (1-3), 182-190.
- Ji, J., Qiu, J., Wong, F. S. and Li, Y. (2008). Enhancement of filterability in MBR achieved by improvement of supernatant and floc characteristics via filter aids addition. *Water Research*, 42 (14), 3611-3622.
- Jordan, H. van Barneveld, O. Gerlich, Kleine-Boymann, M. and Ullrich, J. (2002).Ullmann's Encyclopedia of Industrial Chemistry. In: Phenol. Wiley-VCH Verlag.
- Judd, S. (2004). A review of fouling of membrane bioreactors in sewage treatment. *Water Science and Technology*, 49 (2), 229-235.
- Judd, S. (2005) Fouling control in the submerged membrane bioreactors. *Water Science Technology*, 51 (6-7), 27-34.

- Judd, S. (2006). The MBR Book: Principles and applications of membrane bioreactor in water and wastewater treatment. (2<sup>nd</sup> Ed.). Amsterdam: Elsevier
- Judd. S. (2008). The MBR Book: The status of membrane bioreactor technology. Trends in Biotechnology, 26 (2), 109-116.
- Jusoh, N. and Razali, F. (2008). Microbial Consortia From Residential Wastewater for Bioremediation of Phenol in a Chemostat. *Journal Teknologi Universiti Teknologi Malaysia*, 48(F), 51-60.
- Kabsch-Korbutowicz, M. (1992). Membrane biofouling. *Environmental Protection Engineering*, 18 (1-2), 125-144.
- Kang, I. J., Yoon, S. H. and Lee, C. H. (2002). Comparison of the filtration characteristics of organic and inorganic membranes in a membranecoupled anaerobic bioreactor. *Water Research*, 36 (7), 1803-1813.
- Kim J.S., Lee C.H., Chun H.D. (1998). Comparison of untrafiltration characteristics between activated sludge and BAC sludge. *Water Research*, 32 (11), 3443-3451.
- Kimura, K., Miyoshi, T., Naruse, T., Yamato, N., Ogyu, R. and Watanabe, Y. (2008). The difference in characteristics of foulants in submerged MBRs caused by the difference in the membrane flux. *Desalination*, 231 (1-3), 268-275.
- Krauth, K. H. and Staab, K. F. (1993). Pressurized Bioreactor with Membrane Filtration for Wastewater Treatment. *Water Resources*, 2 (27), 405.
- Lacoste, B., Drakides, C. and Rumeau, M. (1993) Study of an aerobic concentrated culture reactor coupled to separation by cross-flow micro- or ultra-filtration through inorganic membranes: initial approach to a depollution application. *Revue Des Sciences De L'eau*, 6 (4), 363-380.
- Laspidou, C. S. and Rittmann, B. E. (2002). A unified theory for extracellular polymeric substances, soluble microbial products, and active and inert biomass. *Water Research*, 36 (11), 2711-2720.
- Laszlo, K., Podkoscielny, P. and Dabrowski, A. (2003). Heterogeneity of polymerbased active carbons in the adsorption of aqueous solutions of phenol and 2, 3, 4-trichlorophenol. *Langmuir*, 19 (13), 5287-5294.
- Lawrence, K. W., Zucheng, W. and Nazih, K. S. (2009). Biological treatment process. *Handbook of Environmental Engineering*, 8, 207-281.

- Le-Clech, P., Chen, V. and Fane, A. (2006). Fouling in membrane bioreactors used in wastewater treatment. *Journal of Membrane Science*, 284 (1-2), 17-53.
- Le-Clech, P., Jefferson, B. and Judd, S. (2003). Impact of aeration, solids concentration and membrane characteristics on the hydraulic performance of a membrane bioreactor. *Journal of Membrane Science*, 218 (1-2), 117-129.
- Lee, K. M. (2001). Process Serentak Penjerapan dan Penguraian untuk Pengolahan sebatian Alkilfenol dan Kajian Mekanismenya. Thesis for PhD. USM Malaysia.
- Lee W., Kang S. and Shin H. (2003). Sludge characteristics and their contribution to microfiltration in submerged membrane bioreactor. *Journal of Membrane Science*, 216 (1), 217-227.
- Lee, J., Kim, J., Kang, I., Cho, M., Park, P. and Lee, C. (2001). Potential and limitation of alum or zeolite addition to improve the performance of a submerged membrane bioreactor. *Water Science and Technology*, 43 (11), 59-66.
- Li Y.Z., He Y.L., Liu Y.H., Yang S.C. and Zhang G.J. (2005a). Comparison of filtration characteristics between biological powdered activated carbon sludge and activated sludge in submerged membrane bioreactor. *Desalination*, 174 (3), 305-314.
- Li, J.F., Yang, F. L., Li, Y.Z., Wong, F.S. and Chua H.C. (2005b). Impact of biological constituents and properties of activated sludge on membrane fouling in a novel submerged membrane bioreactor. *Desalination*, 225 (1-3), 356-365.
- Li, X., Gao, F., Hua, Z., Du, G and Chen, J. (2005c) Treatment of synthetic wastewater by a novel MBR with granular sludge developed for controlling membrane fouling. *Separation and Purification Technology*, 46 (1-2), 19-25.
- Liang, S., Liu, C. and Song, L. (2007). Soluble microbial products in membrane bioreactor operation: behaviors, characteristics, and fouling potential. *Water Research*, 41 (1), 95-101.
- Liao, B. Q., Kraemer, J. T. and Bagley, D. M. (2006). Anaerobic membrane bioreactors: applications and research directions. *Critical Reviews in Environmental Science and Technology*, 36 (6), 489-530.

- Lim, A.L. and Bai, R. (2003). Membrane fouling and cleaning in microfiltration of activated sludge wastewater. *Journal of Membrane Science*, 216 (1-2), 279-290.
- Linkfield, T. G., Suflita, J. M. and Tiedje, J. (1989). Characterisation of the acclimation period before anaerobic dehalogenation of halobenzoates. *Applied and Environmental Microbiology*, 55 (11), 2773-2778.
- Long Jiang, H. E., Hwatay, J., Maszenan, A. M. and LeeTay, S.M. (2006). Enhanced phenol biodegradation and aerobic granulation by two coaggregating bacterial strains. *Environmental Science and Technology*, 40 (19), 6137-6142.
- Lyko, S., Wintgens, T., Al-Halbouni, D., Baumgarten, S., Tacke, D., Drensta, K., Janot, A., Dott, W., Pinnekamp, J. and Merlin, T. (2008). Long term monitoring of a full scale municipal membrane bioreactors– characterisation of foulants and operational performance. *Journal of Membrane Science*, 317 (1-2), 78-87.
- Magara, Y. and Itoh, M. (1991). Effect of operational factors on solid/liquid separation by ultra-membrane filtration in a biological denitrification system for collected human excrete treatment plant. *Water Science and Technology*, 23 (7-9), 1583-1590.
- Manem, J. and Sanderson, R. (1996). Membrane bioreactors. In: Water Treatment Membrane Processes, Wiesner, M.R. (ed). McGraw-Hill.
- Marrot, B., Barrios-Martinez, A., Moulin, P. and Roche, N. (2006). Biodegradation of high phenol concentration by activated sludge in an immersed membrane bioreactor. *Biochemical Engineering Journal*, 30 (2),174-183.
- Masse, A., Sperandio, M. and Cabassud, C. (2006). Comparison of sludge characteristics and performance of a submerged membrane bioreactor and an activated sludge process at high solids retention time. *Water Research*, 40 (12), 2405-2415.
- McCarthy A.A., O'Shea D.G., Murray N.T., Walsh P.K. and Foley G. (1998). Effect of cell morphology on dead-end filtration of dimorphic yeast Kluyveromyces marxianus Var. marxianus NRRLy2415. *Biotechnology Progress*, 14 (2), 279-285.
- Meng F., Chae S.R., Drews A., Kraume M., Shin H.S., Yang F. (2009). Recent advances in membrane bioreactors (MBRs): Membrane fouling and membrane material. *Water Research*, 43 (6), 1489-1512.

- Meng, F., Shi, B., Yang, F., Zhang, H. (2007). Effect of hydraulic retention time on membrane fouling and biomass characteristics in submerged membrane bioreactors. *Bioprocess and Biosystems Engineering*, 30 (5), 359-367.
- Meng, F., Zhang, H., Yang, F., Zhang, S., Li, Y. and Zhang, X. (2006). Identification of activated sludge properties affecting membrane fouling in submerged membrane bioreactors. *Separation and Purification Technology*, 51 (1), 95-103.
- Metcalf and Eddy, Inc. (2003). Wastewater Engineering Treatment and Reuse (4<sup>th</sup> Ed.) New York, N. Y.: The McGraw-Hill Companies Inc.
- Metzger, U., Le-Clech, P., Stuetz, R. M., Frimmel, F. H. and Chen, V. (2007). Characterisation of polymeric fouling in membrane bioreactors and the effect of different filtration modes. *Journal of Membrane Science*, 301 (1-2), 180-189.
- Nagoka, H. and Nemoto, H. (2005). Influence of extracellular polymeric substance on nitrogen removal in an intermittently aerated membrane bioreactor. *Water Science and Technology*, 51 (11), 151-158.
- Nakanishi K., Tadokoro T., Matsuno R. (1987). On the specific hydraulic resistance of cakes of microorganisms. *Chemical Engineering Communication*, 62 (1-6), 187-201.
- Ng, C. A., Sun, D. and Fane, A. G. (2006). Operation of membrane bioreactor with powdered activated carbon addition. *Separation Science and Technology*, 41 (7), 1447-1466.
- Nywening, J.P. and Zhou, H. (2008) Membrane bioreactor operation and optimisation: quantification of particle size contributions to membrane fouling, in: proceedings of water environment federation (WEFTEC) Conference, Chicago, USA.
- Ognier, S., Winiewski, C. and Grasmick, A. (2002). Characterisation and modeling of fouling in membrane bioreactors. *Desalination*, 146 (1-3), 141-147.
- Owen, G, Bandi, M., Bandi, J. A. and Churchouse, S. J. (1995). Economic Essessment of membrane processes for water and waste water treatment. *Journal of Membrane Science*, 102, 77-91.
- Pang, C. M., Hong, P., Guo, H. and Liu, W. T. (2005). Biofilm formation characteristics of bacterial isolates retrieved from a reverse osmosis membrane. *Environmental Science and Technology*, 39 (19), 7541-7550.

