

**TREATMENT OF SYNTHETIC PRODUCED WATER USING HYBRID
MEMBRANE PROCESSES**

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**A project report submitted in partial fulfilment of the
requirements for the award of Bachelor of Engineering
(Hons.) Chemical Engineering**

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DECLARATION

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

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ABSTRACT

Production of produced water generated from oil and gas industries increases significantly, resulting in various environmental issues. Membrane filtration technology are found to be the promising alternatives to treat oily wastewater. Therefore, this research was aimed to treat the produced water with hybrid microfiltration (MF) and ultrafiltration (UF) processes. The pre-treatment MF membrane was fabricated with polyethersulfone (PES), n-methyl-2-pyrrolidone (NMP) and polyvinylpyrrolidone (PVP) through phase inversion process. The UF membranes contained additional component which was titanium dioxide (TiO₂) nanoparticle ranging from 0 wt.% to 1.0 wt.%. The fabricated membranes were characterized using scanning electron microscope (SEM), energy-dispersive X-ray spectroscopy (EDX), Fourier transform infrared spectrometer (FTIR) and water permeability test, whereas the membrane performances were analysed in terms of permeate flux, oil removal and flux recovery ratio. The increase in TiO₂ nanoparticles enhance the pore formation, porosity and pure water permeability due to improved hydrophilicity. The permeate flux of UF membranes increased with the increase of TiO₂ nanoparticles and pressure. The initial oil concentration was 556.33 mg/L. The oil removal rate after MF process was only 52.35 %, whereas the oil rejection efficiency was found to be in the range between 82.34 % and 95.71 % for UF process. It should be highlighted that the overall oil removal rate could achieve as high as 97.96 %. Based on the results, PES membrane incorporated with 1.0 wt.% was proved to be the most promising membrane since it exhibited the best separation performance in oil removal at a transmembrane pressure of 3 bar. The membrane cleaning process was best performing at 1.0 M NaOH with a recovery rate of 52.18 %, whereby individual NaOH solution was proved to be not sufficient to remove the foulants completely.

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LIST OF SYMBOLS / ABBREVIATIONS

A	effective area of the membrane, m^2
C_f	concentration of feed solution, mg/L
C_p	concentration of permeate, mg/L
J	pure water flux, $L / (m^2 \cdot h)$
l	membrane thickness, m
ΔP	operational pressure, Pa
Q	volume of the permeate water per unit time, m^3/h
R	oil retention (%)
r_m	average pore size, m
t	sampling time, h
w	weight of membrane, g
ε	porosity of membrane (%)
η	water viscosity at 25 °C, Pa·s
ρ	density, g/cm^3
BOD	biochemical oxygen demand
CAG	contact angle goniometer
COD	chemical oxygen demand
EDX	energy-dispersive x-ray spectroscopy
FRR	flux recovery ratio
FTIR	fourier transform infrared spectroscopy
MF	microfiltration
NF	nanofiltration
NMP	n-methyl-2-pyrrolidone
PA	polyamide
PES	polyethersulfone
PTFE	polytetrafluoroethylene
PVDF	polyvinylidene fluoride
PVP	polyvinylpyrrolidone
RO	reverse osmosis
SDS	sodium dodecyl sulfate

SEM	scanning electron microscope
TDS	total dissolved solids
TMP	transmembrane pressure
TOC	total organic carbon
TSS	total suspended solids
UF	ultrafiltration
WFD	european union water framework directive

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CHAPTER 1

INTRODUCTION

1.1 General Introduction

Oily wastewater is defined as the combination of wastewater and oil under different concentrations (Jamaly, Giwa and Hasan, 2015). It is usually produced in several industries, including oil refinery, petrochemical, metallurgy, automotive, machinery, food and beverage (Han et al., 2017; Masoudnia et al., 2014). After the industrial revolution, the amount of oil and grease generated increases due to rapid development in the industries which release oily wastewater as by-product. An increase in the production of oily wastewater leads to a major environmental issue. The discharge of oily wastewater directly from the industries without adequate treatment will result in various types of pollution by contaminating groundwater resources, endangering health of living creatures and even deconstructing natural landscapes (Yu, Han and He, 2017). Therefore, the processes of separating oil droplets from wastewater have gained extensive interests, so that the treated water which meets regulatory standards can be reused in other fields.

The treatment of oily wastewater can be conducted either in physical, chemical or biological route, depending on the types and quantities of pollutants as well as the respective allowable level of specific contaminants (Masoudnia et al., 2014). There are several types of conventional technology, namely flotation, coagulation, flocculation, centrifugal settling, chemical emulsification and biological treatment (Križan Milić et al., 2013). These methods have shown the similarity in disadvantages and limitations. For example, tiny oil droplets are remained in the filter water owing to low oil removal efficiency. Besides, high capital and operating costs are required to maintain proper functioning of the separation systems.

Consequently, many research institutions have investigated in-depth and they have reported on the efficient and feasible alternatives to treat oily wastewater. Membrane-based technology are concluded to be the promising methods in the treatment of stable emulsified oily wastewater (Ong et al., 2013; Wang and Chung, 2015). Among all the membrane-based processes, microfiltration (MF) and ultrafiltration (UF) receive additional attention (Kiss et al., 2013). These membrane filtration systems are able to overcome the limitations of conventional technology by

providing several advantages such as a straightforward operation, stable quality of effluent, high selectivity and high oil removal efficiency as well as low operating investment (Hafidi et al., 2004). Moreover, the outcomes of the treatment of oily wastewater are satisfied because the treated water after MF and UF processes is almost free-of-oil and meets the environmental standards.

1.2 Importance of the Study

The importance of this study was to perform hybrid membrane processes to remove oil emulsion from wastewater and to evaluate the performance on oil removal efficiency by adding additive. The selection of type of polymer material and additive was investigated to ensure best separation performance could be achieved. The oil concentration of treated oily wastewater were measured in order to assure the final oil content able to meet the environmental guidelines. The study on membrane cleaning provided the understanding on capability of membrane recovery.

1.3 Problem Statement

Oily wastewater is one of the dominant sources of water pollution and air pollution. Due to the presence of hazardous contaminants in the wastewater, the conditions of water, air and soil as well as the human health are greatly affected. For instance, the hydrocarbon and oil found in the wastewater will evaporate to the atmosphere under sunlight, resulting in air pollution (Jamaly, Giwa and Hasan, 2015). Besides, water pollution is caused by the contamination of the sources of drinking water and groundwater. Nowadays, production of oily wastewater increases greatly owing to the high demand for industrial products. In fact, the amount of produced water generated from oil and gas industries increases significantly. The impurities in produced water may cause adverse and toxic effects to the environment. Hence, treatment of produced water has gained a lot of concerns and the researchers have conducted many studies and experiments on different methods.

The traditional methods consist of certain major disadvantages and limitations, whereby membrane filtration processes, especially microfiltration and ultrafiltration are found to be the promising alternatives to treat oily wastewater. However, the intrinsic hydrophobic nature of most of the membrane materials will lead to serious fouling issue, affecting the permeate flux and oil removal efficiency. To overcome the fouling problem, greater transmembrane pressure is needed to achieve the same

permeance and the operating cost will eventually increase. Therefore, an appropriate membrane material has to be studied and chosen wisely to maximize the oil rejection. Besides, some additives have to be added in order to enhance the performance of the filtration system. Moreover, the types of operating parameters which will influence the overall performance have to be figured out and the related researches have to be carried out to identify the most satisfactory operating condition. Lastly, a cleaning agent is required to clean the fouled membrane by mitigating or eliminating the foulants.

1.4 Aim and Objectives

This study was aimed to treat synthetic produced water with hybrid microfiltration (MF) and ultrafiltration (UF) processes and to perform cleaning in fouled membrane.

The objectives of this project were enumerated as follows:

- i. To characterize the polyethersulfone (PES) based MF and UF membranes in terms of membrane structure, membrane porosity and elemental composition.
- ii. To identify the performance of fabricated MF and UF membranes in terms of permeate flux and oil rejection by using a dead-end filtration system.
- iii. To evaluate the performance on oil removal by adding different concentrations of titanium dioxide (TiO_2) into UF membranes.
- iv. To investigate the effect of employing sodium hydroxide (NaOH) solution as cleaning agent on foulant removal.

1.5 Scope and Limitation of the Study

This study was related to membrane filtration technology whereby MF and UF membranes were chosen to demonstrate the separation processes. To attain the objective stated previously, the scope of this study were listed as follows:

- i. Determine the optimal composition of membrane dope solution.
- ii. Study the membrane characterization in terms of membrane morphology, membrane porosity and hydrophilicity.
- iii. Use MF as a pre-treatment method before the feed solution flowing through UF membranes.
- iv. Investigate the performance of treated synthetic oily wastewater under different pressures in a dead-end filtration unit.
- v. Perform membrane cleaning by immersing the fouled membrane in alkali solution.

The limitations existed in this study were listed as follows:

- i. The produced water generated directly from oil and gas industry usually contains a high concentration of various contaminants which are not easily to be filtered. Hence, in this case, synthetic produced water which was collected from a tank depot cleaning company was known as tank dewatering produced water.
- ii. The performance of oil retention efficiency is affected by a lot of operating parameters, including transmembrane pressure, oil feed concentration, pH, temperature, velocity and others. Due to limited duration to complete this study, this research was only focused on transmembrane pressure.

1.6 Contribution of the Study

Throughout this research, several conclusive information was obtained such as the most desirable composition of UF membrane dope solution, optimal operating conditions and the performance of NaOH solution as a membrane cleaning agent. Sharing of the knowledge obtained from this study could help to improve future work of other researchers in membrane filtration field.

1.7 Outline of the Report

The following chapters of this study consisted of literature review, methodology and work plan, results and discussion as well as conclusions and recommendations. A fundamental understanding on current membrane-based technology, membrane materials and characterization, effects of operating variables as well as the significant membrane fouling problem and the appropriate cleaning method used to tackle this issue, were discussed in the chapter of literature review. Based on the analysis from previous researches, a most suitable methodology was proposed to achieve better performance of oil rejection. According to proposed methodology, the membrane characterization tests were conducted prior to membrane performance tests. The results for permeate flux, oil rejection and flux recovery ratio were discussed in that chapter. A conclusive summary and recommendations for future work were then discussed in the last chapter.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction of Produced Water

The largest byproduct or waste stream generated in the oil and gas industry is known as produced water or oilfield brine. Produced water is a composite of organic and inorganic components which mainly involves the dissolved and dispersed oil compounds, dissolved formation minerals, production chemicals, produced solids as well as the dissolved gases (Igunnu and Chen, 2012). The properties of produced water varies with the location of oilfield, lifetime of the reservoir, operating condition of the drilling process and the types of hydrocarbon being produced (Nasiri and Jafari, 2017). The typical ranges for characteristics of produced water in global oilfields are summarised in Table 2.1.

