MEMBRANE FOULING AND CLEANING STUDY FOR DRINKING WATER TREATMENT USING INTEGRATED MEMBRANE SYSTEM

by

NOORLAILA BINTI MOHAMED NOR

Thesis submitted in fulfilment of the requirements for the degree of

Master of Science

FEBRUARY 2015

ACKNOWLEDGEMENTS

First and foremost, a great thankful to Allah the Almighty for blessing me with strength, good health and ease my journey to complete my study. My deepest gratitude to my late parents, Tuan Haji Mohamed Nor Zainul and Puan Nazehah Mat, my brothers and sisters, nephews and nieces for their endless love, understanding, prayers, patience and financial assistance that supported me through the whole course of study.

I wish to express my genuine appreciation to my supervisor, Dr Suzylawati Ismail who provided me an enthusiastic, motivating, inspiration and critical atmosphere during my study. Without her continued support, this thesis would not have been completed. I believe that all her advices and comments are for the benefit of my research. A special gratitude goes to Mr Ahmad Suhaimi Jaafar, my site supervisor and their team in Kolej KEDA, Sik, Kedah for helping me throughout my research work. It was a great pleasure for me to conduct my research with their constructive comments.

My sincere appreciation extends to all the staffs and technicians in School of Chemical Engineering for their guidance in various occasions. A special acknowledgement to my dearest colleagues, Syahida Farhan, Nur Atiah, Roswani, Nur Farhana, Mohd Shahir and Mohd Usman for the overwhelming and wonderful ideas which helps me a lot. All of your views and comments are very useful indeed.

Last but not least, thank you to each one of you who keep praying for my success. May Allah bless all of you. Thank you.

TABLE OF CONTENTS

ACKN	OWLEDGEMENT	ii
TABLE	C OF CONTENTS	iii
LIST O	F TABLES	vii
LIST O	F FIGURES	viii
LIST O	F PLATES	X
LIST O	F SYMBOLS	xi
LIST O	F ABBREVIATIONS	xii
ABSTR	AK	xiii
ABSTR	ACT	XV
CHAPT	TER 1 – INTRODUCTION	
1.1	Raw water supply in Malaysia	1
1.2	Water quality in Malaysia	4
1.3	Drinking water treatment	6
	1.3.1 Conventional drinking water treatment system	6
	1.3.2 Membrane separation technology	8
	1.3.3 Integrated membrane system	8
1.4	Problem statements	9
1.5	Research objectives	11
1.6	Scope of study	11
1.7	Organization of thesis	12
CHAPT	TER 2 – LITERATURE REVIEW	
2.1	Membrane technology	14
	2.1.1 Type of membrane process	14

	2.1.2 Application in drinking water production	16
2.2	Integrated membrane system	18
	2.2.1 Hybrid membrane processes	18
	2.2.2 Pre-treatment process	19
	2.2.3 Post-treatment process	20
2.3	Membrane fouling	21
	2.3.1 Type of membrane fouling	22
	2.3.2 Membrane foulant	24
	2.3.3 Fouling mechanism	25
2.4	Membrane cleaning	26
	2.4.1 Type of membrane cleaning	27
CHAPT	ER 3 – MATERIALS AND METHOD	
3.1	Overall experimental flowchart	29
3.2	Materials and chemicals	31
	3.3.1 Materials	31
	3.3.2 Chemicals	32
3.3	Design of pilot scale integrated membrane system	32
	3.3.1 Pre-treatment	34
	3.3.2 Ultrafiltration	34
	3.3.3 Post-treatment	35
	3.3.4 Sampling point	36
3.4	Water quality test	36
	3.4.1 pH	36
	3.4.2 Total dissolved solid (TDS)	37
	3.4.3 Turbidity	37

	3.4.4 Total organic carbon (TOC)	37
	3.4.5 Total coliform and Escherichia coli (E.coli)	37
3.5	Membrane performance	38
	3.5.1 Effect of transmembrane pressure	38
	3.5.2 Effect of raw water quality	39
3.6	Membrane fouling study	39
3.7	Physical cleaning	40
	3.7.1 Effect of backwashing pressure	40
	3.7.2 Effect of backwashing duration	40
3.8	Chemical cleaning	41
	3.8.1 Effect of different cleaning agent	41
	3.8.2 Effect of chemical concentration	41
	3.8.3 Effect of cleaning time	41
3.9	Flux recovery	42
3.10	Membrane morphology	42
3.11	Membrane lifespan estimation	42
CHAPTER	4 – RESULTS AND DISCUSSION	
4.1	Process description	44
4.2	Water quality test	46
	4.2.1 Raw water quality	46
	4.2.2 Treated water quality	46
4.3	Membrane performance study	48
	4.3.1 Effect of transmembrane pressure	49
	4.3.2 Effect of raw water quality	51
4.4	Membrane fouling study	54