- Papadimitriou, Ch., Palaska, G., Lazaridou, M., Samaras, P. and Sakellaropoulos, G. P. (2007). The effects of toxic substances on the activate sludge microfauna. *Desalination*, 211 (1-3), 177-191.
- Philips, S., Rabaey, K. and Verstraete, W. (2003). Impact of iron salt in activated sludge and interaction with nitrite and nitrate. *Bioresource Technology*, 88(3), 229-239.
- Pujols, R. and Canler, J.P. (1992). Biosorption and dynamics of bacterial population in activated sludge. *Water Research*, 26 (2), 209–212.
- Radovic, L. R., Moreno-Castilla, C. and Rivera-Utrilla, J. (2000) Carbon materials as adsorbents in aqueous solutions, in: L. R. Radovic (Ed.), Chemical and Physical Carbon, vol. 27. (pp. 224-227). New York: Marcel Dekker.
- Richard, M., Brown, S. and Collins, F. (2003). Activated sludge microbiology problems and their control. 20<sup>th</sup> Annual USEPA National Operator Trainers Conference, Buffalo, NY.
- Rog'erio Jos'e Ara'ujo L'Amoura, Eduardo Bessa Azevedo, Selma Gomes Ferreira Leite, M árcia Dezotti (2008). Removal of phenol in high salinity media by a hybrid process (activated sludge + photocatalysis). *Separation and Purification Technology*, 60 (2), 142–146.
- Rosenberger S., Evenblij H., te Poele S., Wintgens T. and Laabs C. (2005). The importance of liquid phase analyses to understand fouling in membrane assisted activated sludge processes- six case studies of different European research groups. *Journal of Membrane Science*, 263 (1-2), 113-126.
- Rosenberger, S., Kruger, U., Witzig, R. Manz, W., Szewzyk, U. and Kraume, M. (2002). Performance of a bioreactor with submerged membranes for aerobic treatment of municipal wastewater. *Water Research*, 36 (2), 413-420.
- Rosenberger, S., Laabs, C., Lesjean, B. Gnirss, R., Amy, G., Jekel, M. and Schrotter, J. C. (2006). Impact of colloidal and soluble organic material on membrane performance in membrane bioreactors for municipal wastewater treatment. *Water Research*, 40 (4), 710-720.
- Sablani S.S., Goosen M.F.A., Al-Belushi R. and Wilf M. (2001). Concentration polarization in ultrafiltration and reverse osmosis: a critical review. *Desalination*, 141 (3), 269-289.

- Saravanan, P., Pakshirajan, K. and Saha, P. (2008). Growth kinetics of an indigent mixed microbial consortium during phenol degradation in a batch reactor. *Bioresource Technology*, 99 (1), 205-209.
- Schmidt, R. J. (2005). Industrial catalytic processes-phenol production. *Applied Catalysis A: General*. 280 (1), 89-103.
- Sezgin, M., Jenkins, D. and Parker, D. S. (1978). A unified theory of filamentous activated sludge. *Journal Water Pollution Control*, 50 (2), 362-381.
- Shane Trussell, R., Merlo, R. P., Hermanowicz, S. W. and Jenkins, D. (2007). Influence of mixed liquor properties and aeration intensity on membrane fouling in a submerged membrane bioreactor at high mixed liquor suspended solids concentrations. *Water Research*, 41 (5), 947-958.
- Singer, P. L. and Yen, C. (1980). Adsorption of alkyl phenols by activated carbon. In: Activated carbon adsorption of organics from the aqueous phase (McGuire, M. J. and Suffet, I. H., ed.) (pp 167-189). Michigan: Ann Arbor Science.
- Smith, P. J., Vigneswaran, S., Ngo, H. H., Ben-Aim, R. and Nguyen, H. (2005). Design of generic control system for optimizing back flush duration in a submerged membrane hybrid reactor. *Journal of Membrane Science*, 255 (1-2), 99-106.
- Song, K. G., Kim, Y. and Ahn, K. H. (2008). Effect of coagulant addition on membrane fouling and nutrient removal in a submerged membrane bioreactor. *Desalination*, 221 (1-3), 467-474.
- Stoutharner, S., Verseveld, H. W. and Eikelboom, D. H. (1995). Aerobic domestic wastewater treatment in a pilot plant with complete sludge retention by crossflow filtration. *Water Resource*, 29 (4), 1179-1189.
- Sun D.D., Hay C.T. and Khor S.L. (2006). Effects of hydraulic retention time onbehavior of start-up submerged membrane bioreactor with prolonged sludge retention time. *Desalination*, 195 (1-3), 209-225.
- Sun, Y., Wang, Y. and Huang, X. (2007). Relationship between sludge settleability and membrane fouling in a membrane bioreactor. *Frontiers of Environmental Science and Engineering in China*, 1(2), 221-225.
- Terzyk, A. P. (2007). The impact of carbon surface chemical composition on the adsorption of phenol determined at the real oxic and anoxic conditions. *Applied Surface Science*, 253 (13), 5752-5755.

- Teychence, B., Guigui, C., Cabassud, C., Amy, G. (2008). Toward a better identification of foulant species in MBR processes. *Desalination*, 231 (1-3), 27-34.
- Thompson, G. and Forster, G. (2003). Bulking in activated sludge plants treating paper mill wastewater. *Water Resources*, 37 (11), 2636-2644.
- Thompson, T. L. and Yates Jr., J. T. (2006). Surface science studies of the photoactivation of TiO2 new photochemical processes. *Chemical Review*, 106 (10), 4428-4453.
- Throop W. M. (1975/1977). Alternative methods of phenol wastewater control. *Journal of Hazardous Materials*, 1, 319-329.
- Ueda, T. and Hata, K. (1999) Domestic wastewater treatment by a submerged membrane bioreactor with gravitational filtration. *Water Research*, 33 (12), 2888-2892.
- Ueda, T., Hata, K., Kikuoka, Y. and Seino, O. (1997). Effect of aeration on suction pressure in a submerged membrane bioreactor. *Water Resource*, 31 (3), 489-494.
- Uygur, A. and Kargi, F. (2004). Phenol inhibition of biological nutrient removal in a four-step sequencing batch reactor. *Process Biochemistry*, 39 (12), 2123-2128.
- Van Dijk L. and Roneken G. C. G. (1997). Membrane bioreactors for wastewater treatment: the state of art and new developments, *Water Science* andTechnology, 35 (10), 35-41.
- Van Kaam, R., Anne-Archard, D., Alliet Gaubert, M., Albasi, C. (2008). Rheological characterization of mixed liquor in a submerged membrane bioreactor: Interest for process management. *Journal of Membrane Science*, 317 (1-2), 26-33.
- Wang, Z., Wu, Z., Yin, X. and Tian, L. (2008). Membrane fouling in a submerged membrane bioreactor (MBR) under sub-critical flux operation: membrane foulant and gel layer characterization. *Journal of Membrane Science*, doi:10.1016/j.memsci.2008.07.035.
- Weissermel, K., Weissermel, H. and Arpe, J. (1997). Industrial Organic Chemistry (3<sup>rd</sup> Ed.). (pp. 346-365). Germany: Wiley-VCH Verlag GmbH.
- Wicaksana, F., Fane, A. and Chen, V. (2006) Fibre movement induced by bubbling using submerged hollow fibre membranes. *Journal of Membrane Science*, 271 (1-2), 186-195.

- Wiesner, M. R. and Aptel, P. (1996). Mass transport and permeate flux and fouling in pressure-driven processes. Water Treatment Membrane Processes, M. R. Wiesner (ed), McGraw-Hill Companies Inc.
- Wisniewski C., Grasmick A. (1998). Floc size distribution in a membrane bioreactor and consequences for membrane fouling. *Colloids and Surfaces* A: Physiochemical and Engineering Aspects, 138 (2-3), 403-411.
- Wittcoff, H. A. and .Reuben, B. G. (1996). Industrial Organic Chemistry. (pp. 236-255) Chichester: John Wiley and Sons.
- Yamato, N., Kimura, K., Miyoshi, T., Watanabe, Y. (2006). Difference in membrane fouling in membrane bioreactors (MBRs) caused by membrane polymer materials. *Journal of Membrane Science*, 280 (1–2), 911–919.
- Yang, W., Cicek, N. and Ilg, J. (2006). State-of-the-art of membrane bioreactors: worldwide research and commercial applications in North America. *Journal of Membrane Science*, 270 (1-2), 201-211.
- Yigit, N. O., Civelekoglu, G., Harman, I., Koseoglu, H. and Kitis, M. (2009). Effects of various backwash scenarios on membrane fouling in a membrane bioreactor. *Desalination*, 237 (1-3), 346-356.
- Ying, Z. and Ping, G. (2006). Effect of powdered activated carbon dosage on retarding membrane fouling in MBR. Separation Science and Technology, 52 (1), 154-160.
- Yoong, E. T., Lant, P. A. and Greenfield, P. F. (2000). In Situ respirometry in an SBR treating wastewater with high phenol concentrations. *Water Resource*, 34(1), 239-245.
- You, H. S., Huang, C. P., Pan, J. R. and Chang, S. C. (2006). Behavior of membrane scaling during crossflow filtration in the anaerobic MBR system. *Separation Science and Technology*, 41 (7), 1265-1278.
- You, H. S., Tseng, C. C., Peng, M. J., Chang, S. H., Chen, Y. C. and Peng, S., H. (2005). A novel application of anaerobic membrane process in wastewater treatment. *Water Science and Technology*, 51 (6-7), 45-50.
- Yu S.L., Zhao F.B., Zhang X. H., Jing G.L., Zhen X.H. (2006). Effect of components in activated sludge liquor on membrane fouling in a submerged membrane bioreactor. *Journal of Environmental Sciences*, 18 (5), 897-902.

- Yu, H. L., Liu, L. Q., Tang, Z. Q., Yan, M. G., Gu, J. S. and Wei, X. W. (2008).Mitigated membrane fouling in an SMBR by surface modification. *Journal of Membrane Science*, 310 (1-2), 409-417.
- Yu, H. Q. (1994). Study on the characteristics and mechanism of SBRs for the treatment of refractory/ toxic wastewater, PhD thesis, Tongji University, Shanghai, China.
- Yu, H. Q. and Gu, G. W. (1996). Treatment of phenolic wastewater by sequencing batch reactors with aerated and unaerated FILLS. *Waste Management*, 16 (7), 561-566.
- Yu, H. Y., Hu, M. X., Xu, Z. K., Wang, J. L. and Wang, S. Y. (2005a). Surface modification of polypropylene microporous membranes to improve their antifouling property in MBR: NH<sub>3</sub> plasma treatment. *Separation and Purification Technology*, 45 (1), 8-15.
- Yu, H. Y., Xie, X. Y., Hu, M. X., Xu, Z. K., Wang, J. L. and Wang, S. Y. (2005b). Surface modification of polypropylene microporous membranes to improve its antifouling property in MBR: CO<sub>2</sub> plasma treatment. *Journal* of Membrane Science, 254 (1-2), 219-227.
- Yu, H. Y., Xu, Z. K., Lei, H., Hu, M. X. and Yang, Q. (2007). Photoinduced graft polymerization of acrylamide on polypropylene microporous membranes for the improvement of antifouling characteristics in a submerged membrane bioreactor. *Separation and Purification Technology*, 53 (1), 119-125.
- Zhang B., Yamatoto K., Ohgaki S. and Kamiko N. (1997). Floc size distribution and bacterial activities in membrane separation activated sludge processes for small-scale wastewater treatment and reclamation. *Water Science Technology*, 35 (6), 37-44.
- Zhang, G., Ji, S., Gao, X. and Liu, Z. (2008). Adsorptive fouling of extracellular polymeric substances with polymeric ultrafiltration membranes. *Journal of Membrane Science*, 309 (1-2), 28-35.
- Zhang, J., Chua, H.C., Zhou, J. and Fane, A.G. (2006a). Factors affecting the membrane performance in submerged membrane bioreactors. *Journal of Membrane Science*, 284 (1-2), 54-66.
- Zhang, J. S., Chua, C. H., Zhou, J. T. and Fane, A. G. (2006b). Effect of sludge retention time on membrane bio-fouling intensity in a submerged membrane bioreactor. *Separation Science and Technology*, 41 (7), 1313-1329.