Table 2.1: Properties of Worldwide Oilfield Produced Water (Martel-Valles, Foroughbakchik-Pournavab and Benavides-Mendoza, 2016; Tibbetts et al., 1992)

Parameter	Unit	Values
Density	kg/m ³	1014 - 1140
pH Value		4.3 - 10
Total Organic Carbon (TOC)	mg/L	0 - 1500
Chemical Oxygen Demand (COD)	mg/L	1,220
Biochemical Oxygen Demand (BOD)	mg/L	499.3 - 12 353
Total Suspended Solids (TSS)	mg/L	1.2 - 1000
Total Dissolved Solids (TDS)	mg/L	100 - 400 000
Total Oil	mg/L	2 - 565

The treatment of produced water becomes an significant issue due to its high commercial value in the aspects of recycling and reusing in petroleum industry operations, becoming the source of fresh water for irrigation and wildlife consumption as well as replacing the source of drinking water (Fakhru'l-Razi et al., 2009). Hence, current industries have applied several types of technology for produced water treatment.

2.1.1 Formation of Produced Water

As referring to Figure 2.1, the typical petroleum reservoir consists of naturally forming rock and underground fluids such as gas, oil and formation water. The formation water will migrate to the surface along with the hydrocarbon, oil and gas during oil recovery as reported by Rawindran, Krishnan and Sinnathambi (2017). For the purpose of sustaining hydraulic pressure and improving the oil recovery levels, additional water will be injected to the reservoir because extraction of oil and gas reduces the reservoir pressure (Fakhru'l-Razi et al., 2009). Besides, the production of formation water with hydrocarbons increases when the production of oil and gas raises. Consequently, the produced water which consists of formation water, injected water and hydrocarbon is generated.

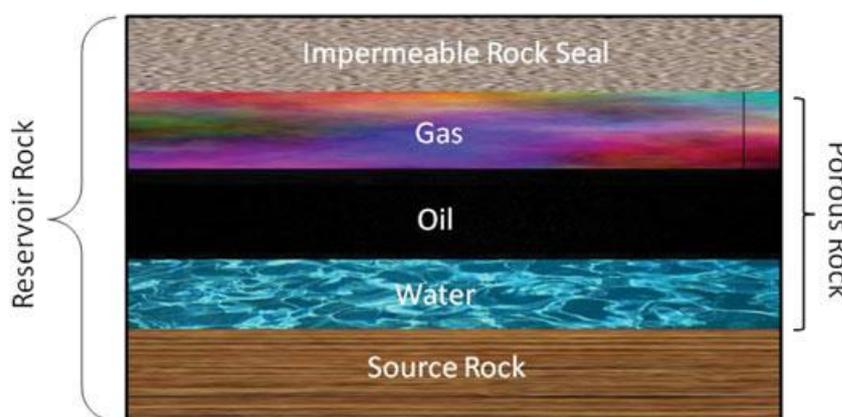


Figure 2.1: Diagram of Typical Reservoir (Igunnu and Chen, 2012)

2.1.2 Control of Produced Water Discharge

The impurities in produced water may cause adverse and toxic effects to the environment. Hence, the produced water has to be treated before discharge to the sea in order to meet the environmental regulations. According to the research by Fakhru'l-Razi et al., (2009), regulatory guidelines for produced water discharge offshore after certain treatment are different for several countries, but the average permitted limit has been set at 40 mg/L. With the increase in environmental concern, more stringent standards have been stipulated by many countries as summarised in Table 2.2. Based on the study by Igunnu and Chen (2012), the European Union Water Framework Directive (WFD) initiated the 'zero discharge' action in 2000 to provide a strong protective system for aquatic organisms. The action was further supported and responded by Norwegian Oil Industries Associations. Moreover, many oil and gas

companies have attempted to achieve zero discharge of pollutants and contaminants in produced water.

Table 2.2: Permitted Oil and Grease Limits for Produced Water Discharge by Several Countries (Fakhru'l-Razi et al., 2009; Neff, 2002)

Country	Monthly Average (mg/L)	Daily Maximum (mg/L)
Australia	30	50
Canada	30	60
China	10	-
Mediterranean Sea	40	100
Nigeria	40	72
North-East Atlantic	30	-
USA	29	42

2.2 Fundamental of Membrane Technology

Typical pressure-driven separation processes comprise microfiltration, ultrafiltration, nanofiltration and reverse osmosis. The contaminants include tiny particles, microorganisms, dissolved organic matter and monovalent salts are removed by four different types of mechanisms depending on the pore sizes while the filtered permeate passes through the membrane (Fane, 1996). Figure 2.2 shows the types of contaminants being separated by different membrane separation process with respective pore sizes.

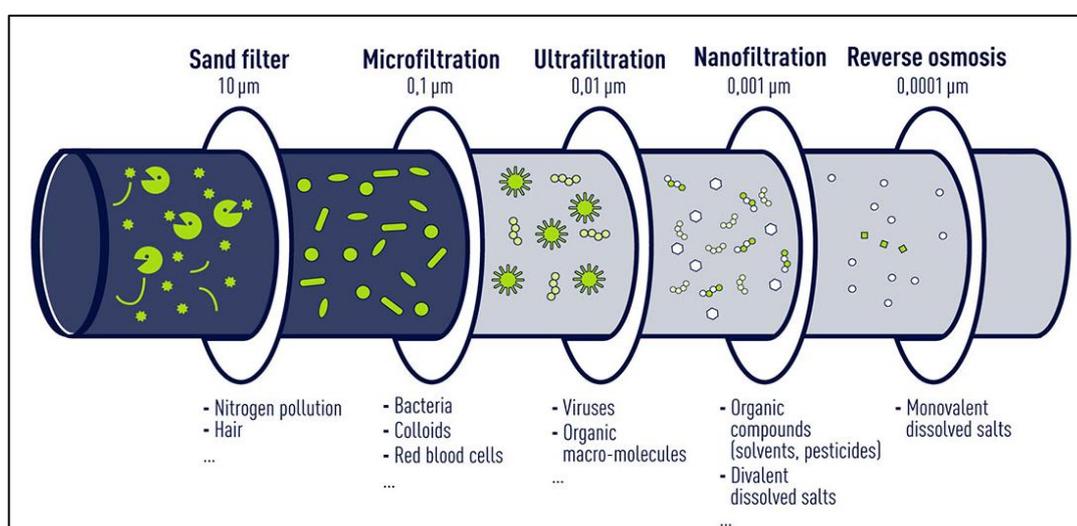


Figure 2.2: Comparison between Membrane Technology (SUEZ, n.d.)

2.2.1 Microfiltration (MF)

Microfiltration is a membrane technique in which the porous membranes trap suspended particles with diameters ranging from 0.1 to 10 μm (Baker, 2012; Juholin, 2016). The particles with greater sizes are suitable to be separated using conventional cake filters. The optimal operating pressure is approximately from 1 to 2 bar (Juholin, 2016).

2.2.2 Ultrafiltration (UF)

For ultrafiltration process, a finely porous membrane is designed to remove microorganisms, dissolved macromolecules and tiny colloidal particles with diameters in the range of 0.01 to 0.1 μm (Baker, 2012). Besides, the membranes have the ability to separate dissolved particles with molecular weights between 300 and 500000 (Esfahani et al., 2014). The process typically operates at pressure of 1 to 10 bar which is slightly higher than microfiltration (Juholin, 2016). He and Jiang (2008) claimed that ultrafiltration is a well-known effective method to filter oil emulsions and droplets with diameters less than 20 μm due to its low energy consumption and high oil removal efficiency but the major drawback is the reduction of flux caused by membrane fouling.

2.2.3 Nanofiltration (NF)

Nanofiltration is a separation technique which capable to separate multivalent salts, pesticides as well as herbicides with sizes smaller than 2 nm (Esfahani et al., 2014). The operating pressure of conventional nanofiltration varies between 10 to 25 bar (Juholin, 2016) but recent study shows that the membrane able to function at relatively low pressure of 2 bar with an extraordinary advantage of maintaining high rejection of multivalent ions (Labban et al., 2017). The sieving process depends on the particle sizes and also the effects of electrical charge between membrane materials and the ions (Juholin, 2016). Nanofiltration is commonly being applied in the desalination industry.

2.2.4 Reverse Osmosis (RO)

Reverse osmosis is widely used in the water purification industry to separate salts and monovalent ions from water. Greater pressure at the range of 15 to 80 bar is exerted to overcome the osmotic pressure (Juholin, 2016). Ions with diameter about 0.1 nm are removed by concentration difference and pure water is then forced through the non-porous membrane from concentrated solution into a low concentration solution

(Kucera, 2015). Drioli and Giorno (2010) found that reverse osmosis was suitable for oily wastewater treatment as the permeate was free of oil.

2.2.5 Hybrid Membrane Technology

The comparison of advantages and disadvantages of the four types of membrane technology is summarised in Table 2.3. Each of the membrane technology has its own superiority and limitation. Juholin (2016) also explained that a stand-alone membrane process has the difficulty of producing highly purified product due to higher fouling tendency of the synthetic membranes. Therefore, hybrid membrane processes have been developed sustainably for the purpose of achieving higher oily particles removal efficiency and reducing the requirement for membrane cleaning. The hybrid membrane processes are best defined as an integration of at least two techniques which offer better performance than a stand-alone system.

Many researchers have tried to combine distinct membrane system. The fundamental theory of hybrid membrane process is the permeate flow from the first separation system will be treated as the feed pass through the second filtration process. Most of the suspended particles and contaminants can be removed by the first separation technique and thus, the final permeate after the hybrid membrane processes is relatively clean enough and is usually free of oil. For example, microfiltration and ultrafiltration processes are frequently applied as pre-treatment technique for nanofiltration and reverse osmosis (Juholin, 2016).

