MIXED MATRIX POLYSULFONE MEMBRANE ENTRAPPED WITH SILICON DIOXIDE AND POLYVINYLPYRROLIDONE FOR OIL EMULSION REMOVAL

by

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Thesis submitted in fulfillment of the

requirements for the degree of

Master in Science

JANUARY 2014

ACKNOWLEDGEMENT

In the name of Allah, the Most Beneficent and the Most Merciful. Alhamdulillah, all praises to Allah the Almighty for giving me strength and patience to complete my research project and dissertation.

Firstly and foremost, I would like to express my sincere appreciation to my main supervisor Prof. Dr Abdul Latif bin Ahmad for his encouragement, guidance, trust, critics, and ideas in finishing my thesis. Big thanks to my assistance supervisor Dr. Ooi Boon Seng for the collaboration and helpful guidelines.

As my enrolment from 2011 to 2014, I would like to express my appreciation to the Dean; Prof Dr. Azlina Harun @ Kamaruddin, Deputy Dean of Research and Graduate Studies; Assoc. Prof. Dr. Ahmad Zuhairi bin Abdullah, all lectures, technicians and staffs of School Chemical Engineering, Universiti Sains Malaysia (USM). I am thankful for their cooperation and assistance especially in formalities matters.

Then, I would like to give thanks to Institute Postgraduate Studies (IPS) and USM Membrane Cluster for the awarded scholarship. In addition to that, I would like to thank to my valuable friends and colleagues; Farah, Mira, Ogy, Wani, Afrizal, Ayshah, Kak Dayah, Kak Anis, Kak Zaika, Kak Azi, and Abang Jami for rendering their help, kindness and moral support toward me.

My special thanks and dedication to my lovely husband, Abdul Fattah bin Haji Ismail, my lovely father, Hussain bin Shaikh Omar, and to my lovely mother, Nazli bt Abu Bakar, for their moral supports, patience and financial supports during the study. And not forgetting to my in law’s family. I might not be able to achieve what I want to be without the support from all.

Kharulnisa Nadiah bt Hussain,

January 2014

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LIST OF ABBREVIATIONS

AFM	Atomic Force Microscopic
Ag	Silver
$Al(OH)_3$	Aluminium hydroxide
$Al_2(SO_4)_3$	Aluminium sulphate
Al_2O_3	Aluminium oxide
$AlCl_3$	Aluminium chloride
ANOVA	Analysis of variance
ATR-FTIR	Attenuated Total Reflectance – Fourier Transform Infrared
$CaCl_2$	Calcium chloride
CCD	Central composite design
CF	Compaction factor
CPVP	Chlorinated polyvinyl chloride
DOE	Design of experiment
DMAc	N-N- Dimethylacetamide
DR	Decay ratio
EQA	Environmental Quality Act
FESEM	Field Emission Scanning Electron Microscopy
FTIR	Fourier Transform Infrared
FRR	Flux recovery ratio
IR	Infrared
MD	Membrane distillation
MF	Microfiltration
MMMs	Mixed matrix membranes
MWCO	Molecular weight cut off
NF	Nanofiltration
NIPS	Non solvent induce phase separation
NTU	Nephelometric Turbidity Units
P	Probability
PEG	Poly(ethylene glycol)

PES	Polyether sulfone
PSf	Polysulfone
PVA	Poly (vinyl alcohol)
PVDF	Poly(vinylidene fluoride)
PVP	Polyvinylpyrrolidone
PW	Permeation water
PWF	Pure water flux
R	Rejection
R^2	Correlation factor
RFR	Relative flux reduction
RO	Reverse osmosis
RSM	Response surface methodology
SiO_2	Silicon dioxide
S/N	Signal-to-noise
TiO_2	Titanium dioxide
ZnO	Zinc oxide
ZnSe	Zinc-selenium

LIST OF SYMBOLS

A	Membrane area
C_o	The initial concentration of oil in water emulsion
C_p	The oil concentration in the permeate
J	Membrane permeation flux
J_p	Oil flux
J_{pure}	Pure water flux
$J_{permeate}$	Permeation flux
J_{wash}	Pure water flux after washing
J_{w1}	Permeate water flux
J_{w2}	Permeate water flux at cleaning condition
kV	kiloVolt
m_n	Mass of absorbed water
m_p	Mass of the dry membrane
r	Membrane pore radius
V	Volume of permeate water
Δt	Time taken for permeate collected
ΔP	Pressure differential
α	Alpha value
ε	Porosity
ρ_n	Density of water
ρ_p	Density of PSf
θ	Wetting angle
γ	Surface tension of wetting liquid
R_p	The peak to valley of the line
R_q	Root mean square roughness
R_a	Roughness average

MATRIX POLYSULFON MEMBRAN CAMPURAN TERPERANGKAP DENGAN SILICON DIOKSIDA DAN POLYVINYLPYRROLIDONE UNTUK PENYINGKIRAN EMULSI MINYAK