- Zhang, S., Yang, F., Liu, Y., Zhang, X., Yamada, Y., Furukawa, K. (2006c).Performance of a metallic membrane bioreactor treating simulated distillery wastewater at temperatures of 30 to 45 °C. *Desalination*, 194 (1–3), 146–155.
- Zhang, S. T., Qu, Y. B., Liu, Y. H., Yang, F. L., Zhang, X. W., Furukawa, K. and Yamada, Y. (2005). Experimental study of domestic sewage treatment with a metal membrane bioreactor. *Desalination*, 177 (1-3), 83-93.
- Zhang, S., Yang, F. I., Meng, F. G., An, P. and Wang, D. (2007). Comparison of membrane fouling during short-term filtration of aerobic granular sludge and activated sludge. *Journal of Environmental Sciences*, 19 (11), 1281-1286.
- Zhou, J., Yang, F. L., Meng, F. G., An, P., Wang, D. (2007). Comparison of membrane fouling during short-term filtration of aerobic granular sludge and activated sludge. *Journal of Environmental Sciences*, 19 (11), 1281– 1286.

## Appendix A

## Chemical Oxygen Demand (APHA 5220-C Closed Reflux & Titrimetric Method)

Organic compounds such as phenol can be fully oxidised to carbon dioxide and water in the presence of strong oxidising agent under acidic conditions. Therefore, COD test was employed to determine the amount of organic compounds in samples. Four reagents were required in the closed reflux, titrimetric method.

### i) Standard potassium dichromate digestion solution, 0.01667 M:

To prepare this, about 500 mL of distilled water was added to into a primary standard grade, previously dried at 150 °C for 2 hours of 4.903 g  $K_2Cr_2O_7$ , 167 mL concentrated  $H_2SO_4$  together with 33.3 g HgSO<sub>4</sub>. The mixture was dissolved by continuing stirring. The mixture was cooled to room temperature and then diluted to 1000 mL. This mixture was named as digestion solution stored in a 1 L reagent bottle in a cool dry place.

### ii) Sulphuric acid reagent:

10.11 g of  $Ag_2SO_4$  reagent grade, crystal or powder was added to concentrated  $H_2SO_4$  at a rate of 5.5 g  $Ag_2SO_4/kg H_2SO_4$ . When  $Ag_2SO_4$  was fully dissolved in  $H_2SO_4$ , the solution was topped up with  $H_2SO_4$  to 1 L. The solution was let to stand 1 to 2 days to dissolve. The solution was then stored in a 1 L reagent bottle.

iii) Ferroin indicator solution:

The indicator solution was purchased commercially.

iv) Standard ferrous ammonium sulphate titrant (FAS), approximately 0.1 M:

To prepare this, 39.2 g of Fe  $(NH_4)_2(SO_4)_2.6H_2O$  was dissolved in distilled water. 20 mL of concentrated  $H_2SO_4$  was added later. The mixture was cooled and to be diluted to 1000 mL with distilled water. The solution needed was standardised daily against standard  $K_2Cr_2SO_7$  digestion solution as follow:

5.00 mL digestion solution was pipetted into a small beaker. 10 mL reagent water was added to substitute for sample. The solution was cooled to room temperature. 1 to 2 drops of ferroin indicator were added and the solution was then titrated with FAS.

## Appendix A

## Chemical Oxygen Demand (APHA 5220-C Closed Reflux & Titrimetric Method)

Molarity of FAS solution

= (Volume 0.01667M  $K_2Cr_2O_7$  solution titrated, ml / Volume FAS used

in titration, ml) X 0.1

(Equation A.1)

## COD test for sample:

Effluents from SBR and MBR were subjected to COD test after being drawn out. 2.5 mL of the effluent sample (without filter) was added to 1.5 mL potassium dichromate digestion reagent in a 16 X 100 mm culture tube. Then, 3.5 mL of sulphuric acid reagent was added slowly into the culture tube to make up a total final volume of 7.5 mL Two blanks (used 2.5 mL distilled water) were prepared on every test to ensure no other organic material interfered the COD of the sample being measured. When all the reagents were mixed in culture tube, the tube was inserted into pre-heated aluminium block on hot plate which had been calibrated to the temperature of 140 °C-170 °C. After 2 hours of reflux, the culture tube was removed from the aluminum block and cooled to room temperature. The solution was then titrated with standardised FAS solution. Minimum distilled water was used to rinse the residue solution in the tube and cap. Ferroin indicator was used as an indicator. The end point was reached when the colour of the solution changes from bluegreen to red-brown. The volume of titrant (FAS) used to titrate the sample was used to calculate COD. The mathematical model to calculate the COD is given by:

COD as mg O<sub>2</sub>/L = (A-B) x M x 8000 mL sample (Equation A. 2)

Where A is the volume of FAS used for blank (distilled water); B is the volume of FAS used for sample; M is the molarity of FAS and 8000 is the miliequivalent weight of oxygen X 1000 ml/L.

## Appendix B

## Phenol Concentration Determination

Determination of phenol concentration in the sample was performed by UV-spectrophotometer (Perkin-Elmer Lambda 35 Series). The sample was scanned over the wavelength range from 190 to 400 nm with lambda maximum at 269 nm (Singer and Yen, 1980). For each scanned peak obtained, the area-to-base under the peak was integrated using Winlab software. After integration, the concentrations of phenol in the sample could be calculated from the calibration curve of area-to-base data against the standard solution of phenol.

## Appendix C

## Mixed Liquor Suspended Solids (APHA 2540-D Total Suspended Solids Dried at 103°C-105°C)

MLSS refers to the suspended or non filterable solids concentration in the mixture of wastewater and suspended culture that is used in activated sludge processes. To measure MLSS, 100 ml of mixed liquor was collected from the reactor. The MLSS was separated from the water by filtered through 45 mm Whatman Glass Fiber Filter Paper. The filter papers together with MLSS were dried in oven at 100 °C for 24 hours. The concentration of sludge was expressed as MLSS in the unit of mg/L.

$$\frac{MLSS = Weight of sludge(g)}{0.1 L} \times \frac{1000 \text{ mg}}{g}$$
(Equation C. 1)

## Appendix D

## Sludge Volume Index (APHA 2710-D Sludge Volume Index)

Sludge volume index was used to determine the settling characteristics of the sludge. The suspended solids concentration or MLSS of the well-mixed sample and the data of 30 minutes settled sludge volume ( $SV_{30}$ ) were required to calculate SVI. To obtain  $SV_{30}$ , 100 mL of well-mixed suspension was let to settle in a 100 mL measuring cylinder. The sludge volume after 30 minutes of settling time was expressed in term of millilitres per litres. SVI could thus be determined by dividing the  $SV_{30}$  (ml/L) with MLSS (mg/L).

SVI = 
$$\frac{\text{Settle sludge volume SV}_{30} (\text{mL/L})}{\text{Mixed Liquor Suspended Solids MLSS (mg/L)}}$$
(Equation D. 1)

<b>1</b>	
Concentration, (mg/L)	SOUR, mg O2/ (g MLVSS.h)
0	13.69
60	12.88
100	12.35
200	11.73
500	10.04
1000	8.84
1500	7.63
2000	5.85

Specific Oxygen Uptake Rate

# Specific Oxygen Uptake Rate

				P	
At	base-mix	At 20	mg/L Phenol	At 60	mg/L Phenol
Time(s)	$DO(mg O_2/L)$	Time(s)	DO (mg $O_2/L$ )	Time(s)	DO (mg $O_2/L$ )
10	6.51	10	5.89	10	6.76
20	5.12	20	5.64	20	5.75
30	5.55	30	5.51	30	5.60
40	5.44	40	5.32	40	5.51
50	5.21	50	5.00	50	5.26
60	4.99	60	4.87	60	5.12
70	4.73	70	4.59	70	4.92
80	4.48	80	4.34	80	4.68
90	90 4.26		4.19	90	4.45
100	100 4.04		3.93	100	4.26
110	3.81	110	3.74	110	4.02
120	3.54	120	3.52	120	3.80
130	3.31	130	3.34	130	3.54
140	3.10	140	3.09	140	3.35
150	2.89	150	2.92	150	3.12
160	2.66	160	2.65	160	2.92
170	2.41	170	2.45	170	2.73
180	2.22	180	2.25	180	2.54
190	2.00	190	2.05	190	2.23
200	1.81	200	1.85	200	2.04
210	1.58	210	1.65	210	1.84
220	1.40	220	1.45	220	1.64
230	1.21	230	1.30	230	1.44
240	1.04	240	1.13	240	1.28
250	0.88	250	0.98	250	1.11
260	0.74	260	0.85	260	0.94
270	0.60	270	0.70	270	0.79
280	0.49	280	0.59	280	0.65
290	0.39	290	0.50	290	0.54
300	0.30	300	0.40	300	0.41
310	0.23	310	0.32	310	0.33
320	0.17	320	0.25	320	0.26
330	0.12	330	0.19	330	0.21
340	0.10	340	0.14	340	0.15
350	0.08	350	0.11	350	0.11
360	0.08	360	0.10	360	0.08

DO Measurement with Time at Varying Feeding Compositions:

# Specific Oxygen Uptake Rate

At 100	mg/L Phenol	At 200	At 200 mg/L Phenol		At 500 mg/L Phenol	
Time	DO (mg	Time	DO (mg	Time	DO (mg	
(s)	O <sub>2</sub> /L)	(s)	O <sub>2</sub> /L)	(s)	O <sub>2</sub> /L)	
10	6.19	10	6.60	10	6.15	
20	5.98	20	5.69	20	6.02	
30	5.83	30	5.82	30	5.95	
40	5.65	40	5.69	40	5.74	
50	5.46	50	5.47	50	5.62	
60	5.23	60	5.33	60	5.56	
70	5.04	70	5.11	70	5.42	
80	4.82	80	4.86	80	5.26	
90	4.58	90	4.71	90	5.00	
100	4.36	100	4.51	100	4.83	
110	4.17	110	4.4	110	4.73	
120	3.91	120	4.17	120	4.53	
130	3.73	130	3.97	130	4.31	
140	3.51	140	3.76	140	4.15	
150	3.32	150	3.53	150	3.91	
160	3.05	160	3.34	160	3.77	
170	2.88	170	3.17	170	3.58	
180	2.67	180	2.95	180	3.38	
190	2.41	190	2.77	190	3.26	
200	2.23	200	2.55	200	3.21	
210	2.05	210	2.36	210	3.06	
220	1.86	220	2.20	220	2.87	
230	1.66	230	2.00	230	2.7	
240	1.47	240	1.82	240	2.55	
250	1.30	250	1.66	250	2.33	
260	1.12	260	1.48	260	2.17	
		270	1.3	270	2.00	
		280	1.15	280	1.78	
		290	1.01	290	1.62	
				300	1.46	
				310	1.31	
				320	1.16	
				330	1.01	

DO Measurement with Time at Varying Feeding Compositions:

# Specific Oxygen Uptake Rate

			<u>r</u>
At 1000	mg/L Phenol	At 200	0 mg/L Phenol
Time (s)	DO (mg O <sub>2</sub> /L)	Time (s)	$DO (mg O_2/L)$
10	6.18	10	6.1
20	5.99	20	5.45
30	5.86	30	5.59
40	5.85	40	5.7
50	5.77	50	5.73
60	5.52	60	5.63
70	5.51	70	5.54
80	5.37	80	5.57
90	5.22	90	5.33
100	5.11	110	5.29
110	4.96	130	5.12
120	4.85	150	5.01
130	4.7	170	4.75
140	4.51	190	4.6
150	4.32	210	4.38
160	4.26	230	4.27
170	4.14	250	4.02
180	3.92	270	3.88
190	3.8	290	3.62
200	3.63	310	3.5
210	3.49	330	3.32
220	3.33	350	3.1
230	3.2	370	2.95
240	3.03	390	2.71
250	2.9	410	2.54
260	2.73	430	2.36
270	2.58	450	2.18
280	2.45	470	2.01
290	2.29	490	1.8
300	2.13	510	1.62
310	2.01	530	1.45
320	1.87	550	1.27
330	1.71	570	1.09
340	1.59		
350	1.43	1	

DO Measurement with Time at Varying Feeding Compositions:

## Appendix F

## Phenol Volatilisation Test

Time (hour)	Phenol (mg/L)	COD (mg/L)
0	84.42	216.24
1	72.13	225.74
2	72.47	178.22
3	71.84	162.38
4	74.53	160.79
5	78.22	173.47
6	74.41	175.05
7	73.00	224.16
8	90.08	206.73

## (a) At low phenol concentration

## (b) At intermediate phenol concentration

 L		
Time (hour)	Phenol (mg/L)	COD (mg/L)
 0	506.90	1200.00
1	416.82	1168.32
2	426.07	1057.43
3	407.62	1057.43
4	431.28	1049.5
5	401.57	994.06
6	417.60	962.38
7	418.57	1200.00
8	473.44	1215.84

## (c) At high phenol concentration

Time (hour)	Phenol (mg/L)	COD (mg/L)
0	714.64	1734.65
1	692.20	1671.29
2	685.90	1671.29
3	695.46	1750.50
4	689.11	1893.07
5	673.62	1893.07
6	714.88	1576.24
7	702.30	1702.97
8	698.06	1687.13

# Appendix G

Sequencing Batch Read	ctor Study
-----------------------	------------

Day	COD (mg/L)	Phenol (mg/L)	MLSS (g/L)	SVI (ml/g)	MLVSS (g/L)	Effluent Suspended Solids (g/L)	Waste Sludge (g/L)
1	14.95	0.126				0.084	0.126
2	7.80	0.051	11.51	16.50	9.60	0.034	0.051
3	7.87	0.097				0.065	0.097
4	11.31	0.072	12.33	16.21	10.60	0.048	0.072
5	3.96	3.090	10.54	17.08	10.82	2.060	3.090
8	20.59	0.045	12.12	17.32	10.75	0.030	0.045
9	8.71	0.080	11.76	17.85	10.47	0.053	0.079
10	24.55	0.054	11.18	17.88	8.67	0.036	0.054
11	33.74	0.012	12.40	17.73	11.33	0.008	0.012
12	45.15	0.032				0.021	0.031
14	1.58	0.027				0.018	0.027
15	32.64	0.041	11.09	19.82	9.30	0.027	0.040
16	32.64	0.118	11.70	17.93	9.74	0.079	0.118
17	13.50	0.116	11.15	18.83	9.31	0.077	0.115
18	24.80	0.123	10.17	19.65	8.52	0.082	0.123
19		0.149				0.099	0.148
21	47.33						
22	63.65	0.191	10.06	20.86	8.31	0.127	0.190
23	55.49	0.241	12.16	17.26	10.61	0.161	0.241

Day	COD (mg/L)	Phenol (mg/L)	MLSS (g/L)	SVI (ml/g)	MLVSS (g/L)	Effluent Suspended Solids (g/L)	Waste Sludge (g/L)
24	42.40	0.091				0.061	0.091
25	64.00	0.084	8.80	19.32	7.73	0.056	0.084
26	56.00	0.249				0.166	0.249
28	76.80	0.151				0.101	0.151
29	213.07	1.881	7.17	15.32	6.40	1.254	1.881
30	23.76	0.039	5.76	22.55	5.09	0.026	0.039
31	46.73	0.136	6.37	17.24	5.61	0.091	0.136
32	94.26	0.180				0.120	0.180
33	64.62	0.184	7.14	14.00	6.30	0.123	0.184
35	73.73	0.277	6.40	23.41	5.69	0.185	0.277
36	31.37	0.265	6.05	23.12	5.39	0.177	0.265
37	45.49	0.187	6.34	20.50	5.59	0.125	0.187
38	61.96	0.147	6.48	20.04	5.73	0.098	0.147
43	60.77	0.328	5.74	19.15	5.12	0.219	0.328
44	50.00	0.172	5.48	20.12	4.86	0.115	0.172
45	30.00	0.195	5.39	20.39	4.82	0.130	0.195
46	65.38	0.162	5.66	19.41	5.09	0.108	0.162
49	59.20	0.523	5.17	23.19	4.66	0.349	0.523
50	43.43	0.108	5.48	21.87	4.98	0.072	0.108
51	50.29	0.126	4.90	20.38	4.41	0.084	0.126
							0.157
52	26.23	0.157	5.01	19.93	4.52	0.105	

Day	COD (mg/L)	Phenol (mg/L)	MLSS (g/L)	SVI (ml/g)	MLVSS (g/L)	Effluent Suspended Solids (g/L)	Waste Sludge (g/L)
53	10.33	0.103	4.86	18.48	4.30	0.069	0.103
56	36.56	0.093	5.83	22.27	5.32	0.062	0.093
57	41.33	0.108	5.60	21.42	5.07	0.072	0.108
58	42.40	0.237	5.78	20.75	5.22	0.158	0.237
59	17.60	0.048	6.08	18.07	5.55	0.032	0.048
60	15.20	0.058	5.20	23.06	4.70	0.038	0.058
63	44.69	0.006	5.55	23.40	5.02	0.004	0.006
64	5.49	0.025				0.017	0.025
65	24.66	0.069	5.49	23.67	4.91	0.046	0.069
66	63.50	0.018	6.19	24.19	5.32	0.012	0.018
67	2.35	0.078	8.91	14.58	5.22	0.052	0.078
68	12.29	0.022				0.015	0.022
70	4.57	0.069	5.78	27.64	5.16	0.046	0.069
71	85.46						
72	41.14	0.039	5.93	21.99	5.41	0.026	0.039
74	21.37	0.087	5.65	24.74	4.93	0.058	0.087
77	19.59	0.021	5.94	23.56	5.34	0.014	0.021
78	32.65	0.036	5.58	25.09	4.90	0.024	0.036
79	12.80	0.034	6.68	22.44	6.09	0.023	0.034

Day	COD (mg/L)	Phenol (mg/L)	MLSS (g/L)	SVI (ml/g)	MLVSS (g/L)	Effluent Suspended Solids (g/L)	Waste Sludge (g/L)
80	4.80	0.025	5.60	24.99	4.95	0.017	0.025
81	31.20	0.006	7.05	19.90	6.33	0.004	0.006
82	7.76	0.018	7.23	20.73	6.47	0.012	0.018
84	7.76	0.034	6.80	22.04	5.82	0.023	0.034
85		0.019	6.38	25.06	5.27	0.013	0.019
86	30.10	0.006	7.10	22.51	5.99	0.004	0.006
87	18.82	0.021	6.97	22.92	5.57	0.014	0.021
88	4.71	0.062	7.20	23.61	5.86	0.041	0.062
91	9.41	0.015	7.22	22.15	6.47	0.010	0.015
92	45.49	0.022				0.015	0.022
93	28.24	0.039	7.88	20.30	6.57	0.026	0.039
94	6.27	0.070	6.43	26.40	5.81	0.046	0.070
95	12.55	0.235	8.38	17.88	7.53	0.157	0.235
100	9.90	0.088				0.059	0.088
102	49.22						
103	58.67	0.100	7.99	21.28	7.05	0.067	0.100
105	33.52	0.018	7.35	21.76	6.61	0.012	0.018
106	7.62	0.055	8.76	21.67	7.50	0.037	0.055
107	10.67	0.008	8.78	19.35	7.87	0.005	0.008
108	45.76	0.070	8.43	18.97	7.44	0.047	0.070

Dav	COD (mg/L)	Phenol (mg/L)	MLSS (g/L)	SVI (ml/g)	MLVSS (g/L)	Effluent Suspended	Waste Sludge (g/L)
Duy	00D (111g/L)	Thener (hig/L)		5 VI (III/G)	1111 ( 55 ( <u>6</u> / <u>L</u> )	Solids (g/L)	(gil)
109	25.60	0.057	8.67	19.60	7.68	0.038	0.057
110	17.60	0.042	9.79	19.40	8.78	0.028	0.042
113	25.60	0.058				0.039	0.058
114	99.20	0.012	10.71	19.60	9.38	0.008	0.012
115	25.37	0.250	8.67	20.75	7.61	0.167	0.250
116	23.82	0.012	7.27	22.00	6.50	0.008	0.012
117	137.73	0.030	6.45	20.14	5.77	0.020	0.030
118	27.44	0.024	8.15	18.39	7.33	0.016	0.024
119	7.77	0.088	10.83	20.30	9.43	0.059	0.088
120	9.50	0.049	8.59	23.26	7.67	0.033	0.049
121	36.80	0.070	9.38	20.24	8.35	0.047	0.070
122	9.60	0.037	10.88	20.20	9.67	0.025	0.037
123	30.40	0.016	10.57	21.75	9.41	0.011	0.016
124	28.80	0.090	11.34	20.26	9.94	0.060	0.090
126	45.60	0.061	11.69	18.81	10.27	0.041	0.061
127	35.20	0.018	11.01	19.97	9.05	0.012	0.018
128	0.80	0.039	12.22	18.81	10.19	0.026	0.039
129	46.40	0.031	11.78	21.20	9.80	0.021	0.031
130	20.80	0.037	9.73	21.56	8.04	0.025	0.037
131	80.00	0.042	12.32	17.85	10.06	0.028	0.042

Day	COD (mg/L)	Phenol (mg/L)	MLSS (g/L)	SVI (ml/g)	MLVSS (g/L)	Effluent Suspended Solids (g/L)	Waste Sludge (g/L)
132	73.60	0.037	12.02	19.96	10.13	0.025	0.037
133	20.00	0.058	11.67	19.70	9.65	0.039	0.058
134	30.40	0.064	12.84	21.02	11.51	0.043	0.064
135		0.033				0.022	0.033
136	12.80	0.018	11.61	19.79	10.14	0.012	0.018
137	6.00	0.013	10.99	20.00	9.68	0.009	0.013
138	30.80	0.058	14.37	18.08	12.44	0.039	0.058
141	18.40	0.015	13.11	22.87	11.55	0.010	0.015
142	30.80	0.442	12.10	20.64	10.42	0.295	0.442
143	20.40	0.528	12.57	23.06	10.91	0.352	0.528
144	3.60	0.669	11.13	22.45	9.82	0.446	0.669
145	24.00	6.496	12.61	22.19	10.89	4.331	6.496
146							
147	21.60	1.015	13.23	20.39	11.70	0.677	1.015
148	14.80	0.094	13.72	22.58	11.77	0.063	0.094
150	19.20	0.628	13.25	23.38	11.61	0.419	0.628
151	20.00	4.162	11.88	21.87	10.48	2.775	4.162
155	3.20	0.085	11.31	21.21	10.08	0.057	0.085
156	25.60	0.619	9.98	22.04	8.88	0.413	0.619
157	40.80	0.778	12.71	24.38	10.91	0.519	0.778