Table 2.3: Advantages and Disadvantages of Membrane Technology (He and Jiang, 2008; Igunnu and Chen, 2012)

Technology	Advantages	Disadvantages
Microfiltration (MF)	<ul style="list-style-type: none"> • Low energy consumption • Act as a pretreatment method for nanofiltration or reverse osmosis 	<ul style="list-style-type: none"> • Membrane Fouling • Require periodic cleaning of membrane • Require disposal or recycle treatment for the waste produced during membrane cleaning
Ultrafiltration (UF)	<ul style="list-style-type: none"> • High oil retention efficiency • No essentiality for chemical additives • Low energy consumption • Act as a pretreatment method for nanofiltration or reverse osmosis 	<ul style="list-style-type: none"> • Membrane Fouling • Require periodic cleaning of membrane • Require disposal or recycle treatment for the waste produced during membrane cleaning
Nanofiltration (NF)	<ul style="list-style-type: none"> • High pH tolerance • Does not require disposal for solid waste • High rejection of multivalent ions 	<ul style="list-style-type: none"> • High energy cost due to high operating pressure • Require backwashing cycles • Cannot withstand feed temperatures above 45 °C
Reverse Osmosis (RO)	<ul style="list-style-type: none"> • High pH tolerance 	<ul style="list-style-type: none"> • High energy cost due to high operating pressure • Cannot withstand feed temperatures above 45 °C

2.3 Membrane Materials

The common materials used to fabricate membranes for oily wastewater separation processes are polymer and ceramic. Polymeric membrane is a synthetic membrane which has better oil rejection efficiency compared to organic membrane. On the other hand, ceramic membranes are mainly made from clays of nitrides and metal oxides (Igunnu and Chen, 2012).

2.3.1 Polymeric Membrane

There are several types of polymeric membranes which are frequently applied in membrane filtration such as polyvinylidene fluoride (PVDF), polyamide (PA), polyether sulfone (PES), polytetrafluoroethylene (PTFE) and others. Zeman and Zydney (1996) stated that the basic principles for choosing appropriate polymer membranes are based on availability, affordability and compatibility with the membrane technology.

Masoudnia et al. (2014) applied hybrid microfiltration with PVDF and ultrafiltration with PES and the oil rejection level was successfully reached up to 100 % compared to stand-alone membrane. Orecki, Tomaszewska and Karakulski (2006) also developed a hybrid membrane system to treat model oil solutions from bilge water treatment with ultrafiltration and nanofiltration. The oil concentration was less than 8 ppm after ultrafiltration with PVDF membrane whereas the remaining oil from ultrafiltration permeate was removed completely after nanofiltration with PA membrane. Besides, PVDF membrane was employed in an ultrafiltration model to treat produced water and the oil content could be reduced to less than 1 ppm (Yu, Han and He, 2017).

Other than PVDF, PA membranes possess high tensile strength and better resistance to chlorinated components. Besides, they are more superior than other polymeric membranes due to the hydrophilic nature without any wetting agent. Therefore, PA membrane with additives of montmorillonite and calcium chloride dihydrate was adopted by Medeiros et al. (2017) to treat oily wastewater and the result was satisfied as the rejection of oil and grease was lower than 20 ppm, meeting the minimum requirement for discharge of produced water. Moreover, Singh, Purkait and Das (2011) reported that the oil rejection was in the range of 94 % to 98 % for microfiltration with PA membrane

2.3.2 Ceramic Membrane

Ceramic membranes have been widely used in oily wastewater industry. Nakamura and Matsumoto (2013) demonstrated separation of oil-in-water emulsion with alumina microfiltration and ultrafiltration and the result illustrated that the oil particles were completely rejected at low oil feed content. Besides, a tubular aluminium oxide microfiltration system was demonstrated by Abadi et al. (2011) to treat the wastewater effluent from Tehran refinery. The oil content of the permeate generated from the system was found to be less than 4 ppm while the efficiency of TOC removal was greater than 95 %.

2.3.3 Comparison between Polymeric and Ceramic Membrane

Vatai et al. (2009) investigated the comparison between polymeric and ceramic membrane by using polyaryletherketone and zirconia to separate oil-in-water emulsion with ultrafiltration. From the experiments, ceramic membrane was more advantageous in the aspect of membrane productivity but the oil rejection level was not satisfied because of its hydrophobic nature and greater pore sizes which contributed to the initial oil permeation. Based on the studies on separation performance of both of the membrane materials, the comparison between their advantages and disadvantages is summarised and is tabulated in Table 2.4. Therefore, polymeric materials are concluded to be the superior material to fabricate membranes for combination of microfiltration and ultrafiltration due to their affordable-prices and hydrophilic properties after surface modification.

Table 2.4: Advantages and Disadvantages of Polymer and Ceramic Membranes (Igunnu and Chen, 2012; Ikhsan et al., 2017; Vatai et al., 2009)

Membrane Material	Advantages	Disadvantages
Polymer	<ul style="list-style-type: none"> • Low cost • High oil removal efficiency • Low energy requirement • Extensive variability of barrier properties and structures 	<ul style="list-style-type: none"> • Less available to separate volatile components • High tendency of membrane fouling • Short life cycle (seven years) compared to ceramic membrane • Requires chemical treatment for membrane cleaning
Ceramic	<ul style="list-style-type: none"> • Narrow and well-distributed pore size • High selectivity and productivity • High thermal, mechanical and chemical stability • Long life cycle (more than ten years) compared to polymer membrane 	<ul style="list-style-type: none"> • High cost • High tendency of membrane fouling • Limited availability of pore size range • Not a relatively advanced development compared to polymer membranes • Requires chemical treatment for membrane cleaning

2.4 Membrane Characteristics

Zhu et al. (2014) studied the intrinsic property of polymeric membranes and concluded that these oleophilic membranes had to be modified with hydrophilic additives during phase inversion process in order to avoid adhesion of oily particles on the membrane surfaces. This is because hydrophobic membranes such as PVDF and PES usually foul more than hydrophilic surface (DiGiano, 2001). Contact angle is a decisive parameter to determine the wettability of membrane surface as illustrated in Figure 2.3. For hydrophilic membrane, the contact angle tends to be as low as zero degree because the water droplets are able to spread out on the surface and pass through the pore spontaneously without pressure force (Zeman and Zydney, 1996). In fact, the fouling problem of hydrophilic membrane can be avoided but the attraction of oily particles are not effective as a hydrophobic membrane. On the other hand, hydrophobic membrane will repel the water and form a contact angle of greater than ninety degrees due to less contact with the membrane surface (Cheryan, 2010).

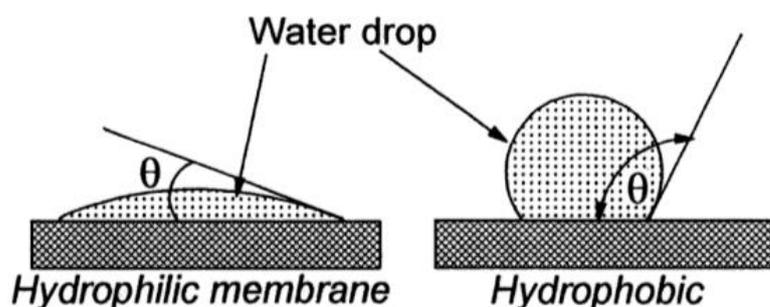


Figure 2.3: Contact angle (Cheryan, 2010)

Fouled oils will be retained and removed easily after the formation of compact hydrated layers. Owing to the hydrophilic property of poly(methyl methacrylate) (PMMA), Ochoa, Masuelli and Marchese (2003) reported that the PVDF with higher PMMA concentration decrease the fouling rate and COD of permeate. An application of PVDF ultrafiltration membrane with polyvinylpyrrolidone (PVP) and 2 wt.% titanium dioxide (TiO_2) nanoparticles as additives was developed by Ong et al. (2013) to enhance the water permeability and fouling resistance. Besides, poly(acrylic acid) and polyethylene glycol were also being employed for membrane fabrication through chemical reactions for the main purpose of improving hydrophilicity.

2.5 Effects of Operating Parameters

The performance on oil removal efficiency depends on several operating parameters, such as transmembrane pressure (TMP), concentration of oil feed solution and temperature.

2.5.1 Transmembrane Pressure (TMP)

According to the study by Ramli, Bolong and Yasser (2013), transmembrane pressure (TMP) is defined as the pressure required to force the feed solution passing through membrane pores whereas the permeate flux is the flowrate per unit membrane area for permeate. Both of the transmembrane pressure and permeate flux are inter-related. As referring to Darcy's Law, permeate flux varies linearly to TMP and membrane area but inversely proportional to the viscosity of solution and transport resistance.

Masoudnia et al. (2014) conducted experiments on treatment of oily wastewater varying TMP of MF and UF process from 1 to 3 bar and 3 to 8 bar respectively. As referring to Figure 2.4, the results followed Darcy's Law because higher permeate flux was generated at 3 bar which was the highest TMP in the MF process. The permeate produced from MF process was treated as the feed solution for UF process which contained a concentration of 500 ppm. The outcomes disobeyed Darcy's Law at relatively higher TMP as illustrated to Figure 2.5. The results showed that the permeate flux at 8 bar was lower than the permeate flux at 7 bar. Higher TMP also increased fouling rate while significantly reduced the oil retention rate and permeate flow of the fouled membrane. This situation could be explained by the accumulation of oil droplets on the membrane surface when the droplets were forced through the membrane pores. Singh, Purkait and Das (2011) also stated that at higher TMP, concentration polarization of oily particles on the membrane surface would occur, resulting in lower oil rejection efficiency.