ABSTRAK

Membran telah diketahui secara meluas untuk merawat air beremulsi. Teknologi membran yang baru telah direka untuk mengatasi fenomena hidrofobik yang sering berlaku semasa penapisan minyak beremulsi. Dalam kajian ini, polysulfone (PSf) telah di fabrikasi bersama zarah nano silikon dioksida (SiO_2) untuk mengubahsuai mofologi membran dan polyvinylpyrrolidone (PVP) ditambahkan untuk mengelakan pergumpalan dan mengekalkan kestabilan SiO_2 pada permuka membran melalui kaedah fasa penyongsangan. Tujuan kajian ini di jalankan adalah untuk menghasilkan membran yang boleh menghasilkan fluks dan kecekapan penolakan yang tinggi dengan memanipulasikan beberapa faktor. Pada peringkat awal, kajian menunjukkan bahawa setiap faktor memberi impak kepada fizikal membran seperti saiz liang dan taburannya, morfologi membran dan UF fluks. Oleh itu, kajian ini di teruskan untuk mengkaji hubungkait bagi setiap faktor dan respon, sekali gus mengoptimumkan nilai faktor dengan menggunakan Kaedah Gerak Balas Permukaan (RSM) di tambah dengan pusat rekabentuk komposit (CCD). Setiap kepekatan faktor telah di variasikan dari 13 kepada 17 wt.% bagi PSf, 1 kepada 3 g bagi SiO_2/100 g jumlah rumusan, dan 2 kepada 4 g bagi PVP/100 g jumlah rumusan. Kepekatan bagi PSf dan PVP didapati memberikan kesan yang tinggi kepada fluks air tulen dan fluxs air tulen selepas cuci. Sementara itu, kepekatan bagi SiO_2 memberi kesan yang tinggi kepada penyerapan fluks. Model yang diperolehi daripada ANOVA bagi setiap respon adalah boleh dipercayai dan telah disahkan apabila peratusan bagi prestasi ramalan dan eksperimen adalah 2.56% bagi fluks air

tulen, 7.40% bagi penyerepan fluks dan 0.30% bagi fluks air tulen selepas di cuci. Faktor yang memberi nilai yang optimum berdasarkan jumlah fluks yang tinggi adalah pada kepekatan PSf = 17 wt.%, SiO_2 = 1 g and PVP = 2 g yang menghasilkan fluks yang tertinggi iaitu fluks air tulen (83.22 ± 1.56 L/m^2h), penyerapan fluks (2.75 ± 1.78 L/m^2h) dan fluks air tulen selapas cuci (66.12 ± 1.06 L/m^2h). Jangka hayat bagi membran yang optimum telah dinilai berdasarkan empat kali penapisan bagi menentukan kebolehan penggunaan semula membran. Keputusan telah menunjukkan bahawa membran yang optimum mampu mengekalkan fluks sebanyak 17.72 L/m^2h selepas empat kali penapisan, di mana ia membuktikan bahawa membran ini mempunyai sifat pemulihan fluks. Sementara itu, membran ini mampu mengekalkan flux bg air tulen selepas cuci sebanyak 25.06 L/m^2h. Ia membuktikan bahawa optimum membrane ini boleh di guna pakai berulang kali dan dapat mengurangkan kos operasi.

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MIXED MATRIX POLYSULFONE MEMBRANE ENTRAPPED WITH SILICON DIOXIDE AND POLYVINYLPYRROIDONE FOR OIL EMULSION REMOVAL

ABSTRACT

Membranes have been known widely to treat emulsified water. New membrane technology has been fabricated to overcome hydrophobic phenomenon that occurred during separation of oil emulsion. In this study, polysulfone (PSf) membranes were fabricated with silicon dioxide (SiO_2) nanoparticles to modify the membrane morphology and polyvinylpyrrolidone (PVP) is added to avoid agglomeration as well as to maintain the stability of SiO_2 on membrane's surface via phase inversion. The aim for this research is to determine the membrane that could produce high flux and high rejection efficiency by manipulating several parameters such as concentration of PSf, SiO_2 and PVP. As preliminary study, the result shows that each of the parameter affects the membrane physical characteristic such as pore size and distribution, membrane morphology and UF flux. Therefore, further studies have been done to investigate the relationship between each parameters and desired response, thus optimize the parameters by using response surface methodology (RSM) coupled with central composite design (CCD). The parameters has been varied from 13 to 17 wt.% of PSf, 1 to 3 g of SiO_2/100 g of casting solution and 2 to 4 g of PVP/100 g of casting solution concentration respectively. It is found that PSf and PVP concentration have the greatest effect on pure water flux and pure water flux after washing. Meanwhile, concentration of SiO_2 greatly affect on the permeation flux. Model obtained from ANOVA analysis for each of the response was reliable and validated since the percentage of predicted and experimental performance was 2.56% for pure water flux (PWF), 7.40% for permeation flux (PF)

and 0.30% for pure water flux after washing. The optimum synthesis parameters that analysed by RSM based on higher fluxes was PSf = 17 wt.%, SiO_2 = 1 g and PVP = 2 g which exhibits highest permeation flux (83.22 ± 1.56 L/m^2h), permeation flux (2.75 ± 1.78 L/m^2h) and pure water flux after washing (66.12 ± 1.06 L/m^2h), respectively. The optimum membrane was also evaluated in terms of long-term UF with four runs to determine the reused property. The result shows the oil emulsion solution flux of the optimum membrane retained at 17.72 L/m^2h after four runs, which proves a satisfactory flux recovery property. Meanwhile, the pure water flux after washing was retained at 25.06 L/m^2h. It reveals that the optimum membrane can be reused for few times and can reduce operational cost.

CHAPTER ONE

INTRODUCTION

1.1 General

1.1.1 Introduction of membrane

Every year, there is new separation technology have been developed to be applied in various industries. Currently, membrane technology is one of the advanced separation technology has been identified to have more advantages compared to conventional separation technology (Judd, 2010). This technology keeps on improving from time to time to gain higher efficiency to be more economical and affordable.

The evolution of membrane technology started in 1960 (So *et al*., 1973). Generally, membrane technology was developed to compete among other conventional separation processes such as water desalting, water purification and gas separation. Not only that, membrane technology also widely being used for the medical treatment (Clara *et al*., 2005). Until now, researchers work hard to improve the quality of the membrane.