	4.4.1 Flux decline	54
	4.4.2 Fouling mechanism	55
4.5	Membrane cleaning	57
	4.5.1 Physical cleaning	57
	4.5.2 Chemical cleaning	58
	4.5.2 (a) Effect of different cleaning agent	59
	4.5.2 (b) Effect of chemical concentration	60
	4.5.2 (c) Effect of cleaning time	61
	4.5.3 Comparison between physical and chemical cleaning	62
	4.5.4 Membrane morphology	63
4.6	Membrane lifespan estimation	66
	4.6.1 Without membrane cleaning	66
	4.6.2 With membrane cleaning	67
CHAPTEI	R 5 – CONCLUSIONS AND RECOMMENDATIONS	
5.1	Conclusions	69
5.2	Recommendations	70
BIBLIOG	RAPHY	71
APPENDI	CES	
Appendix A	A - Experimental data	84
Appendix I	3 - Membrane fouling prediction	85
Appendix (C - Membrane cleaning	95
Appendix D - Membrane lifespan estimation		104
Appendix E - Drinking water quality test 1		
LIST OF I	PUBLICATIONS AND PROCEEDING	112

LIST OF TABLES

		Page
Table 1.1	Percentage of state supplied with treated water in	3
	2012	
Table 1.2	Raw water supply directly from river in 2012	4
Table 3.1	Membrane characteristics data	31
Table 3.2	Chemicals used for membrane cleaning	32
Table 4.1	Raw water quality	46
Table 4.2	Water analysis results	48
Table 4.3	R^2 value for each model fitting	56
Table 4.4	Estimated membrane lifespan with membrane	68
	cleaning	

LIST OF FIGURES

		Page
Figure 1.1	Percentage of raw water supply in 2009	2
Figure 1.2	Water quality of river basins monitored in Malaysia	5
	for 2011 and 2012	
Figure 1.3	Conventional drinking water treatment	7
Figure 2.1	The range of different separation processes based	15
	on sizes	
Figure 2.2	Schematic diagram of a pilot scale hybrid	19
	membrane process for drinking water treatment	
Figure 2.3 (a)	Four types of fouling mechanisms (Complete pore	26
	blocking)	
Figure 2.3 (b)	Four types of fouling mechanisms (Standard pore	26
	blocking)	
Figure 2.3 (c)	Four types of fouling mechanisms (Intermediate	26
	pore blocking)	
Figure 2.3 (d)	Four types of fouling mechanisms (Cake filtration)	26
Figure 3.1	Process flow chart	30
Figure 3.2	Schematic diagram for pilot scale integrated	33
	membrane system	
Figure 3.3	Electromagnetic spectrum	35
Figure 4.1	Permeate flux at different TMP	50
Figure 4.2 (a)	Flux decline during filtration on sunny day	52
Figure 4.2 (b)	Flux decline during filtration on rainy day	52

Figure 4.3	Flux reduction after six hours filtration on different	53
	raw water concentration	
Figure 4.4	Percentage of flux recovery at different	58
	backwashing condition	
Figure 4.5	Percentage of recovery after membrane cleaning	59
	using different cleaning agent	
Figure 4.6	Percentage of recovery for different concentration	61
	of NaClO	
Figure 4.7	Percentage of recovery for different cleaning time	62
Figure 4.8	Recovery rate for different cleaning method	63
Figure 4.9 (a)	Fouled membrane at 1,000x magnification	64
Figure 4.9 (b)	Fouled membrane at 10,000x magnification	64
Figure 4.10 (a)	Cleaned membrane at 1,000x magnification	65
Figure 4.10 (b)	Cleaned membrane at 10,000x magnification	65
Figure 4.11 (a)	New membrane at 1,000x magnification	65
Figure 4.11 (b)	New membrane at 10,000x magnification	65
Figure 4.12	Estimated flux decline without membrane cleaning	66
Figure 4.13	Estimated flux reduction with membrane cleaning	67

LIST OF PLATES

		Page
Plate 4.1	Sand filter used in the integrated membrane system	44
Plate 4.2	Ultrafiltration membrane module	45
Plate 4.3	Ultraviolet light disinfection unit	45

LIST OF SYMBOLS

- *dt* Time difference
- *dV* Volume different
- *exp* Exponent
- J Flux
- *J*₀ Initial flux
- *J*_A Flux after cleaning
- J_B Flux before cleaning
- J_t Flux at time, t
- *K* Constant
- t Time

LIST OF ABBREVIATIONS

- APHA APHA American Public Health Association
- E.Coli Escherichia coli
- MF Microfiltration
- NF Nanofiltration
- RO Reverse Osmosis
- SEM Scanning Electron Microscope
- TDS Total dissolved solid
- TOC Total organic carbon
- TMP Transmembrane pressure
- UF Ultrafiltration
- WHO World Health Organization