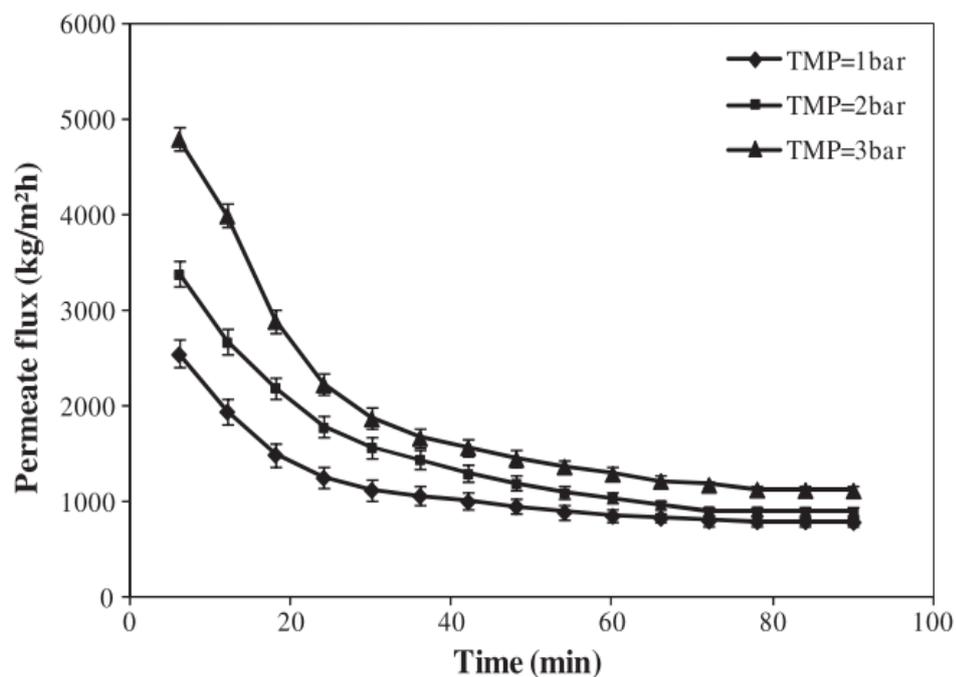


Figure 2.4: Time Dependency of Permeate Flux of MF Process for Different TMP at Feed Concentration of 3000 ppm (Masoudnia et al., 2014)

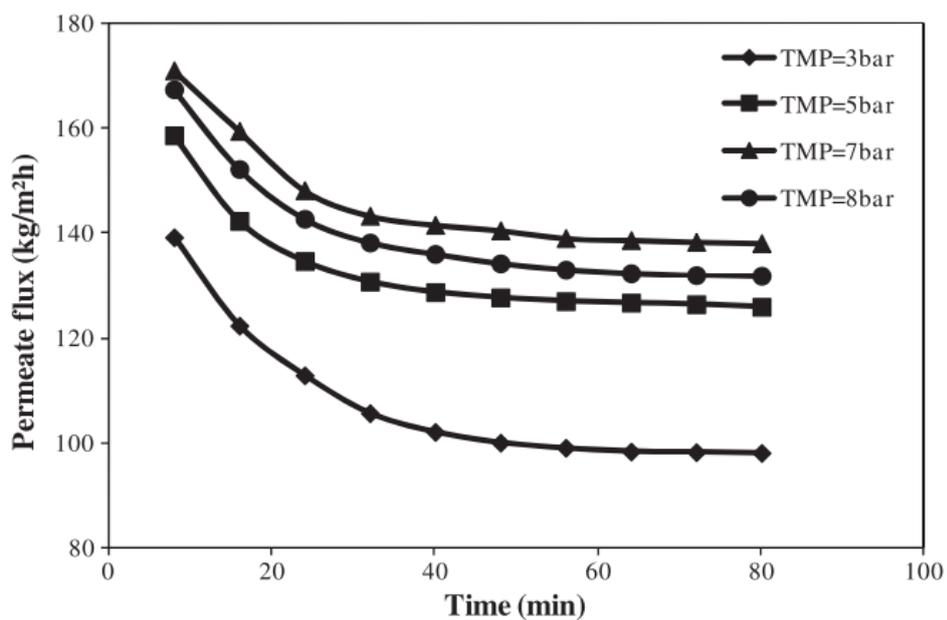


Figure 2.5: Time Dependency of Permeate Flux of UF Process for Different TMP at Feed Concentration of 500 ppm (Masoudnia et al., 2014)

2.5.2 Oil Feed Concentration

The effects of oil feed concentration on permeate flux and oil rejection for microfiltration were investigated by Masoudnia et al. (2014). The results indicated that the 96.1 % of oil can be removed with the oil feed concentration of 500 ppm but when the oil content of the feed solution reaches 3000 ppm, only 79.98 % of oil can be rejected. This situation could be explained by the presence of concentration polarization at high feed concentration which causes the formation of a thick gel layer and reduction of permeate flux.

Besides, the phenomenon of decline of permeate flux was further proven in the research conducted by Ong et al. (2013). Based on Figure 2.6, although the initial oil retention for different concentrations was less than 85 %, the oil retention kept increasing until achieving nearly 97 % after three hours of operation. Moreover, the oil rejection increased when the oil feed concentration changed from 250 to 1000 ppm because the thicker oil layer could form a complementary selective layer to the membrane barrier. Orecki, Tomaszewska and Karakulski (2006) reported that the oil rejection reaches up to 95 % for the oil feed content between 100 and 400 ppm. In conclusion, the treatment of produced water is effective because the typical scope of oil content is between 2 and 565 ppm as summarised in Table 2.1.

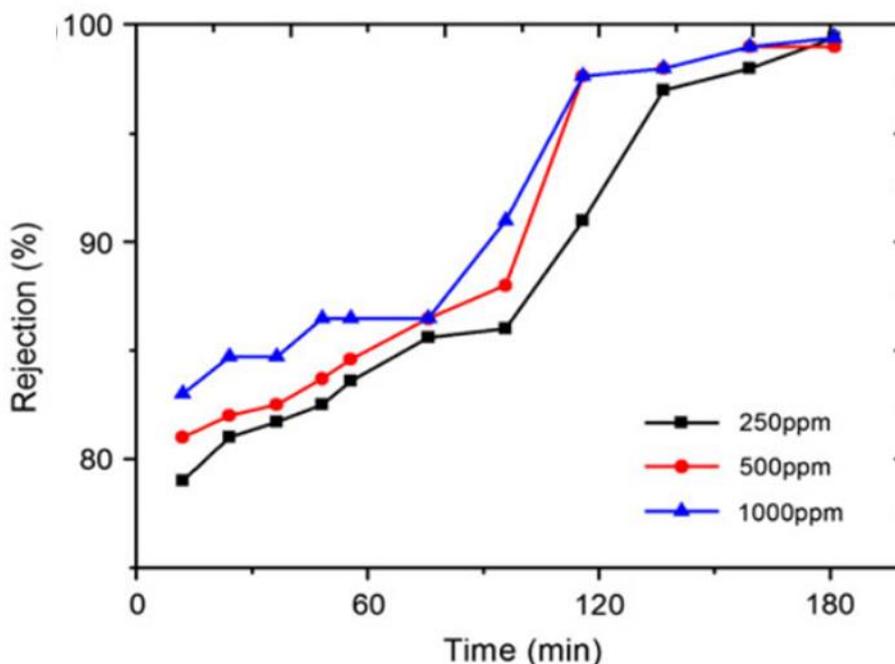


Figure 2.6: Time Dependency of Oil Rejection for Different Oil Concentrations (Ong et al., 2013)

2.5.3 Temperature

Temperature is an essential operating parameter affecting the oil rejection efficiency because it will influence the viscosity of the feed solution. Salahi et al. (2011) reported that higher operating temperature increases the permeate flux and reduces the fouling resistance but there was a limitation above 40 °C. In this case, the oil and grease passed through the membrane easily at higher temperature due to their less viscosity properties but the oil retention efficiencies remained similar from 40 °C until 50 °C. Based on Sadrzadeh, Gorouhi and Mohammadi's (2008) study, higher temperature enhanced the membrane fouling and concentration polarization. Nevertheless, the fouling problem became negligible when membranes with larger pore sizes were employed. Therefore, it could be concluded that operating at higher temperature is an ideal case for membrane separation process but there is still an optimal temperature of around 40 °C.

2.6 Membrane Fouling

Membrane fouling becomes a major barrier to hinder the separation performance of the filtration system for oily wastewater treatment. The contaminants usually accumulate on the membrane surface with prolonged filtration duration, resulting in decline of permeate flux and oil retention efficiency as well as the lifespan of the membrane (Song and Tay, 2010). Basically, there are four types of membrane fouling mechanisms as depicted in Figure 2.7. According to Figure 2.7 (a), at the initial stage of the filtration process, the oil droplets are retained on the membrane surface and they partially block the pore entry since their sizes are greater than the pore sizes. The second type of fouling is the formation of a cake layer, which is caused by accumulation of oil droplets after operating at a period of time. Based on Figure 2.4 (c), if greater transmembrane pressure is applied, the emulsified oil droplets will undergo a wetting transition by reducing the contact angles (Huang, Ras and Tian, 2018). The droplets start to coalesce and transform to viscous oil film on the membrane surface. For the last type of membrane fouling, tiny oil droplets are forced into the membrane pores, leading to the internal pore fouling.