In the past 30 years, membrane process has been introduced to replace conventional separation processes such as crystallization, extraction, adsorption, and distillation (Baker, 2012). Most of industries in Malaysia produce a large amount of chemicals and components which need separation, concentration and purification processes. Besides that, these industries also generate a wide variety of toxic industrial waste which needs to have special treatment before discharging to a public sewer. Wastewater treatment using membrane technology could reduce for few treatment processes manually especially while using chemicals and also give better performance (El-Kayar *et al.*, 1993). UF is a useful process to treat wastewater and could extend the useful life of the washed water and reducing the waste disposal problem.

The membrane has been used mostly for engineering and environment protection. There are so many important factors need to be considered to develop the membrane. Better selection of materials will affect the effectiveness of the membrane (Ren and Li, 2012).

1.1.2 Membrane based oil emulsion removal

As we know, membrane is able to separate different size of particles as shown in Table 1.1. There are few conventional processes to remove oily wastewater/emulsion such as flocculation and coagulation, electrochemical, distillation and adsorption. According to El-Kayar *et al.*, (1993) free floating oil or unstable oil in water emulsion which higher than 50 µm in size can be separated by using conventional process such as skimming and coagulation. For oily wastewater which is less than 50 µm in size is known as stable oil in water emulsion. This particular wastewater cannot be separated efficiently using conventional methods. This is because the micron and submicron emulsion droplet size requires a very long residence time to rise to the top to facilitate gravity separation to occur. Furthermore, the addition of chemicals also cannot break the emulsion effectively (Lonsdale, 1982).

Table 1.1: Membrane processes (Beerlage, 1994).

Process	Pore size (nm)	Materials retained	Materials passed	Pressure (bar)
Microfiltration (MF)	> 50	Particles (bacteria, yeasts, etc.)	Water, salts, macromolecules	< 2
Ultrafiltration (UF)	1-100	Macromolecules, colloids, lattices solutes MW >10,000	Water, salts, sugars	1-10
Nanofiltration (NF)	~ 1	Solutes MW > 500, di- and multivalent ions	Water, sugars, monovalent ions	5-20
Reverse osmosis	Not relevant	All dissolved and suspended solutes (sugar, salts)	Water	15-80

Membrane process is important nowadays compared to other separation methods due to low energy consumption, easy to scale-up, less use of hazardous chemicals and no production of harmful byproducts (Arthanareeswaran *et al*., 2008). Generally, ultrafiltration (UF) membrane is the most commonly used to separate oil emulsion. Maximum total oil and grease concentration discharged after being treated using UF membrane meets the requirement of environmental regulations which is in the range of 10-15 mg/L, (Mueller *et al*., 1997) .

It has been shown that membrane-based separation process promising a good performance compared to other established conventional separation processes. However, the important factor that needs to take into consideration is the material selection which high quality of separation can be achieved. A good material can lead to high permeability and high rejection. In this case, asymmetric membrane is suitable to compensate a low permeate flux. The asymmetric membrane can be prepared by phase inversion in which the membrane dope solution will immerse in the non solvent (Aroon *et al*., 2010b).

As time goes by, membrane become important and the trend shows the demand is increasing compared to other separation technologies separation due to their superior properties (Li *et al*., 2011). The selection of polymers will affect the outstanding properties of the membrane. These polymers do not only have to resist acid and bases, oxidants or reductants, high pressure and high temperature, but also requires to be a good chemical stability that leads to high flux and high selectivity for the applications (Yang *et al*., 2007).

1.1.3 Advantages of membrane technology

Membrane technology becomes important in process engineering operations. There are certain materials naturally difficult to be separated and requires an additional treatment process to be separated (Li *et al*., 2011). If separation was based on size of substances, therefore, membrane technology can promise and offer a better alternative way compared to the other conventional processes such as adsorption, distillation, extraction, leaching and absorption. Thus, membrane technology becomes important and highly demands in most of the industries. They offer a number of significant advantages and attractive properties in order to surpass the other technologies.

Membrane process becomes attractive and important in all industries due to its flexibility and reliable performance. The efficiency using membrane is much better compared to other conventional processes because it provides a boundary for selected materials that can pass through it (Noble and Stern, 1995). Besides that, polymeric membranes are economical suite and the production processes are relatively cheap (Mulder, 1996). In short, less energy required for membrane operation compared to conventional method, thus reduce the operating cost of the process with better performance to protect the environment.

According to previous studies (Lee *et al*., 2001, Savage and Diallo, 2005), membrane provides higher efficiency performance for water after discharged. The structure of the membrane is the major factor contributing to the production of pure water. MF and UF are the processes commonly used for clarification and disinfection because the sizes of its pore are suitable to filter particulate materials and macromolecules as shown in Table 1.1. The process is not only faster in operation, however it ensures safety to be in place because they contain less toxic and it is less time consuming (Chakrabarty *et al*., 2008).

Membrane technology requires low capital investment since the processes and the chemicals involved are relatively less. Not only that, the operation using membrane also can save the cost because less energy consumption as compared to other methods such as distillation, extraction, crystallization and absorption. Furthermore, membrane provides higher efficiency toward separation process. These advantages of the membrane lead to higher demand in all industries (Ismail and Lai, 2004).

1.2 Problem statement

Every year, huge volume of oily wastewater is produced from various activities including extraction, hydrocarbons, food processing, and transportations, textiles and refining (Cheryan and Rajagopalan, 1998). Oil emulsion is generated from oily wastewater and it is exists as stable phase. The efficiency to remove oil from oil emulsion is depends on miscibility or a floating film of the oil at the top of water phase that needs to be removed before it is discharged (He and Jiang, 2008). This is because the degradation rate of oil is slow and it will hinder the oxygenation process of surface water and prevents the penetration of sunlight underneath the water.