Day	COD (mg/L)	Phenol (mg/L)	MLSS (g/L)	SVI (ml/g)	MLVSS (g/L)	Effluent Suspended Solids (g/L)	Waste Sludge (g/L)
158	39.20	1.134	12.59	20.64	11.21	0.756	1.134
159	24.80	1.104	11.52	26.03	10.05	0.736	1.104
161	22.40						
162	4.00	0.045	12.40	24.18	11.04	0.030	0.045
163	9.60	0.042	12.47	24.04	11.17	0.028	0.042
164	16.00	0.081	12.86	24.86	11.56	0.054	0.081
165	17.60	0.048	12.71	24.38	11.42	0.032	0.048
166	20.80	0.060	12.79	25.01	11.44	0.040	0.060
167	17.60	0.283	12.00	24.16	10.66	0.189	0.283
168	50.00	4.183	12.84	26.46	11.19	2.789	4.183
169	29.20	5.647	10.90	29.33	9.61	3.764	5.647
170	40.00	2.043	11.68	29.10	9.98	1.362	2.043
171	16.00	5.366	10.93	31.08	9.32	3.577	5.366
172	86.40	2.780	12.40	27.41	9.82	1.853	2.780
173	62.40	4.962	10.83	30.46	8.96	3.308	4.962
176	19.20	1.699	10.56	30.23	8.81	1.133	1.699
177	28.00	2.601	10.57	31.20	8.72	1.734	2.601
178	39.20	3.859	10.76	30.64	8.63	2.573	3.859
179	28.00	3.294	10.71	30.79	8.80	2.196	3.294
182	43.20	5.643	7.27	45.36	6.23	3.762	5.643
183	34.40	2.850	11.27	28.37	9.52	1.900	2.850

Day	COD (mg/L)	Phenol (mg/L)	MLSS (g/L)	SVI (ml/g)	MLVSS (g/L)	Effluent Suspended Solids (g/L)	Waste Sludge (g/L)
184	58.40	3.420	11.09	27.94	8.85	2.280	3.420
185	34.40	3.547	8.43	33.19	7.19	2.365	3.547
186	11.20	2.796	6.45	48.00	5.52	1.864	2.796
188	14.00	1.495	8.43	42.66	6.53	0.997	1.495
189	16.80	0.208	7.41	44.52	6.40	0.139	0.208
190	39.20	1.168	7.54	43.75	6.24	0.779	1.168
191	30.40	2.550	8.14	42.95	6.63	1.700	2.550
192	14.40	1.777	7.54	43.74	6.53	1.185	1.777
193	21.60	0.313	6.34	50.41	5.08	0.209	0.313
196	18.40	6.601	7.43	43.05	6.10	4.401	6.601
197	24.80	4.684	6.65	48.07	5.60	3.123	4.684
198	10.40	3.445	6.23	49.73	5.09	2.297	3.445
199	12.80	1.824	5.90	49.08	4.63	1.216	1.824
200	12.00	1.587	6.40	49.92	5.58	1.058	1.587
201	27.20	2.155	6.90	44.87	5.87	1.437	2.155

Profile Stud	y for	Seq	uencing	Batch	Reactor
--------------	-------	-----	---------	-------	---------

Time	DO (mg/L)	pН	COD (mg/L)
0	1.47	4.60	19.20
5	0.51	4.75	49.60
10	0.24	4.56	36.80
15	0.21	4.53	44.80
25	0.30	4.47	22.40
35	0.25	4.83	64.00
45	0.30	4.84	36.80
60	0.53	4.86	84.80
75	0.65	4.79	35.20
90	0.71	4.90	41.60
105	0.60	4.83	30.40
120	1.35	4.85	36.80
123	2.41	4.88	24.00
126	3.42	4.92	30.40
130	4.14	4.95	24.00
135	4.39	4.91	30.40
140	5.55	4.95	25.60
145	5.58	4.97	24.00
160	5.68	4.90	54.40
180	6.24	4.73	35.20
210	6.69	4.85	24.00

(a) At Base-Mix

# Profile Study for Sequencing Batch Reactor

Time	DO (mg/L)	pН	Phenol (mg/L)	COD (mg/L)
0	2.33	5.38	N/D	33.85
10	0.02	5.48	1.161	32.31
20	0.04	5.47	9.228	46.15
30	0.04	5.40	9.177	78.46
35	0.04	5.37	8.341	87.60
40	0.03	5.36	5.043	90.77
45	0.02	5.34	5.820	83.20
50	0.01	5.30	4.348	80.00
55	0.01	5.34	2.510	44.62
60	0.02	5.45	0.916	29.23
65	0.31	5.24	0.024	40.00
70	0.58	5.22	N/D	31.10
75	0.79	5.22	N/D	43.08
80	0.98	5.22	N/D	41.40
85	1.02	5.24	N/D	43.90
90	1.01	5.23	N/D	40.00
95	0.96	5.18	N/D	29.23
100	1.06	5.10	N/D	35.40
110	1.30	5.19	N/D	24.62
115	1.59	5.05	N/D	28.60
120	1.90	5.03	N/D	26.15
125	2.58	5.17	N/D	31.10
130	2.46	5.17	N/D	23.08
140	3.15	5.13	N/D	35.38
150	4.70	5.14	N/D	41.54
155	5.00	5.05	N/D	37.90
160	5.30	5.12	N/D	38.90

(b) At 200 mg/L Influent Phenol Concentration

# Profile Study for Sequencing Batch Reactor

Time	DO (mg/L)	pН	Phenol (mg/L)	COD (mg/L)
0	0.07	3.54	15.561	80.25
10	0.05	3.43	64.550	214.66
20	1.15	3.45	72.950	226.70
30	0.48	3.32	81.519	238.50
40	0.66	3.33	85.594	246.14
50	0.16	3.30	86.066	266.11
60	1.47	3.34	85.393	247.20
70	1.82	3.31	81.882	229.25
80	2.04	3.30	80.611	227.71
90	1.54	3.29	74.182	221.10
100	1.10	3.27	70.345	204.67
105	0.88	3.27	67.073	210.00
110	0.81	3.26	56.718	207.74
115	0.74	3.25	42.465	129.41
120	1.54	3.22	32.132	87.94
125	1.26	3.22	17.916	91.90
130	0.86	3.21	7.740	52.20
135	0.84	3.20	N/D	44.93
140	3.76	3.20	N/D	46.60
145	4.98	3.20	N/D	59.60
150	6.00	3.19	N/D	52.61
160	6.04	3.16	N/D	52.80
170	5.84	3.18	N/D	57.10
180	5.84	3.28	N/D	46.46

(c) At 400 mg/L Influent Phenol Concentration

## Profile Study for Sequencing Batch Reactor

#### Time DO (mg/L) Phenol (mg/L) COD (mg/L) pН 3.44 0 6.41 62.410 640.03 20 1.30 3.75 132.680 742.45 1.13 4.34 760.25 40 160.840 60 1.28 4.55 174.950 832.76 1.44 4.90 90 984.35 188.550 120 1.02 5.24 984.25 196.160 0.95 4.23 1088.64 140 193.330 160 0.95 4.96 191.140 984.85 0.97 4.86 192.360 776.72 180 200 0.93 4.74 880.09 186.420 230 1.01 4.63 184.800 896.91 260 1.49 4.14 176.360 806.42 290 1.30 4.01 171.480 745.65 320 1.40 4.24 713.60 153.670 350 1.45 3.95 131.130 710.41 3.97 380 1.92 112.360 633.60 420 1.99 3.57 100.550 627.24 3.97 614.45 480 2.01 97.840 540 2.13 3.65 82.330 540.82 2.09 600 3.77 75.330 521.64

#### (d) At 600 mg/L Influent Phenol Concentration

# Appendix I

Scanning Electron Microscope for Ceramic Filter



# Appendix J

Sludge Size Distr	ibution for	Activated	Sludge	Fed	with	Base-	-mix
Diaage Dille Dibti	10001011 101	1 Iou acoa	Diaage	100	** 1011	Dabe	

$\begin{array}{l} f(D_{p,j}) = \\ n_j/(n_t  D_{p,j}) = \\ normalized \\ number of \\ particles per \\ class width \end{array}$	N(D <sub>p,j</sub> )/n <sub>t</sub> = percent of particles less than upper interval size	n <sub>j</sub> /n <sub>t</sub> = fraction of particles in class	n <sub>j</sub> = number of particles per class	D <sub>p,j</sub> = class midpoint ( m)	D <sub>p,j</sub> = class width ( m)	D <sub>p,max,j</sub> = maximum diameter in class ( m)	$\begin{array}{l} D_{p,min,j} = \\ minimum \\ diameter \\ in class \\ ( m) \end{array}$
0.001449275	4.333333333	0.04333333	26	15.05	29.90	30.00	0.10
0.017	51	0.51	306	45	30.00	60.00	30.00
0.014333333	43	0.43	258	75	30.00	90.00	60.00
0.000555556	1.6666666667	0.01666667	10	105	30.00	120.00	90.00
0	0	0	0	135	30.00	150.00	120.00
0	0	0	0	165	30.00	180.00	150.00
0	0	0	0	195	30.00	210.00	180.00
0	0	0	0	225	30.00	240.00	210.00
0	0	0	0	255	30.00	270.00	240.00
0	0	0	0	285	30.00	300.00	270.00
0	0	0	0	315	30.00	330.00	300.00
0	0	0	0	345	30.00	360.00	330.00
0	0	0	0	375	30.00	390.00	360.00
D <sub>p,min,j</sub> = minimum diameter in class ( m)	D <sub>p,max,j</sub> = maximum diameter in class ( m)	D <sub>p,j</sub> = class width ( m)	D <sub>p,j</sub> = class midpoint ( m)	n <sub>j</sub> = number of particles per class	n <sub>j</sub> /n <sub>t</sub> = fraction of particles in class	$N(D_{p,j})/n_t =$ percent of particles less than upper interval size	$\begin{array}{l} f(D_{p,j}) = \\ n_j/(n_t  D_{p,j}) = \\ normalized \\ number of \\ particles per \\ class width \end{array}$
---	---	--	---	--	--	---	--
390.00	420.00	30.00	405	0	0	0	0
420.00	450.00	30.00	435	0	0	0	0
450.00	480.00	30.00	465	0	0	0	0
480.00	510.00	30.00	495	0	0	0	0
510.00	540.00	30.00	525	0	0	0	0
540.00	570.00	30.00	555	0	0	0	0
570.00	600.00	30.00	585	0	0	0	0
600.00	630.00	30.00	615	0	0	0	0
630.00	660.00	30.00	645	0	0	0	0
660.00	690.00	30.00	675	0	0	0	0
690.00	720.00	30.00	705	0	0	0	0
720.00	750.00	30.00	735	0	0	0	0
750.00	780.00	30.00	765	0	0	0	0
780.00	810.00	30.00	795	0	0	0	0
810.00	840.00	30.00	825	0	0	0	0
840.00	870.00	30.00	855	0	0	0	0
870.00	900.00	30.00	885	0	0	0	0
900.00	930.00	30.00	915	0	0	0	0