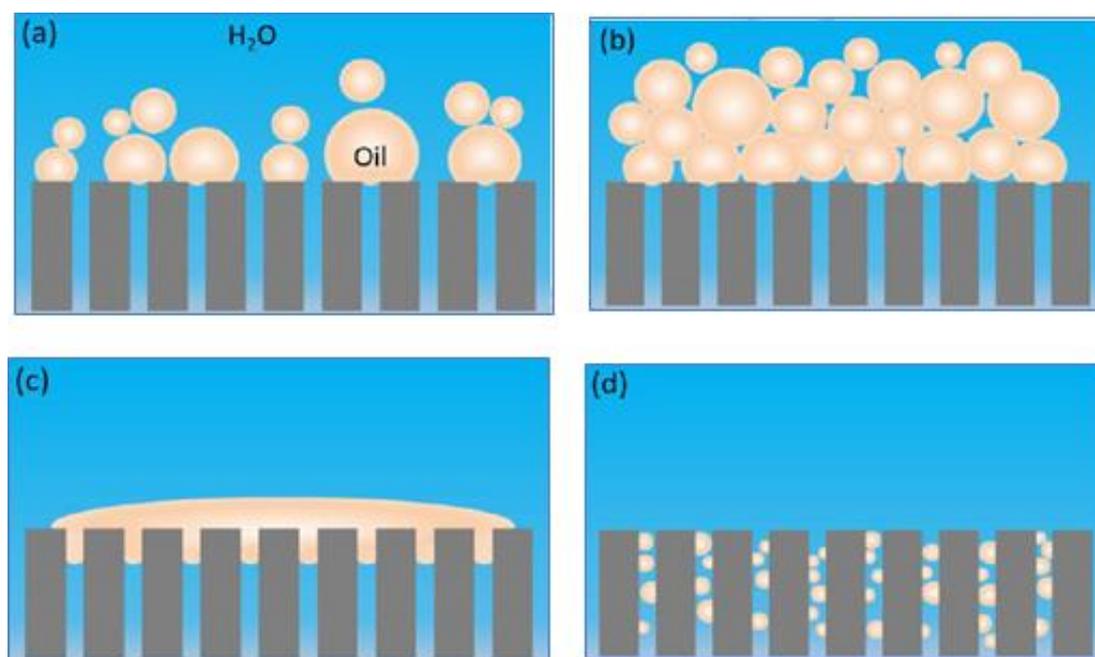


Figure 2.7: Scheme of Membrane Fouling Mechanisms (a) Presence of Partial Blockage of Membrane Pores by Oil Droplets, (b) Formation of Cake Layer on Membrane Surface, (c) Formation of Viscous Oil Film on Membrane Surface, (d) Presence of Oil Droplets within Membrane Pores (Huang, Ras and Tian, 2018)

There are four common types of foulants, namely particulates, organic foulants, inorganic foulants and microbiological organisms (Guo, Ngo and Li, 2012). Understanding the existence of types of the foulants found in the oily wastewater becomes significant for selection of adequate membrane cleaning method. Li and Elimelech (2004) mentioned that the degree of membrane fouling depends on characteristics of foulants, permeate flux, operating conditions of the membrane model and membrane properties such as surface morphology and hydrophilicity as well as the molecular weight cut-off. Hence, the operating conditions have to be controlled and the type of cleaning method has to be chosen wisely for different types of membrane materials and separation techniques.

2.7 Membrane Cleaning

The principal function of a cleaning process is to relieve a substance which is not an original component of the material (Shi et al., 2014). Several criteria have been stipulated for the membrane cleaning in order to provide sufficient permeate flux and efficient removal of foulants. Firstly, the membrane surface cannot be altered during

restoration of initial feed flow (Blanpain-Avet, Migdal and Bénézech, 2009). Besides, the foulants have to be stored in dispersion or solution phase for the purpose of avoiding the re-fouling of cleaned surfaces. Moreover, the cleaning agent should be compatible with the membrane system and stable with time. Lastly, the cleaning agent with high availability and low cost is most likely to be chosen.

The fouled membranes can be cleaned in either physical or chemical method, depending on the condition of fouling membrane and the types of foulants. The fouling problem which exists in either reversible or irreversible form, can be cleaned by different methods. Reversible fouling which occurs because of the formation of a cake layer on the surface of membrane, can be overcome by physical washing method such as backwashing and hydrodynamic scouring (Guo, Ngo and Li, 2012). It is discovered that some of the reversible fouling cannot be backwashed, whereby the fouling has to be treated by chemical cleaning method. For irreversible fouling, pore-blocking and chemisorption mechanisms will give rise to this fouling problem. In this case, the membrane should be replaced or cured by intense chemical or thermal treatment (Huang, Ras and Tian, 2018).

Physical cleaning methods, such as backwashing, hydrodynamic scouring and sponge ball cleaning are used to remove the absorbent particles away from the membrane surface. Sometimes, the physical cleaning method is not effective if the membrane fouling is severe. Therefore, the fouled membrane can be cleaned chemically with the use of chemical cleaning agent, including acid, alkaline, oxidant, surfactant, enzyme and chelating agent (Shi et al., 2014; Zhang and Ma, 2009). Table 2.5 summarises the common functions of chemical cleaning agents and the respective foulants to be removed. The selection of appropriate cleaning agent is primarily owing to the efficiency of dissolving deposited materials on the membrane surface, meanwhile, eliminating the particles without damaging the surface and maintaining the original properties of the membrane (Arnal, García-Fayos and Sancho, 2011).

Table 2.5: General Functions of Chemical Cleaning Agents (Shi et al., 2014)

Cleaning Agents	Functions
Acids	<ul style="list-style-type: none"> • Regulate pH value of solution • Dissolve inorganic precipitates
Alkalis	<ul style="list-style-type: none"> • Regulate pH value of solution • Hydrolyse protein • Reduce number of bonds between the membrane surface and the foulants • Enhance mass transfer rate of cleaning agents to surface of fouled membrane
Oxidants	<ul style="list-style-type: none"> • Oxidize organic particulates • Destroy pathogenic microorganisms
Surfactants	<ul style="list-style-type: none"> • Promote dispersion or suspension of deposited particles • Decrease interfacial tension between liquids and solids • Increase wettability of membrane surface • Eliminate water consumption and rinsing time
Enzymes	<ul style="list-style-type: none"> • Remove biofilm foulants • Catalyse lysis of particular substrates

CHAPTER 3

METHODOLOGY AND WORK PLAN

3.1 Materials

The membrane dope solution consisted of polyethersulfone (PES, MW = 35,000 g/mol), n-methyl-2-pyrrolidone (NMP, MW = 99.13 g/mol), polyvinylpyrrolidone (PVP, MW = 160,000 g/mol) and titanium dioxide (TiO₂, MW = 79.87 g/mol). PES and NMP purchased from EMPLURA® were used as the major membrane forming material and solvent respectively. PVP obtained from R&M Chemicals was chosen as the additive to act as pore former whereas the other additive was TiO₂ nanoparticle from R&M Chemicals.

The remaining chemicals used in the project were sodium sulfate anhydrous (Na₂SO₄, MW = 142.04 g/mol) from DUKSAN, n-hexane (C₆H₁₄, MW = 86.18 g/mol) from EMSURE® and sodium hydroxide (NaOH, MW = 40.00 g/mol) from EMSURE®. All of the materials used in this project were summarised in Table 3.1.

Table 3.1: Materials Used and Their Respective Functions

No.	Material	Function
1	Polyethersulfone, PES	Polymer
2	n-methyl-2-pyrrolidone, NMP	Solvent
3	Polyvinylpyrrolidone, PVP	Additive, pore former
4	Titanium dioxide, TiO ₂	Additive, nanoparticle
5	Sodium sulfate anhydrous, Na ₂ SO ₄	Inert drying agent
6	n-hexane, C ₆ H ₁₄	Oil extraction solvent
7	Sodium hydroxide, NaOH	Cleaning agent

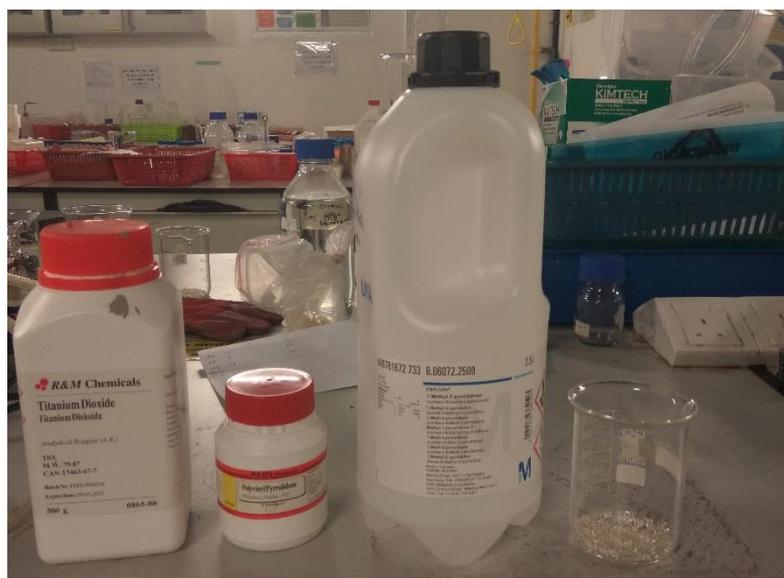


Figure 3.1: Titanium Dioxide, PVP, NMP and PES Used (from left to right)



Figure 3.2: Other Materials Used (a)Sodium Sulfate Anhydrous, (b) n-hexane, (c) Sodium Hydroxide

3.2 Preparation of Membrane Dope Solutions

The membrane dope solutions with different compositions were prepared before the membrane fabrication. The dope solutions consisted of PVDF, NMP, PVP and TiO₂. In this study, one MF membrane was fabricated due to its function of pre-treating the feed solution whereas four UF membranes were fabricated with different compositions. The compositions of five respective sets of membrane dope solutions were summarised in Table 3.2.

Table 3.2: Compositions of Membrane Dope Solutions

Membrane ID	Type of Membrane	Composition (wt. %)			
		PES	NMP	PVP	TiO ₂
M1	MF	12	84.0	4	0
U1	UF	16	83.0	1	0
U2	UF	16	82.9	1	0.1
U3	UF	16	82.5	1	0.5
U4	UF	16	82.0	1	1.0

For MF membrane (M1), the compositions of PES, NMP and PVP were 12, 84 and 4 wt.% respectively, whereas the additive particle was not added into dope solution of M1. However, for UF membranes, the composition of pore forming additive, PVP was set as a constant value of 1 wt.% throughout the experiments. Meanwhile, the polymer loading remained constant at 16 wt.%. Therefore, the characteristics of UF membranes were unique by varying the composition of pore forming additive and solvent. The UF dope solutions or membranes were named as U1, U2, U3 and U4, indicating different compositions of TiO₂ ranging from 0 to 1 wt.%. Lastly, the solvent, NMP would hold the remaining composition of dope solution, achieving a total composition of 100 wt.%.

By knowing the composition of membrane dope solution, the preparation of a homogenous UF dope solution was started by drying the PES pellets overnight in an oven at a temperature of 50 °C to reduce the moisture content. The dried PES pellets were then added into correspond amount of NMP solvent. Subsequently, one weight percent of PVP and pre-weighed correspond amount of TiO₂ particles were added into the mixture to produce the dope solution. The mixture was then stirred agitation at 600 rpm and was heated at 50 °C for approximately four hours as shown in Figure 3.3 in order to obtain a completely-dissolved dope solution. Finally, as illustrated in Figure 3.4, the dope solution was placed in a ultrasonication probe for thirty minutes so that the air bubbles trapped in the solution were completed removed.