Membrane fouling always is the main obstacle for wider implementation of UF, which usually causes rapid declination of flux (Tay and Song, 2005). As a result of membrane fouling, membrane resistance increases with time due to accumulation of foulants on membrane surface and / or inside the membrane. The main consequences of fouling are flux decline, permeate quality deterioration and energy consumption increase. Since operating costs of UF highly depend on membrane useful life, fouling control is essential for increasing membrane operational life thus reducing economics of the process. Therefore, a good membrane that can provide high recovery properties is needed to extend membrane life span as well as to increase membrane permeate flux.

Researchers have come out with the advanced membrane-based separation and it becomes a promising technology for the 21st century. This method relies on pore size of the membrane to separate undesired constituents in waste water (Sonune and Ghate, 2004). The advantage of membrane system is it can compete with more complex treatment such as treating water with high oil content, low mean particle size and high flow rates. He and Jiang (2008) stated that UF is one of the most effective methods to remove oil emulsion in comparison with the conventional methods such as physical and chemical treatment. This is because it produces high oil removal efficiency, no additional chemical required, low energy consumption and small space requirement (Cheryan and Rajagopalan, 1998).

Unfortunately, the chemical nature of the membrane has a major effect on the flux. Most of the research claimed that in order to obtain high flux, polymeric membrane should be hydrophilic in nature (Fane and Fell, 1987). It is a fact that hydrophobic membrane resulting to low flux, while hydrophilic membrane provides high flux. This is because the hydrophilic membrane is preferable to attract water rather than the oil (Cheryan and Rajagopalan, 1998). The important things to determine the quality of discharge water is depending on the rejection efficiency of the membrane. The pore size of the membrane as well as pore in the membrane sublayer play a major role to remove oil emulsion and allowing water pass through it. Maximous *et al*., (2009) stated in their report that high flux provides less fouling.

There are a lot of polymers that being investigated by researchers that can offer favorable properties for membrane matrix. Polysulfone (PSf) is one of the polymers that have good characteristics and can form such asymmetric membrane. It's a low cost polymer, superior film forming ability, good mechanical and anti-compaction properties, strong chemical and thermal stabilities as well as outstanding acidic and alkaline resistance (Yang *et al.,* 2007). However, PSf is hydrophobic in nature that leads to the poor performance of membrane permeability. Due to this many researchers has come out with a new invention to produce high quality membranes. In this current study, the hydrophobic polymeric has been modified to be hydrophilic membrane by the introduction of few additives such as silicon dioxide (SiO_2) nanoparticles and polyvinylpyrrolidone (PVP).

There are a few types of polymers that can be chosen as the matrix. Some of that were modified with the addition of surfactants and inorganic particles in order to raise the properties and performance of the membranes. Yan *et al.,* (2005) has studied the effect of nano-size alumina oxide (Al_2O_3) incorporated in polyvinylidene fluoride (PVDF) to investigate the membrane properties. Other than that, Yang *et al.*, (2007) used titanium dioxide (TiO_2) mixed together in the PSf solution to determine membrane performance. Both of them claimed that the addition of inorganic particles to the dope solution increased the water permeability of a membrane by increasing pore number and pore distribution as well as good antifouling ability.

It is believed that by inserting inorganic materials such as TiO_2 (Yang *et al.*, 2007), SiO_2 (Ahn *et al.*, 2008) and Al_2O_3 (Yan *et al.*, 2005) will decrease the contact angle thus increase the hydrophilicity of the membrane. In general, a small contact angle corresponds to more hydrophilic material. Hydrophilic materials are less sensitive to adsorption compared to hydrophobic so it considered to be able to reduce the fouling resistance.

Among the numerous inorganic materials, SiO_2 nanoparticles are the most convenient and often used due to its mild reactivity and known chemical properties (Yu *et al.,* 2009). The modification of SiO_2 in PSf polymer can enhance the membrane properties (Arthanareeswaran *et al.,* 2008, Yu *et al.,* 2009). However, higher concentration of SiO_2 often results in agglomeration, leading to reduction of membrane permeability as well as reducing antifouling properties. Therefore, the introduction of polyvinylpyrrolidone (PVP) could overcome the agglomeration phenomenon on the membrane surface due to its superior characteristics such as amphipilic, good water solubility and crosslinkable (Al Malek *et al*., 2012). In order to form good membrane with superior properties, it is necessary to optimize the membrane synthesis parameters such as membrane casting thickness, PSf concentration, SiO_2 concentration, and PVP concentration. The modification of polymer membrane with additives could enhance membrane permeability as well as improve antifouling properties.

1.3 Research overview

There are lots of researches have been done by blending inorganic materials with polymer based membrane (Zularisam *et al*., 2011). Polysulfone (PSf) based membrane itself have higher ranking research in the separation process. These membranes keep improving in terms of method, characterization and performance.

In this research, PSf has been blended with SiO_2 nanoparticles to improve membrane hydrophilicity and to increase antifouling property of the membrane. The membrane was fabricated via phase inversion method to form an asymmetric membrane. Asymmetric membrane is useful for removing oil in water emulsion because of the oil droplet itself is deformable (Xu *et al*., 1999). The addition of PVP forms a porous sublayer membrane allowing water pass through the membrane easily. Research investigations were carried out to find the best membrane that could give a higher permeate flux and high oil rejection (Cheryan and Rajagopalan, 1998, Arthanareeswaran *et al.*, 2008, Balta *et al.*, 2012).