KAJIAN PENGOTORAN DAN PERMBERSIHAN UNTUK RAWATAN AIR MINUMAN MENGGUNAKAN SISTEM INTEGRASI MEMBRAN

ABSTRAK

Teknologi membran sedang digunakan secara meluas untuk sistem rawatan air bagi mememperbaiki sistem rawatan air konvensional. Walau bagaimanapun, masih terdapat beberapa batasan dalam penggunaan teknologi membran disebalik kelebihannya kerana pengotoran membran yang mengakibatkan penghasilan yang lebih rendah dan penggunaan tenaga yang lebih tinggi. Pengotoran membran telah menjadi salah satu cabaran utama apabila zarah ditolak terkumpul pada permukaan membran atau di dalam liang. Oleh itu pembersihan membran adalah perlu untuk mengurangkan kesan kotor pada membran. Kajian ini tertumpu ke atas pengotoran dan pembersihan membran semasa pengasilan air minuman. Satu penyelidikan telah dijalankan di Kolej KEDA, Sik, Kedah di mana sistem integrasi membran berskala pandu telah dipasang Air permukaan mentah dari Hutan Lipur Perangin Sik, Kedah telah disalurkan secara langsung kepada sistem. Objektif kajian ini adalah untuk menilai prestasi membran pada keadaan operasi yang berbeza, mengenal pasti mekanisme pengotoran membran dan mencadangkan kaedah pembersihan yang sesuai. Prestasi terbaik untuk ultraturapenapisan yang dicapai di TMP 1.0 bar di mana fluks yang tinggi dihasilkan dan pengurangan fluks lebih rendah diperolehi berbanding TMP 0.5, 1.5 dan 2 bar. Pembentukan lapisan kek telah dijumpai sebagai mekanisme pengotoran yang dominan dan pancuran balik pada 2 bar selama 0.5 minit disimpulkan sebagai kaedah yang paling sesuai yang boleh memulihkan fluks sehingga 83,69 %

berbanding pembersihan kimia menggunakan NaClO. Dengan pancuran balik, membran dijangka boleh digunakan sehingga 1339 hari.

MEMBRANE FOULING AND CLEANING STUDY FOR DRINKING WATER TREATMENT USING INTEGRATED MEMBRANE SYSTEM

ABSTRACT

Membrane technology is being widely applied for water treatment system to enhance the conventional water treatment system. However, there are still some limitations in the application of membrane technology inspite of their advantages due to membrane fouling which resulting to lower production and higher energy consumption. Membrane fouling has been one of the main challenges when the rejected particles accumulated on the membrane surface or inside the pores. Thus membrane cleaning is necessary to minimize fouling effect to the membrane. Current study focus on membrane fouling and cleaning during drinking water production. Research was conducted in Kolej KEDA, Sik, Kedah where a pilot scale integrated membrane system has been installed. The raw surface water from Hutan Lipur Perangin Sik, Kedah was fed directly to the system. The objectives of the research are to evaluate the membrane performance at different operating condition, identify the fouling mechanism of the membrane and propose the appropriate cleaning method. The best performance for the ultrafiltration achieved at TMP 1.0 bar where higher flux produced and lower flux reduction obtained compared to TMP 0.5, 1.5 and 2 bar. Layer cake formation has been found as the dominant fouling mechanism and backwashing at 2 bar for 0.5 minutes was concluded as the most appropriate method which can recover the permeate flux up to 83.69% recovery compared to chemical cleaning using NaClO. By regular backwashing, membrane is expected can be used up to 1339 days.

CHAPTER 1

INTRODUCTION

1.1 Raw water supply in Malaysia

Malaysia is blessed with an abundant supply of water with 21,536 m³ per capita water resources per year or 59 m³ per capita per day (Compendium of Environment Statistics Malaysia, 2010). However, due to its growing economy, Malaysia will need to be more efficient in the water resources management and supply. In the Tenth Malaysia Plan, the National Water Resources Policy marks an important milestone because it will establish a process for ensuring the security of water supply in an era of rapid economic development, growing cities and population growth, all of which have important implications on how Malaysia manages its water resources in the coming years (Compendium of Environment Statistics Malaysia, 2011).

The main source of raw water supply in our country comes from rivers, storage dams and groundwater. As stated in the National Water Study (Peninsular Malaysia) 2000-2050, the government will be focussing on identifying the demand and water resources to meet future needs in Peninsular Malaysia as well as to determine the availability of water resources up to 2050 due to the water demand in domestic industries and others is expected to rise by 63% from 2000 to 2050 (Compendium of Environment Statistics Malaysia, 2013). Thus, an immediate action such as application of new technology or improving the conventional system is needed to remain water sustainability.

Figure 1.1 shows the raw water supply directly from rivers contributed to the highest percentage compared to the storage dams and groundwater supply. According to the statistics recorded by Department of Water Supply and National Water Services Commission, the raw water supply from rivers has increased 23.9% since 2005 to 2009. Total supply of raw water from the storage dams has decreased 34% from 2005 to 2009 where in 2009 Selangor was supplied 84.7% less water than the amount supplied since 2005. At the same time, raw groundwater has been recorded as the second major source of water supply in Kelantan.



☐ Rivers □ Storage dams ■ Groundwater

Figure 1.1: Percentage of raw water supply in 2009 (Compendium of Environment Statistics Malaysia, 2010)

In Malaysia, there are many areas which are not supplied with treated water from the national water services. This might be due to the location which is far from the distribution area. Statistic shown in Table 1.1 recorded the percentage area of state supplied with piped water. It is obviously shown that rural areas in Kelantan, Sabah and Sarawak have a very low percentage of receiving treated water.