D <sub>p,min,j</sub> = minimum diameter in class ( m)	D <sub>p,max,j</sub> = maximum diameter in class ( m)	D <sub>p,j</sub> = class width ( m)	D <sub>p,j</sub> = class midpoint ( m)	n <sub>j</sub> = number of particles per class	n <sub>j</sub> /n <sub>t</sub> = fraction of particles in class	$N(D_{p,j})/n_t =$ percent of particles less than upper interval size	$\begin{array}{l} f(D_{p,j}) = \\ n_j/(n_t  D_{p,j}) = \\ normalized \\ number of \\ particles per \\ class width \end{array}$
930.00	960.00	30.00	945	0	0	0	0
960.00	990.00	30.00	975	0	0	0	0
990.00	1020.00	30.00	1005	0	0	0	0
1020.00	1050.00	30.00	1035	0	0	0	0
1050.00	1080.00	30.00	1065	0	0	0	0
1080.00	1110.00	30.00	1095	0	0	0	0
1110.00	1140.00	30.00	1125	0	0	0	0
1140.00	1170.00	30.00	1155	0	0	0	0
1170.00	1200.00	30.00	1185	0	0	0	0
1200.00	1230.00	30.00	1215	0	0	0	0
1230.00	1260.00	30.00	1245	0	0	0	0
1260.00	1290.00	30.00	1275	0	0	0	0
1290.00	1320.00	30.00	1305	0	0	0	0
1320.00	1350.00	30.00	1335	0	0	0	0

### Appendix K

Sludge Size Distribution for Activated Sludge Acclimatised to 200 mg/L Pher
---

D <sub>p,min,j</sub> = minimum diameter in class ( m)	D <sub>p,max,j</sub> = maximum diameter in class ( m)	D <sub>p,j</sub> = class width ( m)	$\begin{array}{l} \mathbf{D}_{\mathrm{p,j}} = \\ \mathbf{class} \\ \mathbf{midpoint} \\ (\mathbf{m}) \end{array}$	n <sub>j</sub> = number of particles per class	n <sub>j</sub> /n <sub>t</sub> = fraction of particles in class	$N(D_{p,j})/n_t =$ percent of particles less than upper interval size	$\begin{array}{l} f(D_{p,j}) = \\ n_j/(n_t  D_{p,j}) = \\ normalized \\ number of \\ particles per \\ class width \end{array}$
0.10	30.00	29.90	15.05	70	0.11666667	11.66666667	0.003901895
30.00	60.00	30.00	45	467	0.77833333	77.83333333	0.025944444
60.00	90.00	30.00	75	60	0.1	10	0.003333333
90.00	120.00	30.00	105	3	0.005	0.5	0.000166667
120.00	150.00	30.00	135	0	0	0	0
150.00	180.00	30.00	165	0	0	0	0
180.00	210.00	30.00	195	0	0	0	0
210.00	240.00	30.00	225	0	0	0	0
240.00	270.00	30.00	255	0	0	0	0
270.00	300.00	30.00	285	0	0	0	0
300.00	330.00	30.00	315	0	0	0	0
330.00	360.00	30.00	345	0	0	0	0
360.00	390.00	30.00	375	0	0	0	0
390.00	420.00	30.00	405	0	0	0	0

D <sub>p,min,j</sub> = minimum diameter in class ( m)	D <sub>p,max,j</sub> = maximum diameter in class ( m)	D <sub>p,j</sub> = class width ( m)	D <sub>p,j</sub> = class midpoint ( m)	n <sub>j</sub> = number of particles per class	n <sub>j</sub> /n <sub>t</sub> = fraction of particles in class	$N(D_{p,j})/n_t =$ percent of particles less than upper interval size	$\begin{array}{l} f(\mathbf{D}_{p,j}) = \\ \mathbf{n}_j / (\mathbf{n}_t  \mathbf{D}_{p,j}) = \\ \mathbf{normalized} \\ \mathbf{number of} \\ \mathbf{particles per} \\ \mathbf{class width} \end{array}$
420.00	450.00	30.00	435	0	0	0	0
450.00	480.00	30.00	465	0	0	0	0
480.00	510.00	30.00	495	0	0	0	0
510.00	540.00	30.00	525	0	0	0	0
540.00	570.00	30.00	555	0	0	0	0
570.00	600.00	30.00	585	0	0	0	0
600.00	630.00	30.00	615	0	0	0	0
630.00	660.00	30.00	645	0	0	0	0
660.00	690.00	30.00	675	0	0	0	0
690.00	720.00	30.00	705	0	0	0	0
720.00	750.00	30.00	735	0	0	0	0
750.00	780.00	30.00	765	0	0	0	0
780.00	810.00	30.00	795	0	0	0	0
810.00	840.00	30.00	825	0	0	0	0
840.00	870.00	30.00	855	0	0	0	0
870.00	900.00	30.00	885	0	0	0	0
900.00	930.00	30.00	915	0	0	0	0
930.00	960.00	30.00	945	0	0	0	0

D <sub>p,min,j</sub> = minimum diameter in class ( m)	D <sub>p,max,j</sub> = maximum diameter in class ( m)	D <sub>p,j</sub> = class width ( m)	D <sub>p,j</sub> = class midpoint ( m)	n <sub>j</sub> = number of particles per class	n <sub>j</sub> /n <sub>t</sub> = fraction of particles in class	$N(D_{p,j})/n_t =$ percent of particles less than upper interval size	$\begin{array}{l} f(D_{p,j}) = \\ n_j/(n_t  D_{p,j}) = \\ normalized \\ number of \\ particles per \\ class width \end{array}$
960.00	990.00	30.00	975	0	0	0	0
990.00	1020.00	30.00	1005	0	0	0	0
1020.00	1050.00	30.00	1035	0	0	0	0
1050.00	1080.00	30.00	1065	0	0	0	0
1080.00	1110.00	30.00	1095	0	0	0	0
1110.00	1140.00	30.00	1125	0	0	0	0
1140.00	1170.00	30.00	1155	0	0	0	0
1170.00	1200.00	30.00	1185	0	0	0	0
1200.00	1230.00	30.00	1215	0	0	0	0
1230.00	1260.00	30.00	1245	0	0	0	0
1260.00	1290.00	30.00	1275	0	0	0	0
1290.00	1320.00	30.00	1305	0	0	0	0
1320.00	1350.00	30.00	1335	0	0	0	0

#### Appendix L

Sludge	Size ]	Distribution	for A	Activated	Sludge	Acclimatised	to 400	mg/L	Phenol
								0	

$D_{p,min,j} =$ minimum diameter in class ( m)	D <sub>p,max,j</sub> = maximum diameter in class ( m)	D <sub>p,j</sub> = class width ( m)	D <sub>p,j</sub> = class midpoint ( m)	n <sub>j</sub> = number of particles per class	n <sub>j</sub> /n <sub>t</sub> = fraction of particles in class	N(D <sub>p,j</sub> )/n <sub>t</sub> = percent of particles less than upper interval size	$\begin{array}{l} f(D_{p,j}) = \\ n_j/(n_t  D_{p,j}) = \\ normalized \\ number of \\ particles per \\ class width \end{array}$
0.10	30.00	29.90	15.05	0	0	0	0
30.00	60.00	30.00	45	0	0	0	0
60.00	90.00	30.00	75	2	0.00333333	0.333333333	0.000111111
90.00	120.00	30.00	105	10	0.01666667	1.6666666667	0.000555556
120.00	150.00	30.00	135	30	0.05	5	0.001666667
150.00	180.00	30.00	165	36	0.06	6	0.002
180.00	210.00	30.00	195	49	0.08166667	8.166666667	0.002722222
210.00	240.00	30.00	225	82	0.13666667	13.66666667	0.004555556
240.00	270.00	30.00	255	107	0.17833333	17.83333333	0.005944444
270.00	300.00	30.00	285	99	0.165	16.5	0.0055
300.00	330.00	30.00	315	75	0.125	12.5	0.004166667
330.00	360.00	30.00	345	45	0.075	7.5	0.0025

D <sub>p,min,j</sub> = minimum diameter in class ( m)	D <sub>p,max,j</sub> = maximum diameter in class ( m)	D <sub>p,j</sub> = class width (m)	D <sub>p,j</sub> = class midpoint ( m)	n <sub>j</sub> = number of particles per class	n <sub>j</sub> /n <sub>t</sub> = fraction of particles in class	$N(D_{p,j})/n_t =$ percent of particles less than upper interval size	$\begin{split} f(D_{p,j}) &= \\ n_j/(n_t  D_{p,j}) &= \\ normalized \\ number of \\ particles per \\ class width \end{split}$
390.00	420.00	30.00	405	10	0.01666667	1.666666667	0.000555556
420.00	450.00	30.00	435	17	0.02833333	2.833333333	0.000944444
450.00	480.00	30.00	465	6	0.01	1	0.000333333
480.00	510.00	30.00	495	1	0.00166667	0.166666667	5.55556E-05
510.00	540.00	30.00	525	1	0.00166667	0.166666667	5.55556E-05
540.00	570.00	30.00	555	0	0	0	0
570.00	600.00	30.00	585	0	0	0	0
600.00	630.00	30.00	615	0	0	0	0
630.00	660.00	30.00	645	0	0	0	0
660.00	690.00	30.00	675	0	0	0	0
690.00	720.00	30.00	705	0	0	0	0
720.00	750.00	30.00	735	0	0	0	0
750.00	780.00	30.00	765	0	0	0	0
780.00	810.00	30.00	795	0	0	0	0
810.00	840.00	30.00	825	0	0	0	0
840.00	870.00	30.00	855	0	0	0	0
870.00	900.00	30.00	885	0	0	0	0
900.00	930.00	30.00	915	0	0	0	0

D <sub>p,min,j</sub> = minimum diameter in class ( m)	D <sub>p,max,j</sub> = maximum diameter in class ( m)	D <sub>p,j</sub> = class width ( m)	D <sub>p,j</sub> = class midpoint ( m)	n <sub>j</sub> = number of particles per class	n <sub>j</sub> /n <sub>t</sub> = fraction of particles in class	N(D <sub>p,j</sub> )/n <sub>t</sub> = percent of particles less than upper interval size	$\begin{split} f(D_{p,j}) &= \\ n_j/(n_t  D_{p,j}) &= \\ normalized \\ number of \\ particles per \\ class width \end{split}$
930.00	960.00	30.00	945	0	0	0	0
1020.00	1050.00	30.00	1035	0	0	0	0
1050.00	1080.00	30.00	1065	0	0	0	0
1080.00	1110.00	30.00	1095	0	0	0	0
1110.00	1140.00	30.00	1125	0	0	0	0
1140.00	1170.00	30.00	1155	0	0	0	0
1170.00	1200.00	30.00	1185	0	0	0	0
1200.00	1230.00	30.00	1215	0	0	0	0
1230.00	1260.00	30.00	1245	0	0	0	0
1260.00	1290.00	30.00	1275	0	0	0	0
1290.00	1320.00	30.00	1305	0	0	0	0
1320.00	1350.00	30.00	1335	0	0	0	0