The concentration of PSf, PVP, SiO_2 and solvents are estimated using Response Surface Methodology (RSM) in order to estimate the optimization of membrane performance. In this project, N, N-Dimethylacetamide (DMAc) is used as a solvent. It is colorless and high boiling polar solvent. DMAc is a good solvent for a wide range of inorganic and organic materials and it is miscible with water and other hydrocarbon compounds. DMAc also a stable compound because it is stable in the absence of water, acids and bases at temperatures up to boiling point at atmospheric pressure.

PSf, SiO_2 and PVP were dissolved in DMAc and had been cast using phase inversion method. The dope solution was fabricated on a tightly polyester as supporter to support a light membrane. After membrane has been fabricated, the characterization of membrane is done to analyse contact angle, pore distribution and UF filtration performance by constantly maintain the temperature and pressure during operation to ensure consistency.

1.4 Objectives

The objectives for this research area are:

1. To synthesize and characterize the PSf/SiO_2/PVP mixed matrix membrane.
2. To obtain the optimum membrane synthesis parameters such membrane casting thickness, PSf concentration, SiO_2 concentration, and PVP concentration as well as evaluate membrane based on total fluxes.
3. To study the performance of optimized PSf/SiO_2/PVP mixed matrix membrane.

1.5 Organization of thesis

This thesis covered few chapters which include the introduction, literature review, materials and methods, results and discussion and finally the important significant finding were concluded in the last chapters.

Chapter one outlined the overview of the membrane technology and its application in industries. The general of membrane process has been summarized according to the types of the membrane. Based on the technological development of membrane based oil emulsion separation, problem statement was highlighted to address the issue regarding the limitation of PSf hydrophobic in the filtration process and few suggestions to overcome the problem. It was then followed by the objectives which clearly stated out the purpose of this research project. Finally, the organization of the thesis provided the highlighted content for each chapter.

Chapter two represents the review of various research works reported in other literature under the same area. Initially, the selection of membrane has been studied. It followed by the study through review for oil emulsion removal. The comparison between advance separation method and conventional method has been done to obtain highest effectiveness method. The studies of polymeric UF membrane materials, chemistry and morphology including the polymer concentration and additive concentration were reviewed and highlighted. Recent technology to produce mixed matrix membrane including polymer-inorganic nanoparticles with their unique properties and performance were also outlined and discussed. At the end of this chapter, the development of UF membrane from previous studied was discussed.

Chapter three covers the experimental materials and procedures. The laboratory scale of membrane synthesis, characterization and performance were discussed. The overview of the experimental work done was summarized in a flow chart. Details of the procedure information were reported at this section. All the equipments used for characterization were described. The equations for data analysis were also provided.

Chapter four represents all the experimental results obtain throughout the project. This chapter is divided into 4 sections. In the first section, the characterization of oil emulsion has been reported in terms of its size oil droplet and oil concentration calibration. Second section focused on the effect of membrane synthesis parameters on the membrane morphology and UF performance. The optimization of membrane synthesis parameters was done using RSM to obtain higher response, consist of total pure water flux, permeation flux and pure water flux after washing was reported in section three. The last section reported on the performance of optimum membrane in order to investigate the recycling property after a few runs.

Finally, chapter fives reported the conclusion of the experiment and some recommendations that can be used for future research. The conclusion was based on the outline objectives and some recommendations for the future related research were provided.

CHAPTER TWO

LITERATURE REVIEW

2.1 Membrane definition

In the past few decades, membrane separation has become one of the established separation technologies to replace conventional separation method. The membrane is defined as a semipermeable barrier (boundary), used to separate a mixture of two components in feed side, and allowed the selective component of the feed pass through it (Wee *et al.*, 2008). The components that passed through membrane are driven by force or transmembrane pressure which allows mass transfer to occur across the membrane. The component that penetrated into the membrane is known as permeate. Membrane technology is applied for water separation, purification, and gas separation. Figure 2.1 shows the mechanism for membrane separation.

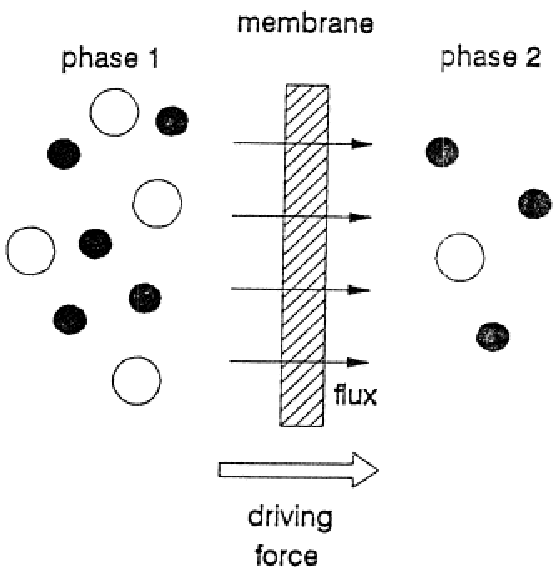

Figure 2.1: Mechanism for membrane separation (Wee *et al.*, 2008).

There are different types of membranes used in separation process, consist of polymeric membrane, inorganic membrane and ceramic membrane. The objective is the same, which is used to separate unwanted molecule and allow the other molecule pass through the membrane by manipulating driving forces to obtain optimum efficiency. These types of membranes could be applied for different range of separation such as MF, UF, reverse osmosis (RO), pervaporation, membrane distillation (MD) and also for medical purpose.