State	Urban area	Rural area
Johor	100	99.5
Kedah	100	96.3
Kelantan	60.8	57.9
Melaka	100	100
Negeri Sembilan	100	99.8
Pahang	100	96.0
Perak	100	99.2
Perlis	100	99
Pulau Pinang	100	99.7
Sabah	99.8	64.2
Sarawak	99.6	63.5
Selangor	100	99.5
Terengganu	99.1	92.9
W. P. Labuan	100	100

Table 1.1: Percentage of state supplied with treated water in 2012(Compendium of Environment Statistics Malaysia, 2013)

Statistics in Table 1.2 shows the amount of raw water supply extracted directly from the river. It is clearly shown that river water is the raw water source for Johor, Kedah, Pahang, Pulau Pinang and Sarawak while Selangor has the highest amount which is more than 4000 million litres per day.

State	Raw water supply, million litres per day
Johor	1001
Kedah	1371
Kelantan	241
Melaka	377
Negeri Sembilan	575
Pahang	1058
Perak	791
Perlis	172
Pulau Pinang	1029
Sabah	751
Sarawak	1152
Selangor	4150
Terengganu	440

Table 1.2: Raw water supply directly from river in 2012 (Compendium ofEnvironment Statistics Malaysia, 2013)

1.2 Water quality in Malaysia

As mentioned before, around 85% of Malaysia's water supply comes from rivers and stream. However, there are few rivers which are polluted thus the water cannot be used directly. Therefore the application of treatment system is needed. Major sources of pollution include improper discharge from sewerage treatment plants, agrobased factories, livestock farming, land clearing activities and domestic sewage. These wastes can be toxic which are not only harmful to humans but also to habitats as well as the environment. The efforts to overcome river pollution are continuously emphasised by the government with the cooperation of the residents.

Figure 1.2 shows the water quality of the rivers in Malaysia. Department of Environment stated that among 140 river basins monitored, there are about 11 rivers are polluted in 2011 and the number has increased to 12 rivers in 2012 while the number of clean rivers has decreased from 76 rivers to 74 rivers from 2011 to 2012. The government is concerned about this issue because the contaminants in the polluted river water may bring harmful to human.



Figure 1.2: Water quality of river basins monitored in Malaysia for 2011 and 2012 (Compendium of Environment Statistics Malaysia, 2013)

The consequences of polluted raw water include the risk of outbreaking waterborne diseases. The microbial and heavy metal contamination in raw water also can affect the food chain and result in serious health impact. The World Health Organization (WHO) reported that every year, 3.4 million people die because of water-related disease (WHO World Water Day Report, 2001).

In United States, there are more than 1,870 waterborne outbreaks associated with drinking water, 883,806 cases of illness and among them 1,165 deaths were reported from 1971 to 2002 (Craun *et al.*, 2006).

Unfortunately, the contaminated raw water might be the main raw water source to the rural area that are not receiving treated water supply from the national water services. Thus, water treatment as well as drinking water treatment is needed to eliminate or reduce contaminant and improve the water quality.

1.3 Drinking water treatment

Drinking water treatment is very important to ensure that the water supply is clean and safe for consumption and daily uses. Previously, conventional water treatment processes have been used to treat raw water. For conventional water treatment method, it is included physical separation techniques for particle removal, biological and chemical treatments to remove suspended solids, organic matter and dissolved pollutants. However, membrane separation replaces or enhances the conventional water treatment methods by the use of selectivity permeable barriers, with pore size to permit the passage of water molecules but small enough to retain a wide range of particulate and dissolved compounds depending on their nature.

1.3.1 Conventional drinking water treatment system

Most of the water treatment plants in Malaysia are using the conventional treatment system. It has been proved that coagulation, flocculation, sedimentation, filtration and disinfection had successfully removed microorganisms, viruses and bacteria (Sarkar *et al.*, 2007). As shown in Figure 1.3, coagulant is added into the raw water and mixed in the rapid mix vessel. Most drinking water treatment plant is using sweep flocculation and require high coagulant dosage. The particles and solids are removed by gravitational settling during sedimentation and followed by filtration to remove the suspended particles. Finally, disinfection process is done and the most

common chemical used for disinfection is chlorine and also known as chlorination process.



Figure 1.3: Conventional drinking water treatment (Lee et al., 2001)

However, studies to improve the conventional water treatment have been done by previous researchers in term or process enhancement and developing a new technology. Lee and his fellow researchers has discovered the different type of flocculant for coagulation which is polymer flocculant and inorganic flocculants used in conventional water treatment plants (Lee *et al.*, 2001). Carvalho Bongiovani in their study combine Moringa Oleifera Lam with anionic polymer to improvise water treatment process (Carvalho Bongiovani *et al.*, 2014).

On the other hand, adsorption also developed and applied in water treatment processes as found by Bhatnagar who used zinc chloride treated activated carbon to remove nitrate from water (Bhatnagar *et al.*, 2008). As for hazardous contaminants, Ayati reported that catalytic applications of Au/TiO₂ nanoparticles can remove pollutants including toxic and organic materials (Ayati *et al.*, 2014). However, some of the water treatment plants have the limitations in treating polluted water for potable use which may affect the availability of water supply in the country.