#### Appendix M

Sludge Size Distribution for	Activated Sludge Acclimatised	to 600 mg/L Phenol
------------------------------	-------------------------------	--------------------

D <sub>p,min,j</sub> = minimum diameter in class ( m)	D <sub>p,max,j</sub> = maximum diameter in class ( m)	$D_{p,j} = class$ width (m)	D <sub>p,j</sub> = class midpoint ( m)	n <sub>j</sub> = number of particles per class	n <sub>j</sub> /n <sub>t</sub> = fraction of particles in class	N(D <sub>p,j</sub> )/n <sub>t</sub> = percent of particles less than upper interval size	$\begin{array}{l} f(D_{p,j}) = \\ n_j/(n_t  D_{p,j}) = \\ normalized \\ number of \\ particles per \\ class width \end{array}$
0.10	30.00	29.90	15.05	10	0.01666667	1.6666666667	0.000557414
30.00	60.00	30.00	45	105	0.175	17.5	0.005833333
60.00	90.00	30.00	75	104	0.17333333	17.33333333	0.005777778
90.00	120.00	30.00	105	82	0.13666667	13.66666667	0.004555556
120.00	150.00	30.00	135	81	0.135	13.5	0.0045
150.00	180.00	30.00	165	36	0.06	6	0.002
180.00	210.00	30.00	195	46	0.07666667	7.666666667	0.002555556
210.00	240.00	30.00	225	32	0.05333333	5.333333333	0.001777778
240.00	270.00	30.00	255	17	0.02833333	2.833333333	0.000944444
270.00	300.00	30.00	285	18	0.03	3	0.001
300.00	330.00	30.00	315	11	0.01833333	1.833333333	0.000611111
330.00	360.00	30.00	345	7	0.01166667	1.166666667	0.000388889
360.00	390.00	30.00	375	5	0.00833333	0.833333333	0.000277778
390.00	420.00	30.00	405	8	0.01333333	1.333333333	0.000444444

D <sub>p,min,j</sub> = minimum diameter in class ( m)	D <sub>p,max,j</sub> = maximum diameter in class ( m)	D <sub>p,j</sub> = class width ( m)	D <sub>p,j</sub> = class midpoint ( m)	n <sub>j</sub> = number of particles per class	n <sub>j</sub> /n <sub>t</sub> = fraction of particles in class	$N(D_{p,j})/n_t =$ percent of particles less than upper interval size	$\begin{array}{l} f(D_{p,j}) = \\ n_j / (n_t  D_{p,j}) = \\ normalized \\ number of \\ particles per \\ class width \end{array}$
420.00	450.00	30.00	435	2	0.00333333	0.333333333	0.000111111
450.00	480.00	30.00	465	6	0.01	1	0.000333333
480.00	510.00	30.00	495	3	0.005	0.5	0.000166667
510.00	540.00	30.00	525	1	0.00166667	0.166666667	5.55556E-05
540.00	570.00	30.00	555	1	0.00166667	0.166666667	5.55556E-05
570.00	600.00	30.00	585	4	0.00666667	0.666666667	0.000222222
600.00	630.00	30.00	615	4	0.00666667	0.6666666667	0.000222222
630.00	660.00	30.00	645	4	0.00666667	0.666666667	0.000222222
660.00	690.00	30.00	675	0	0	0	0
690.00	720.00	30.00	705	2	0.00333333	0.333333333	0.000111111
720.00	750.00	30.00	735	0	0	0	0
750.00	780.00	30.00	765	2	0.00333333	0.333333333	0.000111111
780.00	810.00	30.00	795	0	0	0	0
810.00	840.00	30.00	825	3	0.005	0.5	0.000166667
840.00	870.00	30.00	855	0	0	0	0
870.00	900.00	30.00	885	2	0.00333333	0.333333333	0.000111111
900.00	930.00	30.00	915	0	0	0.333333333	0
930.00	960.00	30.00	945	0	0	0.333333333	0

$\begin{array}{l} f(D_{p,j}) = \\ n_j/(n_t  D_{p,j}) = \\ normalized \\ number of \\ particles per \\ class width \end{array}$	$N(D_{p,j})/n_t =$ percent of particles less than upper interval size	n <sub>j</sub> /n <sub>t</sub> = fraction of particles in class	n <sub>j</sub> = number of particles per class	D <sub>p,j</sub> = class midpoint ( m)	D <sub>p,j</sub> = class width ( m)	D <sub>p,max,j</sub> = maximum diameter in class ( m)	D <sub>p,min,j</sub> = minimum diameter in class ( m)
0	0.333333333	0	0	975	30.00	990.00	960.00
0	0.333333333	0	0	1005	30.00	1020.00	990.00
0	0.333333333	0	0	1035	30.00	1050.00	1020.00
5.55556E-05	0.5	0.00166667	1	1065	30.00	1080.00	1050.00
0	0	0	0	1095	30.00	1110.00	1080.00
0	0	0	0	1125	30.00	1140.00	1110.00
0.000111111	0.333333333	0.00333333	2	1155	30.00	1170.00	1140.00
0	0	0	0	1185	30.00	1200.00	1170.00
0	0	0	0	1215	30.00	1230.00	1200.00
0	0	0	0	1245	30.00	1260.00	1230.00
0	0	0	0	1275	30.00	1290.00	1260.00
5.55556E-05	0.166666667	0.00166667	1	1305	30.00	1320.00	1290.00
0	0	0	0	1335	30.00	1350.00	1320.00

### Appendix N

#### Membrane Permeability of the Ceramic Membrane

(a) In Pure Water

Pressure, kPa	Flux, L/m2.hr
-5	56
-7.5	120
-15	336
-20	400
-25	592
-30	720

(b) In Mixed Liquor

Pressure, kPa	Flux, L/m2.hr
-10	352
-20	736
-25	896
-30	1072
-35	1184

### Appendix O

Time (min)	Relative flux, J/Jo (%)	Time (min)	Relative flux, J/Jo (%)	Time (min)	Relative flux, J/Jo (%)
0	100.00	0	100.00	0	100.00
0	100.00	2	69.76	2	79.20
2	94.99	4	60.46	4	78.90
4	94.99	6	58.13	6	81.48
6	94.99	8	55.81	8	80.00
8	94.99	10	55.81	10	81.48
10	89.99	12	55.81	13	85.18
12	89.99	14	55.81	15	81.48
14	89.99	16	58.13	18	85.18
16	89.99	18	58.13	20	85.18
18	89.99	20	58.13	25	83.33
20	84.99	22	58.13	30	83.10
24	84.99	24	53.48	35	83.10
28	84.99	26	53.90	40	85.80
32	84.99	28	53.48	45	81.60
36	79.99	30	51.16	50	81.00
40	79.99	32	51.16	55	75.60
45	74.99	34	51.16	60	72.22
50	74.99	40	51.16		
55	72.00	45	46.51		
60	69.99	50	48.83		
		55	46.51		
		60	48.83		

Relative Flux of the Ceramic Membrane in sMBR fed with Base-Mix

(c) At -30 kPa

(b) At -15 kPa

#### Appendix P

Time (min)	Relative flux, J/Jo (%)	Time (min)	Relative flux, J/Jo (%)	Time (min)	Relative flux, J/Jo (%)
0	100.00	0	100.00	0	99.99
2	97.43	2	71.05	2	82.35
4	94.87	4	68.42	4	72.05
6	92.30	6	63.15	6	70.58
8	89.74	8	63.80	8	63.23
10	89.74	10	65.78	10	61.76
13	87.17	12	66.20	12	60.29
16	84.61	14	65.60	14	57.35
19	82.05	16	65.78	16	54.41
21	79.48	18	65.78	18	52.94
25	79.48	20	63.15	20	51.47
29	71.79	24	63.60	22	48.52
33	69.23	28	64.60	24	47.05
37	64.10	32	62.10	26	44.11
40	58.80	36	63.80	28	42.64
45	55.70	40	60.52	30	41.17
50	55.90	45	57.89	33	39.70
55	54.50	50	58.30	36	38.23
60	54.00	55	59.30	39	36.76
65	53.00	60	59.30	42	35.29
70	52.10			46	35.29
				50	33.82
				55	32.35
				60	32.35

Relative Flux of the Ceramic Membrane in sMBR fed with 200 mg/L Phenol

(c) At -30 kPa

(b) At -15 kPa

#### Appendix Q

Time (min)	Relative flux, J/Jo (%)	Time (min)	Relative flux, J/Jo (%)	Time (min)	Relative flux, J/Jo (%)
0	100.00	0	100.00	0	100.00
2	80.00	2	80.35	2	62.28
4	69.18	4	71.42	3	56.14
6	62.89	6	51.02	6	35.96
8	60.50	8	34.43	7	30.70
10	54.71	10	28.06	10	21.92
12	50.31	12	24.23	12	21.05
14	42.00	14	22.95	14	18.40
16	38.36	16	21.68	16	17.54
18	32.70	18	20.00	19	14.03
20	28.93	20	21.68	20	14.91
22	25.15	22	20.40	22	14.03
24	23.27	24	19.13	24	13.15
26	22.10	26	16.58	26	12.28
28	22.70	28	15.30	30	13.85
30	20.30	30	14.20	35	14.03
35	19.49	32	12.24	40	13.15
45	21.38	35	12.50		
55	20.12	38	10.90		
		40	9.94		
		50	10.20		
		60	9.94		

Relative Flux of the Ceramic Membrane in sMBR fed with 400 mg/L Phenol

(b) At -15 kPa

(c) At -30 kPa

### Appendix R

Time (min)	Relative flux, J/Jo (%)	Time (min)	Relative flux, J/Jo (%)	Time (min)	Relative flux, J/Jo (%)
0	100.00	0	100.00	0	100.00
2	68.18	2	90.47	4	98.20
5	63.64	4	86.40	6	95.83
6	57.40	5	85.71	8	93.40
8	54.54	7	76.19	10	90.40
10	52.60	10	71.30	12	87.50
13	51.10	12	71.42	14	77.70
15	50.20	15	71.60	16	73.50
20	48.40	17	70.70	18	68.90
25	43.64	20	71.42	24	50.00
30	39.00	25	68.90	26	45.60
35	37.27	30	66.67	28	42.40
40	38.18	35	66.67	30	33.33
50	38.40	40	61.90	32	31.10
		50	57.14	34	28.70
		60	55.00	38	23.60
	-			40	22.10
				42	22.10
				45	21.50
				50	20.30
				60	20.30