2.1.1 Polymeric membranes

Polymeric membranes are the most commonly used in industry. This is because it is relatively economical to fabricate. Polymer materials that are often being used as a matrix based are poly(vinyl alcohol) (PVA) (Gimenes *et al*., 2007), poly(vinylidene difluoride) (PVDF) (Kuo *et al*., 2008), poly(acrylic acid), polyurethane, chitosan (Kanti *et al*., 2004), and cellulose acetate (Chen *et al*., 2009b). Polymeric membranes have a superior characteristic resulted for good water-permselectivity and high permeation flux (Liu *et al*., (2007). This is due to the formation of crosslinked of the polymer during formation of the membrane.

2.1.2 Inorganic membranes

Inorganic membranes (ceramic membranes) normally made from silica, alumina or zeolite has high solvent-resistant properties, and high temperature stability and swelling free (Li *et al*., (2007). These membranes can be used in many applications as it provides high selectivity and permeability. This is because the inorganic particles itself own superior characteristic. Asaeda *et al*., (2001) stated that the porous silica membrane is preferable to obtain high flux on gas permeation but not stable for water. This is because foulants will have higher tendency to clog on the porous structure, thus produce concentration polarization. While, zeolites have unique physical characteristics consists of good pore structure, adsorption properties and their mechanical, chemical and biological stability. It is very useful in the pervaporation applications and gas separation.

2.1.3 Composite membrane

A novel membrane technology that has been developed for industrial usage is the composite membrane. It was prepared by fabricating hydrophilic polymer on porous substrates (Liu *et al*., 2007). The formation of organic-inorganic membrane should achieve membrane stabilization in terms of thermal, chemical and mechanical properties. The porous substrate provides good mechanical support, while crosslinked with hydrophilic polymer membrane significantly suppress excessive swelling of membranes in order to retain high selectivity (Gimenes *et al*., 2007).

2.2 Membrane classification

Membrane can be classified into two categories which are asymmetric and symmetric. Both of them might composed by the same structure which is porous. But, the difference in the behavior of symmetric and asymmetric stacks could be observed on membrane bi-layer systems. The diameter of pores is constant throughout the cross section of the membrane. Meanwhile, an asymmetric membrane has different in pore size starting from the surface until underneath the membrane. Figure 2.2 summarizes the structure exhibits from both of the membranes.

Membrane classification

Symmetrical

- Homogeneous (dense)
- Cylindrical porous
- Porous

Asymmetrical

- Porous
- Porous with dense top layer
- Composite

Figure 2.2: Summarize of membrane classifications (Ismail *et al*., 2002)

2.2.1 Asymmetric structure

Asymmetric membrane is characterized by a non-uniform structure consist of an active top layer or skin supported by a porous sublayer. The formation of asymmetric membrane can be produced by phase inversion process. It involves the process where the polymer in casting solution undergo transition phase from stable phase to unstable phase, consequently causes polymer to precipitate (Scott, 1996). Figure 2.2 shows the structure of asymmetric structure.

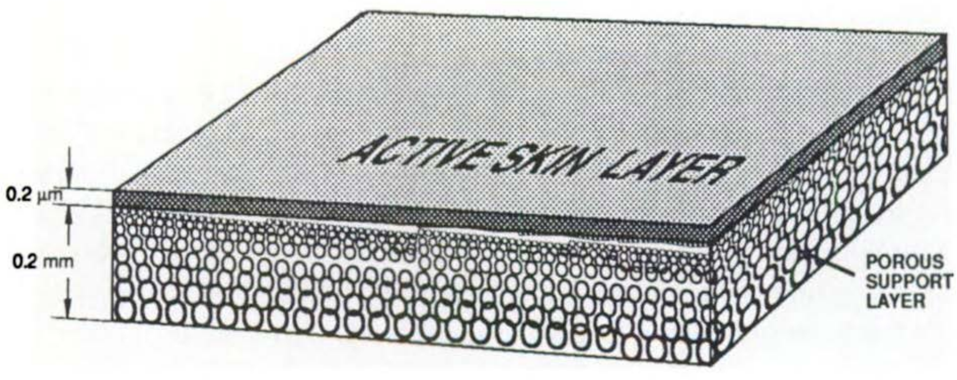

Figure 2.3: Asymmetric membrane structure (Scott, 1996).

Phase inversion induces porous structure in the membrane which is formed from precipitation of a homogeneous polymer solution. This method also can produce microporous symmetric membrane (Scott, 1996). In order to obtain maximum yield of permeability, an active skin layer must be defect-free in order to control only solution/diffusion mechanism. The thickness of skin layer must be as thin as possible in order to improve the permeability. Chung *et al*., (2000) stated that defective skin layer will be produced by a complex mass transfer during exchange of solvent leaves out from the casting solution.

2.2.2 Symmetric structure

Although most of the membranes are asymmetric, some of them might have symmetric structure. The symmetric structure is characterized by a uniform structure, which can be produced by one of the following methods as can be seen in Table 2.1.

Table 2.1: Methods of symmetric structure formation and its applications (Hughes, 1996).

Methods	Application
Sintering or stretching	For manufacture of microporous membranes
Casting	For the manufacture of ion-exchange membranes and membranes for pervaporation
Phase inversion and etching	The manufactured materials function as pore membranes and are used in MF, UF, and dialysis
Extrusion	Materials produced by this method function as diffusion membranes for gas permeation and pervaporation

Symmetric membrane consists of microporous and nonporous structure. It had rigid, highly random voided structure and interconnects pores which differ from the conventional filter (Baker, 2000). In symmetric structure, the macrovoids can be long channel structure and can be sponge-like structure depending on the casting process.