1.3.2 Membrane separation technology

As the technologies are growing and simultaneously the water crisis are becoming an issue by few states in Malaysia, therefore it is appropriate to develop and commercialise a simple, economic and effective water treatment system that function as water purification to serve for small and medium scale populations in the rural areas utilizing the available surface water.

One convincing method in water treatment is the application on membrane technology. Membrane filtration water treatment has been widely used in a few regions in China and United States. Generally, the integrated membrane system might combine a membrane process with conventional processes or any other membrane process. Membrane separation process typically begins with a pre-treatment stage to remove contaminants that would affect the membrane. The pre-treatment process is chosen based on the raw water feed characteristics. For certain cases, post-treatment stage also added to the system that produce the ultra-pure water.

In addition, the membrane system only need a compact space for simple unit process and no or less chemical used during filtration. These advantages show that membrane treatment is very suitable to substitute the conventional water treatment method for the application in the rural area.

1.3.3 Integrated membrane system

Integrated membrane system can be defined as a system that combines two or more membrane processes or as a system integrating a membrane process with other treatment processes. The integrated membrane system is proposed to achieve product requirement as many single processes are not qualified well to produce high quality of treated water or the amount of treated water produced does not achieve the required amount. In typical application, basically the objectives might be minimizing volume of waste for disposal, reducing total dissolved solids, removing total suspended solids, achieving high quality water or minimizing the capital and operating costs.

By using the integrated membrane system, all the objectives can be achieved as several equipments with different functions will be combined in one treatment system thus the treated water produced will have a better quality. Generally, the integrated membrane system might combine a membrane process with conventional processes or any other membrane process.

Membrane separation process typically begins with a pre-treatment stage to remove contaminants that would affect the membrane. Several methods such as activated carbon filtration may be used for chlorine removal, cartridge or deep-bed filters for particle removal, and softening agents to remove minerals that cause hardness in the water. The pre-treatment process is chosen based on the raw water feed characteristics. For certain cases, post-treatment stage also added to the system that produce the ultra-pure water.

1.4 Problem statement

There are various resources for water to be used by consumers including rivers, lakes, sea water and a few more. Water resources from rivers or waterfall with low contaminations can be further treated for the consumption of surrounding populations especially in the rural area. This free raw water supply are not supposed to be consumed directly without treatment as there are already many cases reported on its contamination. For example, thyphoid outbreak in Sungai Chongkak Recreational Park and fatal cases due to leptospirosis in Hutan Lipur Lubuk Yu, Maran, Terengganu. In May 2013, there was a case of one dead and six others warded due to leptospirosis caused by exposure to rat urine at the Lata Bayu Recreational Park in Baling, Kedah. Through 2013, it was reported that 28% from the overall leptospirosis cases are coming from the recreational park visits.

Therefore, an integrated membrane system is needed to treat the raw water source from the rivers for rural area application. However, the rural area residences might not know that membrane fouling will occur which then reduce the membrane lifespan and lower volume of treated water will be produced. On the other hand, the contaminants that naturally exist in the raw water source need to be studied. As for membrane cleaning for rural area application, the appropriate cleaning method is needed to prolong the membrane lifespan.

For this study, a pilot-scale integrated membrane treatment system is installed and the research is conducted at Sik, Kedah which is near to the raw surface water sources from Hutan Lipur Perangin Sik to be used for Kolej KEDA. The water treatment system applying the membranes combining pre-treatment, ultrafiltration and disinfection process. The system is aimed to use less chemical, simple design system but producing higher quality of water.

1.5 Research objectives

The aim of this study is to construct a pilot scale integrated membrane system consists of pre-treatment, membrane filtration and post-treatment for drinking water production. The current study has the following objectives:

- 1) To evaluate membrane performance at different operating conditions
- 2) To identify the fouling mechanism of the membrane
- 3) To propose the appropriate cleaning method for membrane

1.6 Scope of study

The research consists of four phases. For the first phase, the pilot scale integrated membrane system was set up in Kolej Keda, Sik, Kedah to treat the raw water from Hutan Lipur Perangin Sik. Many criteria are considered before the system was finalized to be implemented such as type of membrane filtration process, membrane characteristics and the average production rate. Additional unit processes are added to the membrane system to enhance the product quality and better performance.

Second phase emphasized on water characteristics study. Several water quality tests have been done using standard methods for raw water feed and every unit process. The raw water feed was further analyzed and classified based on the water characteristics results.

In the third phase, membrane performance for the integrated membrane system has been studied on different operational conditions. Membrane fouling continued this study to determine the fouling mechanism and impact on drinking water production. Finally, membrane cleaning study was done by using different cleaning method and operating condition. In addition, the lifespan for the membrane was estimated by calculation based on the recommended cleaning method. The drinking water produced was also send to a commercial laboratory for drinking water quality test.