Relative Flux of the Ceramic Membrane in sMBR fed with 600 mg/L Phenol

(b) At -15 kPa

(c) At -30 kPa

### Appendix S

Without Bubbling		Interm	ittent Bubbling	Continuous Bubbling	
Time	J/Jo (%)	Time	J/Jo (%)	Time	J/Jo (%)
0	100.00	0	100.00	0	100.00
2	95.00	2	84.61	2	75.67
4	95.00	4	80.76	4	72.97
6	95.00	6	76.92	6	70.27
8	95.00	8	73.07	9	67.56
10	90.00	10	84.61	11	64.86
12	90.00	12	76.92	13	62.16
14	90.00	14	53.84	14	59.45
16	90.00	16	65.38	16	64.86
18	90.00	18	61.53	18	62.16
20	85.00	20	57.69	20	59.45
24	85.00	22	57.69	25	62.16
28	85.00	24	55.76	30	62.16
32	85.00	26	46.15	35	56.75
36	80.00	28	53.84	40	54.05
40	80.00	31	53.84	50	56.75
45	75.00	33	48.07	60	62.16
50	75.00	35	53.84	65	59.45
55	70.00	37	65.38	70	54.05
60	70.00	39	53.84	80	56.76
		41	50.00		
		43	61.53		
		45	57.69		
		47	57.69		
		49	53.84		
		51	61.53		
		53	59.61		
		55	57.69		
		57	53.84		
		59	69.23		

# Relative Flux at Varying Bubbling Modes for sMBR Fed with Base-mix At $-7.5~\mathrm{kPa}$

### Appendix T

Without Bubbling		Interm	ittent Bubbling	Continuous Bubbling	
Time	J/Jo (%)	Time	J/Jo (%)	Time	J/Jo (%)
0	100.00	0	100.00	0	100.00
2	80.60	2	70.00	3	82.60
4	79.10	4	68.00	6	77.50
6	81.48	6	92.00	9	76.70
8	80.90	8	70.00	12	74.60
10	81.48	10	74.00	15	73.91
13	82.10	12	72.00	18	71.01
15	81.48	14	72.00	21	72.46
18	81.60	16	68.00	24	72.10
20	82.40	18	72.00	27	72.46
25	82.40	20	90.00	30	73.40
30	82.70	22	90.00	35	73.70
35	83.30	24	90.00	40	74.00
40	82.70	26	80.00	45	75.20
45	83.00	28	78.00	50	74.20
50	81.80	30	78.00	55	74.90
55	79.10	32	76.00	60	74.20
60	77.00	34	68.00	65	78.26
		36	92.00	70	75.36
		38	80.00	75	76.81
		40	74.00	80	78.26
		42	74.00	85	75.36
		44	68.00	90	76.81
		46	92.00		
		49	74.00		
		51	70.00		
		54	68.00		
		56	96.00		
		59	74.00		
		62	80.00		

# Relative Flux at Varying Bubbling Modes for sMBR Fed with Base-mix At $-30~\mathrm{kPa}$

### Appendix U

Without Bubbling		Interm	ittent Bubbling	Continuous Bubbling	
Time	J/Jo (%)	Time	J/Jo (%)	Time	J/Jo (%)
0	100.00	0	100.00	0	100.00
2	97.44	2	74.28	2	51.72
4	94.87	4	68.57	4	41.37
6	92.31	6	82.85	6	37.93
8	89.74	8	71.42	8	37.93
10	89.74	10	68.57	10	37.93
13	87.17	12	57.14	13	37.93
16	84.61	14	77.14	16	37.93
19	82.05	16	68.57	19	37.93
21	79.48	18	60.00	22	37.93
25	79.48	20	54.28	25	37.93
29	71.79	22	82.85	30	40.00
33	69.23	24	65.71	35	37.93
37	64.10	26	60.00	40	37.93
40	58.80	28	77.14	45	39.40
45	55.70	30	60.00	50	40.30
50	55.90	32	57.14	55	37.93
55	54.50	34	54.28	60	41.38
60	54.00	36	82.85		
		38	62.85		
		40	57.14		
		42	74.28		
		44	57.14		
		46	51.42		
		48	65.71		
		50	54.28		
		52	48.57		
		54	57.14		
		56	51.42		
		58	42.85		
		60	62.85		
		62	45.71		
		64	62.85		
		66	51.42		
		68	45.71		
		70	62.85		

# Relative Flux at Varying Bubbling Modes for sMBR Fed with 200 mg/L Phenol At -7.5 kPa

### Appendix V

Without Bubbling		Interm	ittent Bubbling	Continuous Bubbling	
Time	J/Jo (%)	Time	Time J/Jo (%)		J/Jo (%)
0	100.00	0	100.00	0	100.00
2	82.35	2	84.37	2	69.69
4	72.05	4	78.12	4	62.12
6	70.58	6	81.25	6	59.20
8	63.23	8	78.12	8	57.40
10	61.76	10	67.18	10	54.40
12	60.29	12	82.81	12	51.70
14	57.35	14	70.31	14	47.50
16	54.41	16	62.50	16	43.80
18	52.94	18	60.93	18	42.42
20	51.47	20	57.81	20	42.42
22	48.52	22	78.12	22	40.90
24	47.05	24	60.93	24	37.80
26	44.11	26	59.37	26	36.60
28	42.64	28	56.25	28	34.50
30	41.17	30	54.68	30	34.84
33	39.70	32	82.81	32	33.20
36	38.23	34	68.75	34	33.33
39	36.76	36	62.50	36	31.30
42	35.29	38	60.93	40	31.81
46	35.29	40	62.50	45	29.00
50	33.82	42	57.81	50	29.20
55	32.35	44	78.12	55	36.90
60	32.35	46	70.31	60	33.20
		48	67.18		
		50	62.50		
		52	60.93		
		54	59.37		
		56	54.68		
		58	76.56		
		60	65.62		
		62	62.50		
		64	60.93		
		66	56.25		
		68	51.56		

# Relative Flux at Varying Bubbling Modes for sMBR Fed with 200 mg/L Phenol At -30 kPa

### Appendix W

Without Bubbling		Intermittent Bubbling		Continuous Bubbling	
Time	J/Jo (%)	Time	J/Jo (%)	Time	J/Jo (%)
0	100.00	0	100.00	0	100.00
2	80.00	4	90.00	2	64.10
4	69.18	8	70.00	4	63.24
6	62.89	10	80.00	8	42.73
8	60.50	14	85.00	12	32.47
10	54.71	18	80.00	14	25.64
12	50.31	22	70.00	16	20.51
14	42.00	24	100.00	18	20.51
16	38.36	28	100.00	20	17.09
18	32.70	30	100.00	23	15.38
20	28.93	32	90.00	26	12.82
22	25.15	34	90.00	30	14.52
24	23.27	36	85.00	35	11.96
26	22.10	38	75.00	45	12.82
28	22.70	42	65.00	55	13.67
30	20.30	44	80.00		
35	19.49	46	85.00		
45	21.38	48	90.00		
55	20.12	50	80.00		
		52	80.00		
		54	70.00		
		56	100.00		
		60	80.00		
		68	75.00		
		70	65.00		

# Relative Flux at Varying Bubbling Modes for sMBR Fed with 400 mg/L Phenol At -7.5 kPa

### Appendix X

Without Bubbling		Intermittent Bubbling		Continuous Bubbling	
Time	J/Jo (%)	Time	J/Jo (%)	Time	J/Jo (%)
0	100.00	0	100.00	0	100.00
2	62.28	2	85.45	2	77.77
3	56.14	6	78.18	4	69.44
6	35.96	10	69.09	6	44.44
7	30.70	12	87.27	8	38.88
10	21.92	16	80.00	10	27.77
12	21.05	20	69.09	12	16.66
14	18.40	22	76.36	14	13.88
16	17.54	25	72.72	16	12.22
19	14.03	27	67.27	18	10.55
20	14.91	29	80.00	20	8.88
22	14.03	30	72.72	24	6.66
24	13.15	34	65.45	28	6.11
26	12.28	36	76.36	32	5.27
30	13.85	39	65.45	36	4.99
35	14.03	41	76.36	40	4.72
40	13.15	44	65.45		
		46	72.72		
		48	56.36		
		50	69.09		
		52	52.72		
		54	63.63		
		56	58.18		
		58	55.63		
		60	40.00		

# Relative Flux at Varying Bubbling Modes for sMBR Fed with 400 mg/L Phenol At -30 kPa

### Appendix Y

Without Bubbling		Intermittent Bubbling		Continuous Bubbling	
Time	J/Jo (%)	Time	J/Jo (%)	Time	J/Jo (%)
0	100.00	0	100.00	0	100.00
2	68.18	3	86.66	3	60.00
3.6	63.63	6	80.00	6	46.67
6	57.40	9	86.66	9	46.67
8	54.54	12	86.66	12	40.00
10	52.60	15	86.66	14	40.00
13	51.10	18	86.66	16	40.00
15	50.20	21	86.66	18	37.33
20	48.40	24	86.66	20	40.00
25	43.63	27	93.33	25	34.67
30	39.00	30	93.33	28	40.00
35	37.27	33	93.33	30	37.33
40	38.18	36	93.33	35	36.00
50	38.40	40	93.33	40	36.00
		43	93.33		
		46	93.33		
		50	86.66		

# Relative Flux at Varying Bubbling Modes for sMBR Fed with 600 mg/L Phenol At -7.5 kPa

### Appendix Z

Without Bubbling		Intermittent Bubbling		Continuous Bubbling	
Time	J/Jo (%)	Time	J/Jo (%)	Time	J/Jo (%)
0	100.00	0	100.00	0	100.00
4	98.20	3	86.67	2	95.45
6	95.83	9	75.56	4	84.09
8	93.40	11	80.00	6	84.09
10	90.40	15	77.78	8	79.54
12	87.50	18	71.11	10	79.54
14	77.70	20	93.33	12	79.54
16	73.50	22	88.89	15	79.54
18	68.90	24	75.56	18	72.72
24	50.00	28	71.11	21	74.99
26	45.60	32	66.67	24	72.72
28	42.40	34	88.89	27	70.45
30	33.33	36	75.56	30	70.45
32	31.10	40	71.11	33	65.90
34	28.70	44	64.44	36	65.90
38	23.60	46	77.78	39	63.63
40	22.10	48	68.89	42	63.63
42	22.10	50	71.11	45	63.63
45	21.50	54	68.89	48	63.63
50	20.30	58	66.67	52	63.63
60	20.30	63	62.22	56	63.63
		66	55.56	60	54.54
		68	75.56	62	47.72
		70	66.67	64	47.72
		72	57.78	66	47.72
		78	55.56	68	50.00
		80	75.56	70	47.72
		83	68.89	72	49.91
		88	53.33	75	47.72
				80	43.18
				90	47.72

# Relative Flux at Varying Bubbling Modes for sMBR Fed with 600 mg/L Phenol At -30 kPa

#### **BIODATA OF THE AUTHOR**

Ms. Leong Mui Lan was born on 25<sup>th</sup> November 1985 in Seremban. She completed her primary and secondary studies in S.J.K. (C) Yuh Hua Rembau and S.M.K. Undang Rembau, respectively. She moved on to study her Diploma in Chemistry and Biology in Kolej Tunku Abdul Rahman (KTAR), Setapak in 2003. In year 2007, she obtained her first degree in Bachelor of Science (Hons) Chemistry from Universiti Tunku Abdul Rahman (UTAR). She further enrolled in Master of Science in the field of wastewater treatment process, specialised in membrane bioreactor technology. During her postgraduate study, she was employed as teaching assistant to conduct laboratory practical classes in the Faculty of Engineering and Science, UTAR, Setapak.

#### **Published Paper:**

Leong, M. L., Lee, K. M., Lai, S. O. and Ooi, B. S. (2011). Sludge characteristics and performances of sequencing batch reactor at different influent phenol concentrations. *Desalination*, 270, 181-187.