2.3 Ultrafiltration process

There are common problems regarding to the wastewater treatment especially when dealing with contaminants such as oil, grease and some micron size suspended solids. There is a growing awareness by scientist and researcher regarding to this matter in order to approach any coordinate for water treatment. As we know, a large volume of oily wastewater is produced by various industries such as metallurgical industry, pharmaceutical, food and beverage industry as well as petroleum refineries which lead to the serious environmental problem. A common oily wastewater treatment that has been applied recently such as gravity separation and skimming, air-flotation, coagulation, de-emulsification and flocculation have few disadvantages such as low efficiency, high operating cost, corrosive and requires additional chemicals. Most importantly, these common methods could not remove contaminants such as oil and grease in micron size (Chakrabarty *et al*., 2010).

A few studies have been done using membrane filtration especially to remove small droplet of oil in wastewater (Scott *et al*., 2001, Chakrabarty *et al*., 2008, Chen *et al*., 2009a, Chakrabarty *et al*., 2010). There are few types of membrane separation process which are commonly used include MF, UF, nanofiltration (NF) and RO. Among these types of membrane, UF membrane is frequently used to reduce the contaminants in water such as oil, grease and suspended solids. The UF membrane has a small pore diameter size which is in the range of 0.001 µm to 0.2 µm (Li *et al.*, 2006).

Membrane performance and permeate (i.e. pure water) fluxes are primarily affected by the concentration polarization (i.e solute build-up) and fouling (gel layer formation, microbial adhesion and solute adhesion) on the membrane surface. Koltuniewics and Noworyta (1995) summarized that the performance of fluxes highly depends on the concentration polarization. Too much solute accumulates on the membrane surface will decline the total flux which causes high resistance to permeate flow directly pass through the membrane wall. In this case, the characteristic of the membrane and its porous structure are major factors to contribute good membrane-separation process.

Membrane separation is a technology which selectively separates or filtrates materials via pores in the molecular arrangement of a continuous structure. Some of the solute can pass through the pores of the membrane easily whereas some might block on the membrane surface dependent on particle size. Zularisam *et al.,* (2001) stated that in spite of membrane characteristics, the wastewater composition also contributed to the membrane flux and rejection ability.

The synthetic membrane can be fabricated using a large number of different materials. It can be made from organic or inorganic materials such as metal or ceramic, homogenous film (polymers), and heterogeneous solids (polymeric mixes). There are two types of membrane that has been used broadly in industry such as ceramic membrane and polymer membrane. Both of these membranes might be used for oil-in-water emulsion. Organic and inorganic materials itself can be entrapped inside the ceramic and polymer membrane in order to enhance the hydrophilicity.

2.4 Polysulfone membrane

Polysulfone (PSf) is among effective polymer that has high demand for membrane selection material due to their superior characteristics. PSf is an amorphous glassy polymer consist of aromatic ring, sulfone group and ether linkage. Figure 2.4 shows the chemical structure of the PSf membrane.

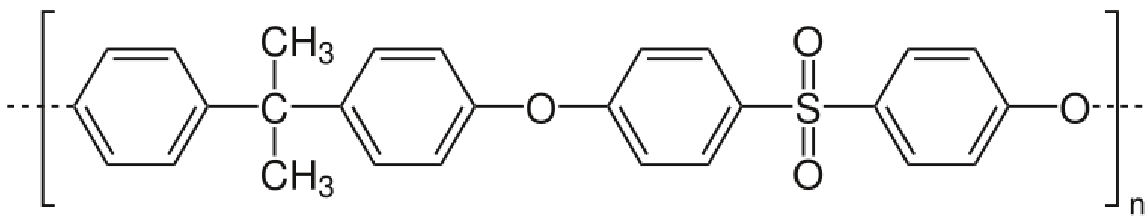

Figure 2.4: Chemical structure of polysulfone (Lai, 2002).

In this study, a mixed matrix membrane (MMMs) is prepared from PSf. Among polymeric materials such as poly(vinyl alcohol) (PVA), polyether sulfone (PES), and poly(vinylidene fluoride) (PVDF), PSf is one of the ideal polymeric membrane because of its high mechanical properties, good heat and chemical stability, easy to process, and favored a good selectivity characteristics stated by Helen J. *et al*., (2012).

Other than that, PSf is a polymer that can form an asymmetric membrane. It is a fact that a good membrane should have high surface porosity and good pore structure in order to obtain high permeability (Chakrabarty *et al*., 2008). Thus, an asymmetric membrane is ideal for this purpose. However, its hydrophobicity characteristic often leads to the membrane fouling and a decline of permeability as stated by Yang *et* al., (2007). This problem severely limits the long term use of these membranes in many filtration systems. Therefore, the modification of PSf membrane is necessary in order to solve these problems.

The addition of the inorganic nanoparticles into the PSf polymer network leads to the formation of nanogap area. Thus, the higher free volume available to provide membrane with higher permeability but the silica nanoparticles must be well distributed (Ng *et al*., 2011). An appropriate amount of silica must studied in doing so, otherwise it will turn to agglomeration among them resulted in the poor permeability performance.

2.5 Polymer blending/composite

2.5.1 Inorganic and nanomaterial additives

Fabrication of mixed matrix membranes (MMMs) has been attempted over the past few years with the addition of inorganic particles. This is due to the compatibility of particles in the polymer in the matrix membrane, and poor distribution of inorganic particle on the membrane. Besides, the size of the pore presence in the membrane, dispersion phase load and particle size also affect the MMMs properties (Aroon *et al*., 2010a). The best selection materials of inorganic particles and polymer must clearly be made as it could exhibits high performance based on permeability and rejection.

Other than that, the casting fabrication technique contributes to the final performance of the MMMs. There are three methods to incorporate the inorganic particle. Figure 2.5 shows a flow chart among these methods for better understanding.