Figure 3.3: Stirring Process For Membrane Dope Solutions



Figure 3.4: Ultrasonication Process For Membrane Dope Solutions

3.3 Preparation of Flat Sheet Membrane

The method used in membrane fabrication process was known as phase inversion technique whereby the solvent and non-solvent would exchange with each other. The well-mixed dope solution was poured and was spread evenly over the smooth surface of a clean glass plate. Subsequently, a casting knife was used to cast the membrane with a thickness of 200 μm . The polymer film was then immersed into the coagulation bath which filled with distilled water. The phase inversion process was said to be carried out completely when the membrane flat sheet was stripped off from the plate.

3.4 Membrane Characterization

The fabricated membranes were examined with various analyses in order to study their structure, properties and functionality.

3.4.1 Scanning Electron Microscope (SEM) Analysis

Before SEM analysis, the membranes were immersed into liquid nitrogen and were fractured to obtain ideal cut structure. The membranes were then sputter coated with gold by using a sputter coater (Model: SC7620, Emitech) as shown in Figure 3.5 before being viewed under SEM. The morphological structures of the membranes such as surface and cross section micrographs images were then analysed by scanning electron microscope (Model: S-3400, Hitachi) as depicted in Figure 3.6 under a wide range of magnification. The focal lengths used were unique for each specimen and the applied voltage was set at 15.0 kV.



Figure 3.5: Sputter Coater (Model: SC7620, Emitech)



Figure 3.6: Scanning Electron Microscope (Model: S-3400, Hitachi)

3.4.2 Energy-dispersive X-ray Spectroscopy (EDX) Analysis

Energy-dispersive X-ray Spectroscopy (EDX) was an analysis technique used simultaneously with SEM to determine the compositions of existing components in the fabricated membranes and the distribution of TiO₂ additive. The membrane sample was cut into small pieces and the active layer on the membrane surface was examined by EDX.

3.4.3 Fourier Transform Infrared Spectrometer (FTIR) Analysis

Fourier Transform Infrared Spectrometer (Model: Nicolet iS10, Thermo Scientific) as illustrated in Figure 3.7 was used to detect the functional groups of the fabricated membranes. After cleaning the specimen holder with alcohol, the background spectrum was collected. The membrane specimen, which was cut into a tiny piece, was placed on the specimen holder for FTIR analysis by taking the spectrum of single-beam sample. The spectrum of the specific sample was obtained from the ratio of the spectrum of single-beam sample to background spectrum.



Figure 3.7: Fourier Transform Infrared Spectrometer (Model: Nicolet iS10, Thermo Scientific)

3.4.4 Membrane Porosity

The membrane porosity was calculated by dividing the total volume of the porous membrane from the pore volume as shown in Equation 3.1. The weight of wet membrane was first measured by using an analytical weight balance before the 24-hour drying process. The weight of dry membrane was then measured in order to obtain the membrane porosity. The measurement was repeated for three times and the average value was recorded for each membrane sample.

$$\varepsilon = \frac{\frac{(w_{wet}-w_{dry})}{\rho_w}}{\frac{(w_{wet}-w_{dry})}{\rho_w} + \frac{w_{dry}}{\rho_p}} \times 100 \% \quad (3.1)$$

where

ε = membrane porosity (%)

w_{wet} = weight of wet membrane, g

w_{dry} = weight of dry membrane, g

ρ_w = density of water, g/cm³

ρ_p = density of polymer, g/cm³

3.4.5 Mean Pore Radius

Guerout-Elford-Ferry equation was used to compute the mean pore radius by the mean of filtration velocity method as shown in Equation 3.2 (Huang et al., 2012).

$$r_m = \sqrt{\frac{(2.9-1.75\varepsilon)8\eta lQ}{\varepsilon A \Delta P}} \quad (3.2)$$

where

r_m = mean pore radius, m

ε = membrane porosity (%)

η = viscosity of water at 25 °C, Pa·s

l = thickness of membrane, m

Q = volume of permeate water per unit time, m³/h

A = effective membrane area, m²

ΔP = transmembrane pressure, Pa

3.4.6 Pure Water Flux

The purpose of pure water permeability test was to investigate the permeability of the fabricated membrane and to examine the membrane fouling issue. This test was conducted after filling the stirred cell (Model: HP4750, Sterlitech) with 300 mL of distilled water. The fabricated membranes were cut into tiny round pieces with the area of 14.6 cm². The MF membrane (M1) was pressurized or experienced compaction with

distilled water at the pressure of 1 bar. The time required to obtain 100 mL of pure water permeate was measured and was recorded. Subsequently, the water permeate flux was then computed by Equation 3.3. The test was repeated for the other membranes (U1, U2, U3 and U4).

$$J_w = \frac{Q_w}{A \times t} \quad (3.3)$$

where

J_w = pure water flux, L/(m²·h)

Q_w = quantity of pure water permeate, L

A = effective membrane area, m²

t = time required to obtain the quantity of pure water permeate, h

3.5 Preparation of Synthetic Produced Water

The synthetic produced water was collected by i-Chem Solution Sdn. Bhd. from a tank depot cleaning company. The company was involved in oil and gas industry and the wastewater from tank cleaning was known as tank dewatering produced water.

3.6 Experimental Setup

The description of dead-end filtration system, operating parameters and the membrane cleaning process was further discussed in this session.

3.6.1 Dead-end Filtration System

The schematic diagram of this experimental setup was depicted in Figure 3.8. The experimental apparatus of the dead-end membrane system included a pressurized cylinder filled with nitrogen gas, a pressure regulator, a stirred cell (Model: HP4750, Sterlitech) and a magnetic stirrer. The diagram of stirred cell was shown in Figure 3.9. The nitrogen gas was used to pressurize the feed solution (either distilled water or synthetic produced water) and to maintain the pressure gradient across the membrane. The stirred cell was continuously stirred on the magnetic stirrer at 680 rpm in order to provide a shear force to reduce the solid cake built up on the membrane surface.

The fabricated membrane (M1) was cut into tiny round pieces with the area of 14.6 cm^2 . The solution was then forced through M1 at the pressure of 2 bar. After the filtration process, the permeate was collected and the volume of permeate was measured by the measuring cylinder. The permeate was then recycled to the stirred cell for UF process. The steps for UF process are similar to the MF module but the membrane inside the stirred cell was changed to UF membrane (U1) and the operating pressure was altered between 3 and 6 bar with an interval of 1 bar. While maintaining the MF process, the whole experiments were repeated with different UF membranes (U2, U3 and U4).

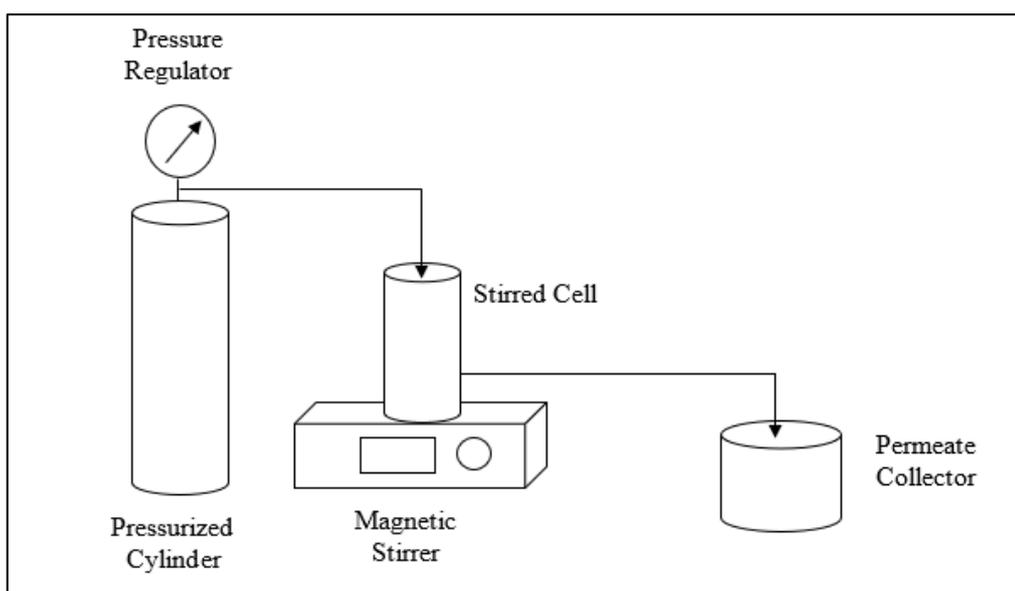


Figure 3.8: Schematic Diagram of Dead-end Filtration System



Figure 3.9: Diagram of Sterlitech HP4750 Stirred Cell System

3.6.2 Permeate Flux

The purpose of oil permeability test was to investigate the permeability of the fabricated membrane and to examine the membrane fouling issue by using the result of pure water flux test as a reference. This test was conducted after filling the stirred cell with 300 mL of synthetic produced water. After the filtration process, the volume of permeate collected was measured every five minutes until 100 mL of permeate was collected. Subsequently, the oil permeate flux was then computed by Equation 3.4. The test was repeated for the other membranes (U1, U2, U3 and U4).

$$J_p = \frac{Q_p}{A \times t} \quad (3.4)$$

where

J_p = oil permeate flux, L/(m²·h)

Q_p = quantity of oil permeate, L

A = effective membrane area, m²

t = time required to obtain the quantity of oil permeate, h

3.6.3 Measurement of Oil Concentration

The measurement of oil concentration was conducted through partition-gravimetric method. Firstly, one hundred millimetres of oil permeate was first collected in a beaker. Four millimetres of 37 % hydrochloric acid was then added drop by drop into the oil permeate. The solution was mixed well and was tested with a pH meter to ensure the maximum of pH 2 was achieved to hydrolysed oil and grease. The mixture was then poured into 500 mL separatory funnel as shown in Figure 3.10 (a). Ten millimetres of n-hexane solvent was added into the separatory funnel for the first oil extraction. The separatory funnel was stoppered and was inverted in order to release the gas through the stopcock. The funnel was then vigorously shaken for two minutes until no more gas escaped. The gas was released at the stopcock every thirty seconds to prevent high pressure accumulates at the end of the stopper.