1.7 Organization of thesis

This thesis consists of five chapters providing all the details and findings of the research. A brief introduction on raw water supply in Malaysia, water quality and drinking water treatment are outlined in Chapter 1 (Introduction). This was followed by problem statements providing some points to set the research direction. Based on the defined problem statement, research objectives and scopes of the study were discussed.

Chapter 2 (Literature Review) reviews all the necessary literatures where it is divided into five sub-chapters. The first sub-chapter focuses on the previous research works on water treatment. The second sub-chapter discusses the studies and development of membrane technology. Brief explanation on integrated membrane system and hybrid membrane processes are presented in the third sub-chapter. For the fourth sub-chapter reviews the membrane fouling approach by the previous researchers and in the final sub-chapter, the past works for membrane cleaning are further discussed.

Chapter 3 (Materials and Method) provides details of materials used and experimental procedures. All the details of the chemicals and how the experimental work has been conducted were elaborated step by step in this chapter. This chapter consists of the description regarding the water quality and characteristics, detailed experimental setup and operating conditions in determining the best performance, fouling mechanism studies and membrane cleaning optimization.

Chapter 4 (Results and Discussion) presents and discusses all the important findings on the present experimental works. The experimental studies were carried out based on the objectives outlined in Section 1.5. The results on membrane performance studies, membrane fouling studies, membrane cleaning studies and the membrane lifespan estimation were discussed.

Chapter 5 (Conclusions and Recommendation) summarizes and concludes all the findings in the current study. Based on the research finding and limitations encountered in the present works, there are a few recommendations to improve for future work.

CHAPTER 2

LITERATURE REVIEW

2.1 Membrane technology

Membrane study has been recorded since middle of 18th century when Jean-Antoine Nollet recognized the relation between a semipermeable membrane and osmotic pressure in 1752 (Strathmann *et al.*, 2006). However, membrane technology started to be applied widely in late 1950s after Loeb and Sourirajan founded very thin asymmetric membranes for reverse osmosis (Wenten, 2002).

Membrane separation processes recently have become a convincing technology which provides effective solutions to meet human, environmental and industrial needs. Membrane separation processes can be used for a wide range of applications and can offer significant advantages over conventional separation such as distillation and adsorption since the separation is based on a physical mechanism. Most membrane separation processes are not using any chemical, biological or thermal change of the component therefore membrane separation is particularly attractive to the food processing, beverage and bio products where the processes products can be sensitive to temperature and solvents compared to distillation and extraction.

2.1.1 Type of membrane processes

Membrane filtration processes are classified according to the membrane pore sizes, which are the size of the particles they are able to retain. There are different processes based on respective membrane pore size such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) as shown in Figure 2.1.



Figure 2.1: The range of different separation processes based on sizes. (Cui *et al.*, 2010)

Among all of the wide variety of membrane filtration, microfiltration (MF) has the largest pore size which is 0.1 to 10 μ m thus falls between ultrafitration membranes and conventional filters. MF is basically used to remove suspended solids, turbidity reduction, giardia and cryptosporidium removal. In industry, MF is used for different applications including drinking water filtration and tertiary wastewater treatment from industry for agricultural irrigation or discharge purposes (Huang *et al.*, 2012; Al-Shammiri *et al.*, 2005; Iritani *et al.*, 2008). Instead of using MF as the main process in the system, MF membrane is also effective as pre-treatment process. This is according to Bae *et al.* (2011) findings which used MF as the pre-treatment process prior to reverse osmosis for seawater treatment compared to the conventional sand-filtration.

Ultrafiltration (UF) refers to filtration process which uses porous membranes to separate microsolutes from macromolecules and colloids with pore diameters between 0.01 to $0.1 \mu m$. Basically UF membranes can remove several viruses, colors and more colloidal natural organic matter as the pore size of the membrane is smaller than the particles contained in the feed.

Nanofiltration (NF) is also a pressure-driven membrane separation process with the separation performance between reverse osmosis (RO) and UF. NF membrane has smaller pore size and can retain molecules with molecular weight fall in the range of 200 to 1000 Da to be compared with UF membrane. Recently, NF has been widely applied for water softening, drinking water purification, industrial process fluid treatment and some textile and dye manufacturing processes (Feng *et al.*, 2013; Hilal *et al.*, 2004; Van der Bruggen, 2013; Giacobbo *et al.*, 2013; Lau and Ismail, 2009).

Among all the membrane technologies, RO membranes have the highest ability for organic and inorganic compounds and microorganisms removal thus provide higher quality product. Nowadays, seawater reverse osmosis (SWRO) plants have been implemented due to the limited availability of fresh and natural water. In term of design, RO have a smaller plant size and simple water treatment process (El-Azizi *et al.*, 2009).

2.1.2 Application in drinking water production

In production of drinking water, membrane technologies are now an option for conventional drinking water treatment process as the quality of the water produced has proved a good quality for human consumption (Mierzwa *et al.*, 2008). Membrane filtration enhances the conventional water treatment as it can effectively remove the particulates, algae, bacteria and viruses. Low pressure membranes including MF and UF are recognized as very attractive processes for producing drinking water. As to be compared to the conventional treatment, membrane process offers several advantages such as little need of chemical agents, good quality of produced water, less production of sludge, compact process and easy automation.