1) Starting with the dispersion of particles for a predetermined period of time and followed by dissolving of polymer (Jiang *et al*., 2005), (Pechar *et al*., 2006). (Figure 2.5 a)
2) The polymer was dissolved in the solvent and stirred for a certain period and inorganic particles were added to the polymer solution (Chong *et al*., 2007), (Zhang *et al*., (2006). (Figure 2.5 b)
3) Particles were dispersed in solvent first and stirred for a fix time, followed by dissolving the polymer in particles-solvent solution (Kim *et al*., (2008), (Rafizah *et al*., 2008). (Figure 2.5 c)

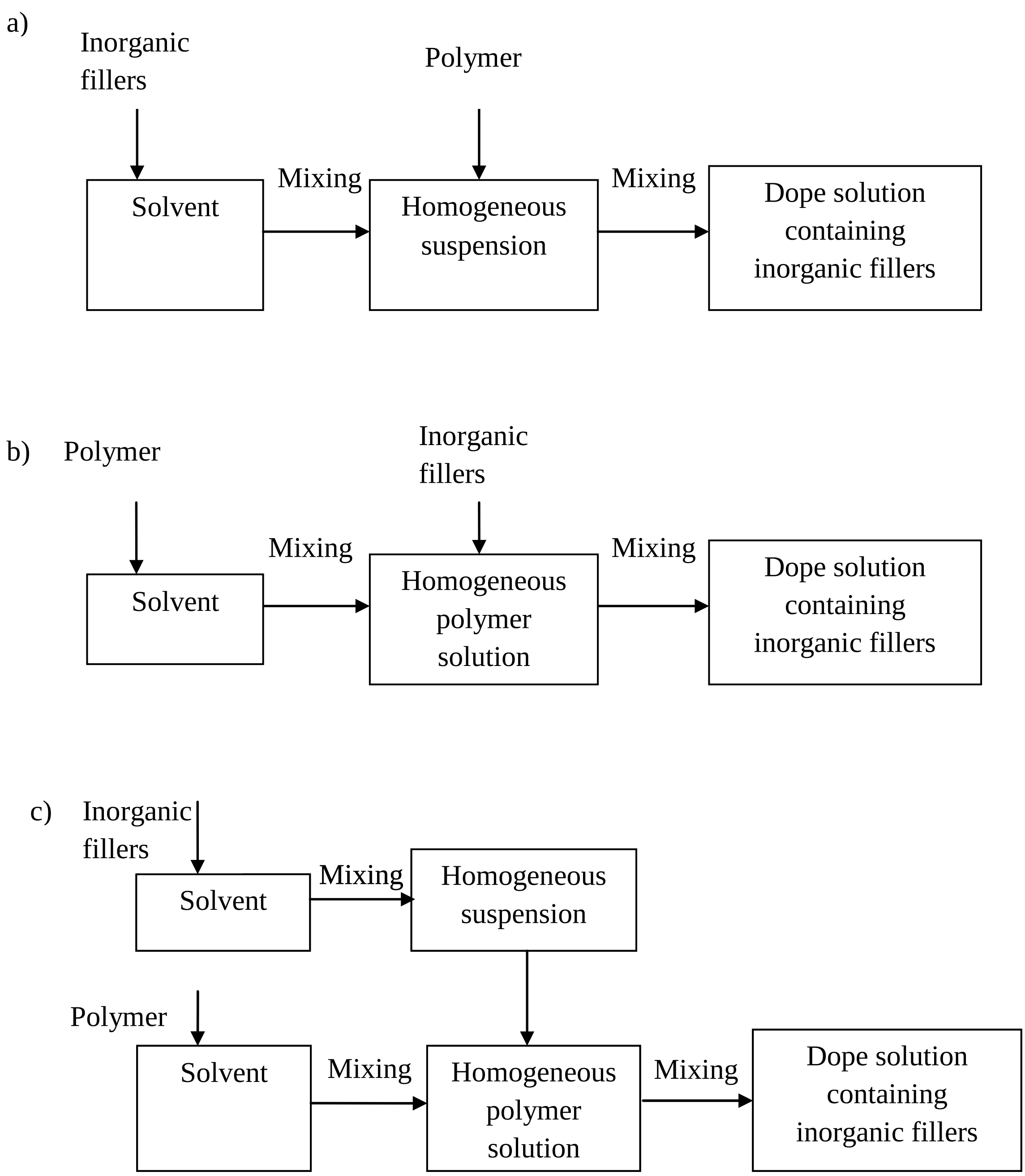

Figure 2.5: Different type of fabrication method (Aroon *et al*., 2010a).

Particles can be classified as nonporous and porous type. Both give different effect in polymeric matrix properties when added into the solution. Generally, porous filler acts as molecular sieving agent in the polymer matrix (Vu *et al*., 2008), and it separates the components by their shape and size. The porous filler offers better permeability than the neat polymeric membrane. However, the nonporous filler improves the separation by increasing matrix torturous pattern and decreasing the diffusion of the larger molecules (Bertelle, 2006). Nano-scale inorganic materials may disrupt the polymer chain packing and increases the free volume between polymer chains and thus increase the diffusion mechanism.

Table 2.2 shows the use of inorganic particles such as silica particles, silver (Ag), zinc oxide (ZnO) and titanium dioxide (TiO_2) in membrane applications. From the current research conducted, it showed that the addition of inorganic particles into polymeric solution enhance the membrane properties. This was due to the great interaction between inorganic particles and polymer membrane which affected the membrane pore size and distribution, surface tension, as well as membrane morphology of the membrane, thus resulted to good membrane permeability.