The separatory funnel was left to stand undisturbed for approximately ten minutes to ensure a perfect separation between the lower water layer and upper solvent layer. The water layer was slowly drained from the separatory funnel into a beaker as depicted in Figure 3.10 (b). Several drops of solvent were allowed to drain into the

water layer to ensure complete transfer of the water layer. The glass funnel was then put in the neck of the conical flask. A piece of filter paper was folded and was put on the glass funnel before adding 5 g of anhydrous sodium sulphate to the filter paper. The solvent was drip-drained into the conical flask through the glass funnel as illustrated in Figure 3.10 (c). The sodium sulphate which mixed with the solvent on the filter paper was gently stirred by a glass rod when the solvent layer was draining.

The water layer collected in the beaker was poured into the separatory funnel. The second and third oil extractions were carried out to ensure the oil content was extracted out completely. Subsequently, the separatory funnel was rinsed with 5 mL of n-hexane to remove any residual oil left on the funnel walls.



Figure 3.10: Oil Extraction Process (a) Experimental Setup, (b) Separation of Water Layer and Solvent Layer, (c) Drip-draining of Solvent Through Glass Funnel

For the measurement of oil concentration, the solvent collected in the conical flask was poured into a 100 mL beaker which had been weighed beforehand. After completely evaporation of solvent, the oil content was retained in the beaker. The weight of the beaker containing residual oil was then measured. The oil concentration was calculated by using Equation 3.5.

$$C = \frac{m_o - m_b}{q} \quad (3.5)$$

where

C = oil concentration, mg/L

m_o = mass of oil and beaker, mg

m_b = mass of plain beaker, mg

Q = quantity of oil, L

3.6.4 Oil Rejection

The initial oil feed concentration and the concentrations after the both MF and UF processes were calculated with Equation 3.5. The oil rejection percentage was then determined through Equation 3.6.

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100 \% \quad (3.6)$$

where

R = oil rejection (%)

C_p = concentration of permeate, mg/L

C_f = concentration of feed, mg/L

3.6.5 Membrane Cleaning

The membrane cleaning process for fouled membrane was conducted in order to identify a proper cleaning method and to provide a reusable membrane with similar oil removal efficiency. Based on the membrane performance test, the oil permeate flux decreased continuously and the oil rejection efficiency reduces along with time. This was because the membrane fouling problem occurs during the filtration process.

Sodium hydroxide (NaOH) was selected as the cleaning agent due to its capability in removing the foulants blocked within the membrane pores and on the membrane surface. There were three concentrations of NaOH solution (0.1, 0.5 and 1.0 M) to be tested in this study. The durations for immersion of fouled membrane into the cleaning agent were 10, 30 and 60 minutes. The cleaning process was performed under room temperature.

3.6.6 Flux Recovery Ratio

The antifouling nature of the membrane had to be accounted by cleaning the fouled membrane immediately once the permeate flux declined drastically. The initial pure water flux was calculated with Equation 3.3 previously. After immersing the membrane into NaOH solution for a certain period, the distilled water was forced through the chemically-cleaned membrane and the pure water flux was determined again with Equation 3.3. Consequently, the flux recovery ratio was calculated with Equation 3.6.

$$FRR = \frac{J_{w2}}{J_{w1}} \times 100 \% \quad (3.7)$$

where

FRR = flux recovery ratio (%)

J_{w1} = initial pure water flux of fresh membrane, L/(m²·h)

J_{w2} = pure water flux of chemically-cleaned membrane, L/(m²·h)

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Membrane Characterization

The characterization tests were conducted after fabrication of flat sheet membrane in order to investigate the elements found in the membranes and to study the structures of the respective membranes. The characterization methods were also assisted in ensuring better incorporation of TiO₂ nanoparticles with the polymeric materials. Therefore, the characterization tests should be carried out and analysed prior to membrane performance tests.

4.1.1 Scanning Electron Microscope (SEM)

The images of cross sectional of membranes were extracted from SEM analysis with different magnification scales and were shown in Figure 4.1.

- (A1) Membrane MF: focal length of 10.0 mm, magnified at 500×
- (A2) Membrane MF: focal length of 9.9 mm, magnified at 2,000×

- (B1) Membrane U1: focal length of 6.0 mm, magnified at 400×
- (B2) Membrane U1: focal length of 6.1 mm, magnified at 2,000×

- (C1) Membrane U2: focal length of 5.4 mm, magnified at 400×
- (C2) Membrane U2: focal length of 5.4 mm, magnified at 2,000×

- (D1) Membrane U3: focal length of 7.1 mm, magnified at 400×
- (D2) Membrane U3: focal length of 7.1 mm, magnified at 2,000×

- (E1) Membrane U4: focal length of 7.4 mm, magnified at 400×
- (E2) Membrane U4: focal length of 7.4 mm, magnified at 2,000×

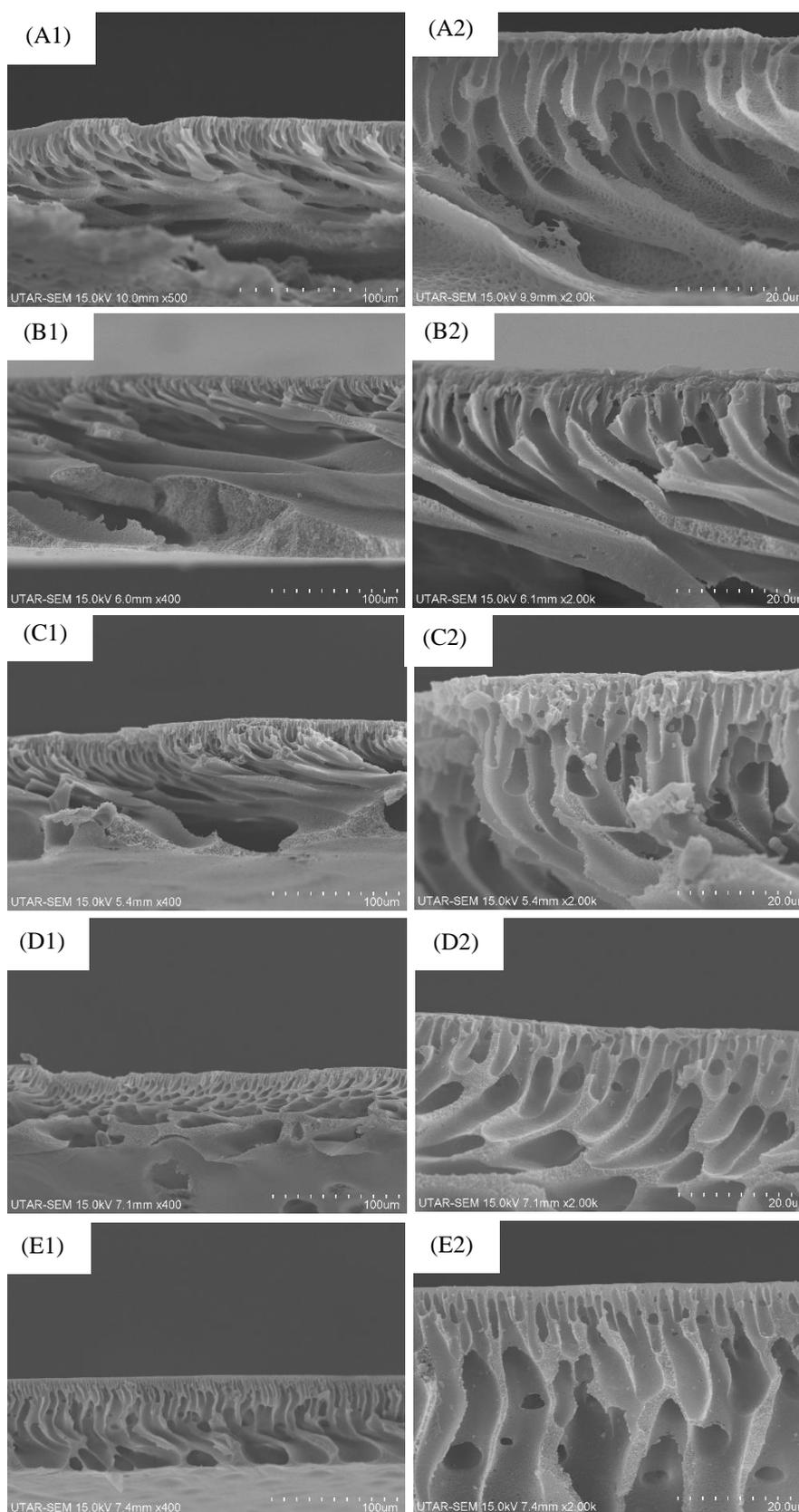


Figure 4.1: SEM Images of Cross Section for Membranes (A) M1, (B) U1, (C) U2, (D) U3, (E) U4 under Different Magnification Scales

As referring to Figure 4.1, most of the membranes illustrates the formation of macrovoid with loosely packed structures. The membrane typically consists of two layers, which are a dense top finger-like layer and a spongy porous support layer. The formation of these structures can be explained by the instantaneous demixing of solvent and polymer during the phase inversion process. There is no apparent difference in the cross-sectional structures of the PES UF membranes since the TiO_2 concentration ranging from 0 wt.% until 1.0 wt% is not significant. However, U4 membrane contains comparatively more finger-like projections because greater amount of hydrophilic TiO_2 contributed in the absorption of water during the phase inversion process. The overall SEM micrographs have proved that higher nanoparticles loading increases the membrane porosity and pore size.

According to Figure 4.2, the dispersion of TiO_2 additives on the surface of UF membranes can be observed from SEM micrographs upon the addition of nanoparticles from 0 wt.% to 1.0 wt.%. M1 membrane might be contained some impurities which caused the top surface rougher compared to others. U1 membrane surface is relatively smooth due to homogeneous mixing at the preparation phase of dope solution. The white dots shown on the Figures 4.2 (c), (d) and (e) indicates the incorporation of TiO_2 additives. U4 membrane with the highest nanoparticles loading shows that the greater number of white dots have greater sizes due to the agglomeration of nanoparticles.