The advanced treatment system with latest technology has been investigated to solve surface water pollution in certain regions in China (Xia *et al.*, 2008). Membrane filtration techniques have been used all over the world because of the advantages of the treatment system. More than 2 million m^3/day of drinking water is produced worldwide using low-pressure membranes in combination with other treatments such as adsorption and coagulation (Laine *et al.*, 2000).

Recently, full-scale UF applications are widely used in Europe and the US while for developing countries, potable water production is facing a very large market for UF membranes because of the lack of drinking water supply in those regions.

In China, membrane processes has been developed for drinking water production since 1997 where their first plant operated in Chang Island of Shangdong Province using nanofiltration membrane (Zheng *et al.*, 2012). This is regarding the issue of their drinking water sources did not meet the requirement due to the pollution of a large portion of surface water and groundwater. Since 2007, membrane processes for drinking water treatment in China increases significantly to the large scale of membrane plants and until now, UF is applied with total capacity of 300,000 m³ per day.

Another latest membrane plant is AQUAPOT which is applied in different locations of Ecuador and Mozambique to increase the drinking water production for human consumption and also for industrial use (Garcia-Fayos *et al.*, 2013). After

several years of research and study, most of the installed plants work successfully producing quality drinking water and even providing water supply for industrial use.

2.2 Integrated membrane system

The application of membrane processes has been recognized due to the advantages offered compared to the conventional mass transfer process. Membranebased hybrid processes have been significantly developed to overcome the limitations when using membrane process alone. The current innovation has definitely improved the productivity of the separation processes.

2.2.1 Hybrid membrane processes

Hybrid membrane process is classified into two categories, the membraneconventional hybrid process and membrane-membrane hybrid process. As for the membrane-conventional hybrid process, a conventional separation process is modified using a membrane process. This combination can reduce the lower capital cost or while maintaining the cost, higher productivity can be achieved. In the second category, the integration of a membrane process and another membrane processes may overcome the problems occur during single membrane process is applied (Suk *et al.*, 2006).

Many conventional separation processes have been applied for a long time and membrane process is now integrated with the conventional process with improved productivity and better quality. One hybrid membrane process has been studied which combines ozonation and microfiltration to improve the permeate quality for surface water treatment (Zouboulis et al., 2014). As for drinking water treatment, hybrid membrane process was also studied for integration with activated carbon as shown in Figure 2.1.



Figure 2.2: Schematic diagram of a hybrid membrane process with integrated activated carbon treatment (Stoquart et al., 2012)

On the other hand, membrane filtration also combined with coagulation for a hybrid process which produced a high quality of drinking water and meet the requirement of WHO (Zularisam et al., 2009).

2.2.2 Pre-treatment process

The pre-treatment process has become an important stage prior to any membrane filtration where foulants which are mainly particles and natural organic matters are removed from the raw water feed during pre-treatment process. Previous studies have proven that pre-treatment process improved the quality of the final product and secured the membrane system (Liang *et al.*, 2008; Dong *et al.*, 2007a). Thus, various types of pre-treatment process are studied recently (Kim *et al.*, 2002).

However, among all the pre-treatment processes, coagulation, ozonation and activated carbon adsorption have been the most familiar application in membrane filtration system. Coagulation is a well-known conventional process and has been chosen due to the lower cost and easy handling. Several researchers have also studied on coagulation pre-treatment (Choi and Dempsey, 2004; Leiknes *et al.*, 2004; Judd and Hillis, 2001; Pikkerainen *et al.*, 2004; Oh and Lee, 2005).

Another effective technology in controlling membrane fouling in water treatment is activated carbon adsorption which is mainly divided into two types namely powder activated carbon and granular activated carbon. Powder activated carbon (PAC) is found out to improve the filtration flux and decrease membrane resistance as studied by Dong *et al.*, (2007b). This is because of the adsorption of PAC to the macromolecular organics and other pollutants thus improving membrane fouling potential. Other researchers also applied PAC as the pre-treatment process on their studies (Tomaszewska and Mozia, 2002; Mozia *et al.*, 2005; Klomfas and Konieczny, 2004). On the other hand, higher initial flux can be achieved using the integrated granular activated carbon (GAC) pre-treatment with membrane filtration yet the membrane fouling can also be decreased (Da Silva *et al.*, 2012).

2.2.3 Post-treatment process

For certain treatment system, post-treatment stage is added to produce ultrapure water by removing trace levels if any residual contaminants present mostly bacteria and viruses. As for drinking water treatment, chlorination has been concluded as the most widely used as the post-treatment process for pathogens disinfection (Li et al., 2002). Stoquart *et al.* (2012) reviewed that granular activated carbon may also be a post-treatment method in the hybrid membrane processes. In Thailand, a hybrid membrane process combined ozonation, membrane filtration and followed by activated carbon filtration has been studied for drinking and service water (Sartor et al., 2008). However, it comes with more disadvantages where the foot print will be increased due to increasing unit processes. In addition, post-treatment can also be enhanced by the addition of ultraviolet (UV) radiation or other features to suit specific circumstances.

2.3 Membrane fouling

Membrane fouling can be defined as the process resulting in loss of performance of a membrane due to deposition of suspended or dissolved particles on the membrane surface, at its pore opening or within the pores. As a result, membrane materials will be affected thus decreased the membrane performance in term of flux decline.

Flux decline is the decrease of permeate volume produced through a membrane as a function of time. This decline is caused by several phenomena during the filtration process. This flux decline related to the pure water flux, can be small for relatively clean feed in ultrafiltration (UF), nanofiltration (NF) or reverse osmosis (RO), but can also be more than 90% especially in more open filtration processes like microfiltration (MF). Typically, flux decline is caused by a decreasing driving force and increased resistance. The main difference between the types of fouling (colloidal fouling, organic fouling, scaling and biofouling) is the nature of the particles that cause the fouling. The difference between types of fouling is made because each type of foulant has an effect on membrane performance and also has its own type of counter measures. In addition, fouling can be divided into reversible and irreversible fouling based on the attachment strength of particles to the membrane surface. Reversible fouling can be removed by backwashing. Formation of a strong matrix of fouling layer with the solute during continuous filtration process will result in reversible fouling being transformed into irreversible fouling layer (Ahmad et al., 2012). Irreversible fouling is normally caused by strong attachment of particles, which is impossible to be removed by physical cleaning. This causes a higher energy use, a higher cleaning frequency and a shorter life span of the membrane.

2.3.1 Type of membrane fouling

Membrane fouling is caused by the deposition of suspended or dissolved solids on the external membrane surface, on the membrane pores or within the membrane pores. Inorganic, biological foulants, suspended solids, colloids, metal oxides and organics are the main species in the feed that contribute to membrane fouling. They are four types of membrane fouling which are inorganic fouling/scaling, particle/colloids fouling, microbial fouling and organic fouling.

Inorganic fouling or scaling is caused by the accumulation of inorganic precipitates such as metal hydroxides and scales on the membrane surface or within pore structure. Precipitates are formed when the concentration of chemical species exceeding their saturation concentration. Scaling is a major concern for reverse osmosis (RO) and nanofiltration (NF) because RO and NF membranes reject inorganic species. For UF and MF, inorganic fouling due to concentration polarization is much less profound but can exist most likely due to interactions between ions and other fouling materials through chemical bonding. Some pretreatment processes for membrane filtration such as coagulation and oxidation which are not designed or operated properly may introduce metal hydroxides on membrane surface or within pore structures. Inorganic fouling or scaling can be a significant problem for make-up water of caustic solutions prepared for chemical cleaning.

Algae, bacteria and certain natural organic matters are contributed to particulate and colloidal fouling. However the differences are from inert particles and colloids like silts and clays. Particles and colloids are referred to biologically inert particles and colloids that are inorganic in nature and are originated from weathering of rocks. They do not really foul the membrane because the flux decline caused by their accumulation on the membrane surface is largely reversible by hydraulic cleaning. Colloidal fouling has given an impact on trace organic contaminant rejection by forward osmosis as mentioned by Xie *et al.* (2014).

Biological fouling is a result of formation of biofilms on membrane surfaces. Once bacteria attach to the membrane, they start to multiply and produce extracellular polymeric substances to form a viscous, slimy, hydrated gel. Severity of biological fouling is greatly related to the characteristics of the feed water.

Organic fouling is found in membrane filtration with source water containing relatively high NOM. Surface water typically contains higher NOM than groundwater, with exceptions. For source water high in NOM, organic fouling is believed to be the most significant factor contributed to flux decline. Yamamura *et al.* (2014) found that hydrophilic fraction of NOM causing the irreversible fouling for MF and UF.

2.3.2 Membrane foulant

From previous studies on water treatment, NOM was found as the main membrane foulant (Margarida *et al.*, 2010; Jermann *et al.*, 2008; Nohwa *et al.*, 2004; Nohwa *et al.*, 2006). NOM refers to a group of carbon-based compounds that are found in surface water and some groundwater supplies which come from various decomposition and reactions in the water supply and its surrounding watershed. Generally NOM is composed of hydrophobic and hydrophilic organic substances exist in raw water (Lin *et al.*, 2014). Common NOM compounds are including proteins, polysaccharides and humic substances. NOM may affect an aesthetically undesirable colour, taste and odour in water but may not bring an adverse effects to human health. However, some NOM compounds are known to react with chlorine and chloramines during the treatment process to produce disinfection by-products (DBPs) such as trihalomethanes (THMs) and haloacetic acids (HAA) that are thought to be carcinogenic or genotoxic.

In most water supplies, majority NOM exists as dissolved compounds and often measured as dissolved organic carbon (DOC) while some NOM occurs as particulate matter or is adsorbed to particulate. NOM compounds are commonly accepted with those light-absorbing chemical structures such as aromatic rings. These structures are known to absorb UV light at specific wavelengths including 254nm thus it is also common to quantify NOM by measuring the amount of UV light it absorbs (UV_{254}) .