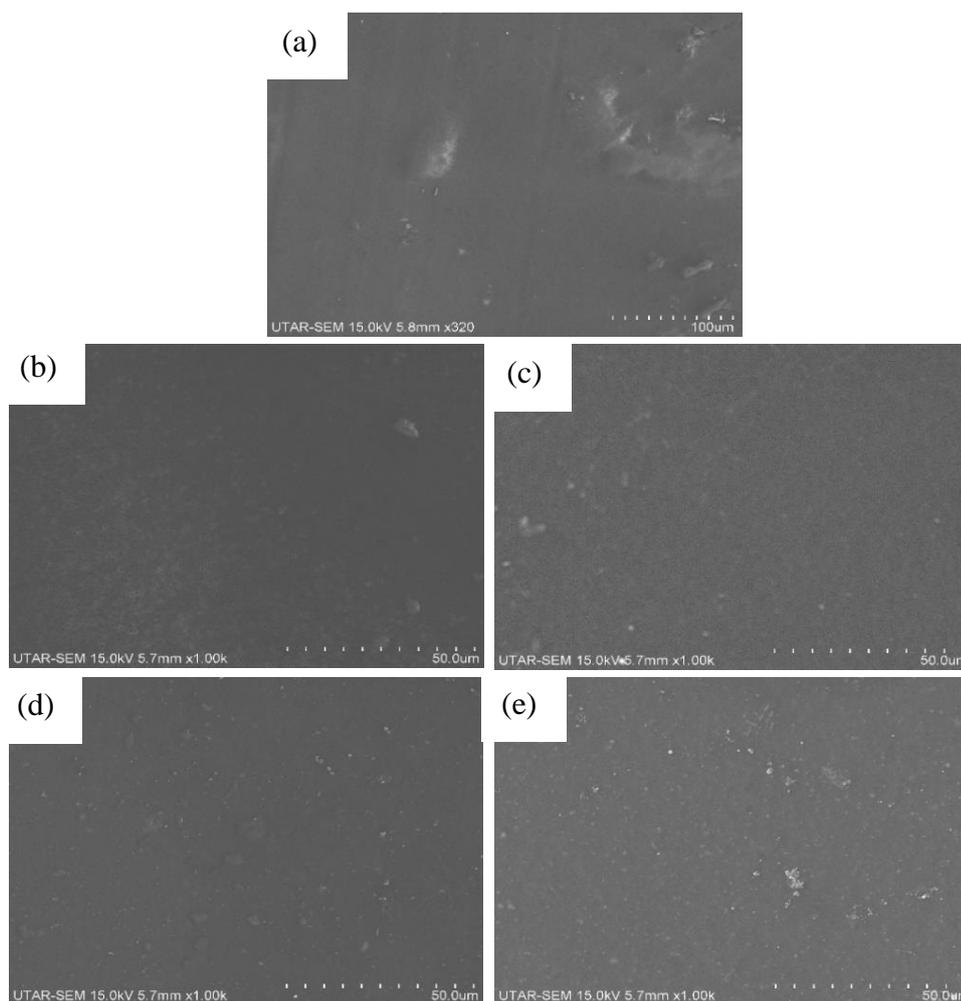


Figure 4.2: SEM Images of Surface Morphology for Membranes (a) M1, (b) U1, (c) U2, (d) U3, (e) U4 under Different Magnification Scales

4.1.2 Energy Dispersive X-ray (EDX)

The EDX analysis provides an individual graph showing the intensity of elements found in the membrane and their specific energies measured in the unit of keV as shown in Appendix A. The graph for each membrane is paired with a table which displays the weight percent and atomic percent of elements. A summary table for all membranes are presented in Tables 4.1 and 4.2.

According to Tables 4.1 and 4.2, the TiO_2 nanoparticles are proved to be incorporated successfully into the polymer dope solution. For all membranes, high proportion of carbon, oxygen and sulphur are detected as the molecular structure of PES consists of these three elements as shown in Figure 4.3. Besides, M1 membrane should not contain any Ti element but 0.11 wt.% has been detected. Moreover, the detectable value of Ti element in U2, U3 and U4 are also different with the actual

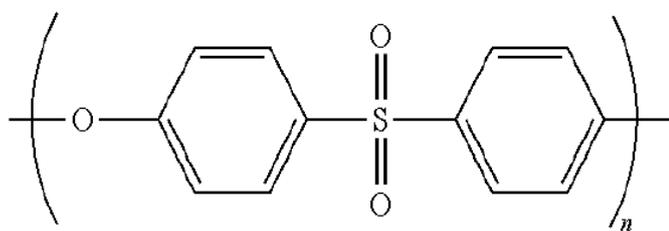
compositions. The deviation may be caused by the statistical error when the X-ray intensity was measured by counting the photons. However, the increasing trend of Ti composition can be observed from U1 to U4 as shown in Table 4.1.

Table 4.1: Weight Percent (wt.%) of Membrane

Element	Weight Percent (wt.%) of Membrane				
	M1	U1	U2	U3	U4
C	60.02	61.16	62.08	60.19	57.05
O	20.09	29.70	22.56	30.65	22.96
S	19.79	09.14	14.89	08.51	16.19
Ti	00.11	00.00	00.46	00.65	03.80

Table 4.2: Atomic Percent (At%) of Membrane

Element	Atomic Percent (At%) of Membrane				
	M1	U1	U2	U3	U4
C	72.71	70.40	73.28	69.54	70.17
O	18.27	25.66	20.00	26.59	21.20
S	08.98	03.94	06.59	03.68	07.46
Ti	00.03	00.00	00.14	00.19	01.17



Polyethersulfone (PES)

Figure 4.3: Chemical Structure of PES

4.1.3 Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR results are demonstrated as transmittance percentage (%) against wavelength (cm^{-1}) for the membrane as depicted in Figures 4.4 and 4.5. The graphs retrieved from FTIR analysis were modified by recognizing the important functional groups and were marked on the specific transmittance peaks. The FTIR test was

conducted to identify the presence of PES composition in the sample specimen. The functional groups for PES include a benzene ring, an ether bond and a sulphone structure as shown in Figure 4.3. The FTIR spectra shows the presence of aromatic C-H stretch between 3000 and 3100 cm^{-1} . Meanwhile, the S=O stretching peaks are found between 1000 and 1200 cm^{-1} . The aromatic C-H bending peaks are located between 680 and 900 cm^{-1} . Therefore, the results strongly indicate the existence of PES in the membranes.

The transmittance peaks located between 3500 and 3700 cm^{-1} represents the stretching peaks of O-H functional group. The result can be explained by the contamination of alcohol on the probe or specimen holder of FTIR during pre-cleaning process before FTIR testing. Low intensity of alcohol bond indicates that there was a little alcohol left without removing it completely.

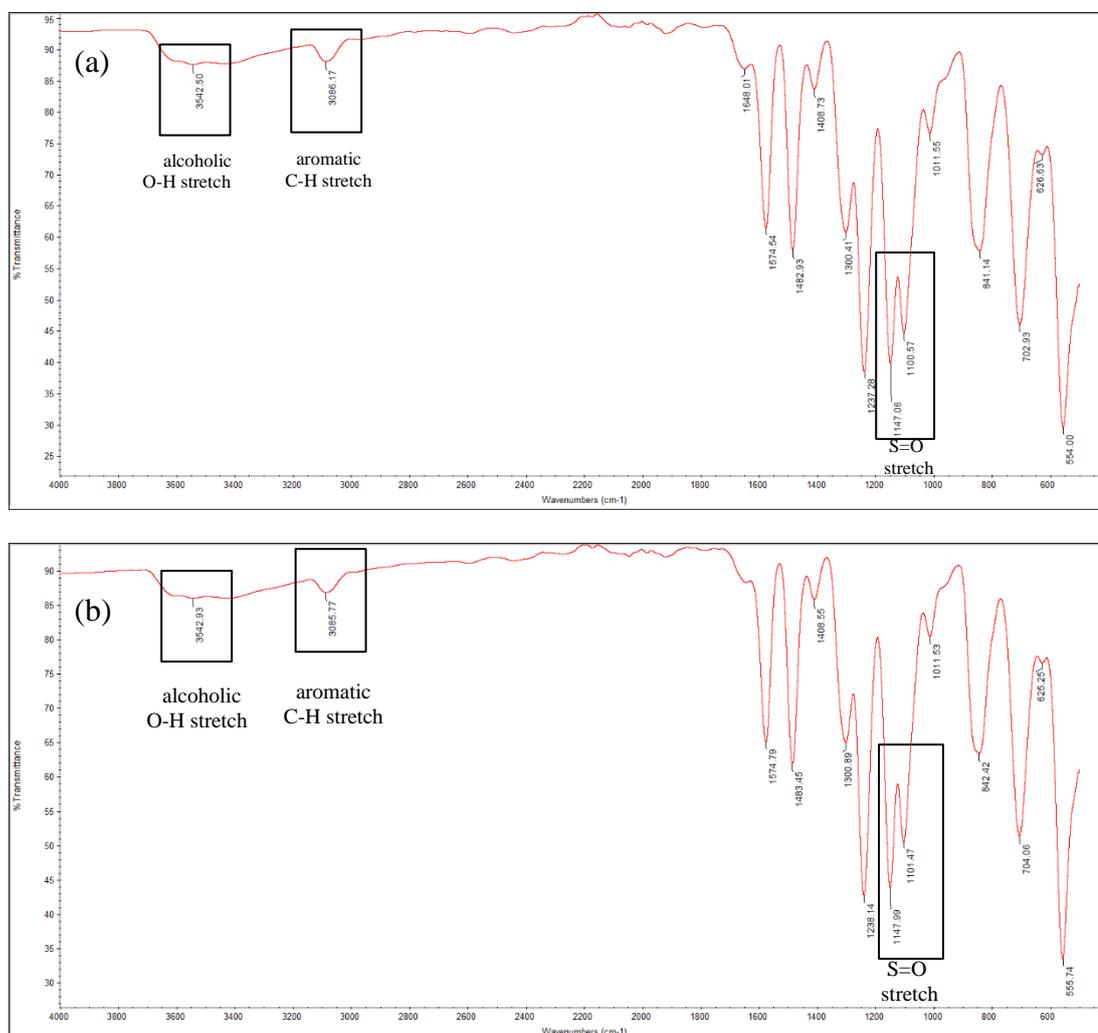


Figure 4.4: FTIR Spectra of Membranes (a) M1, (b) U1

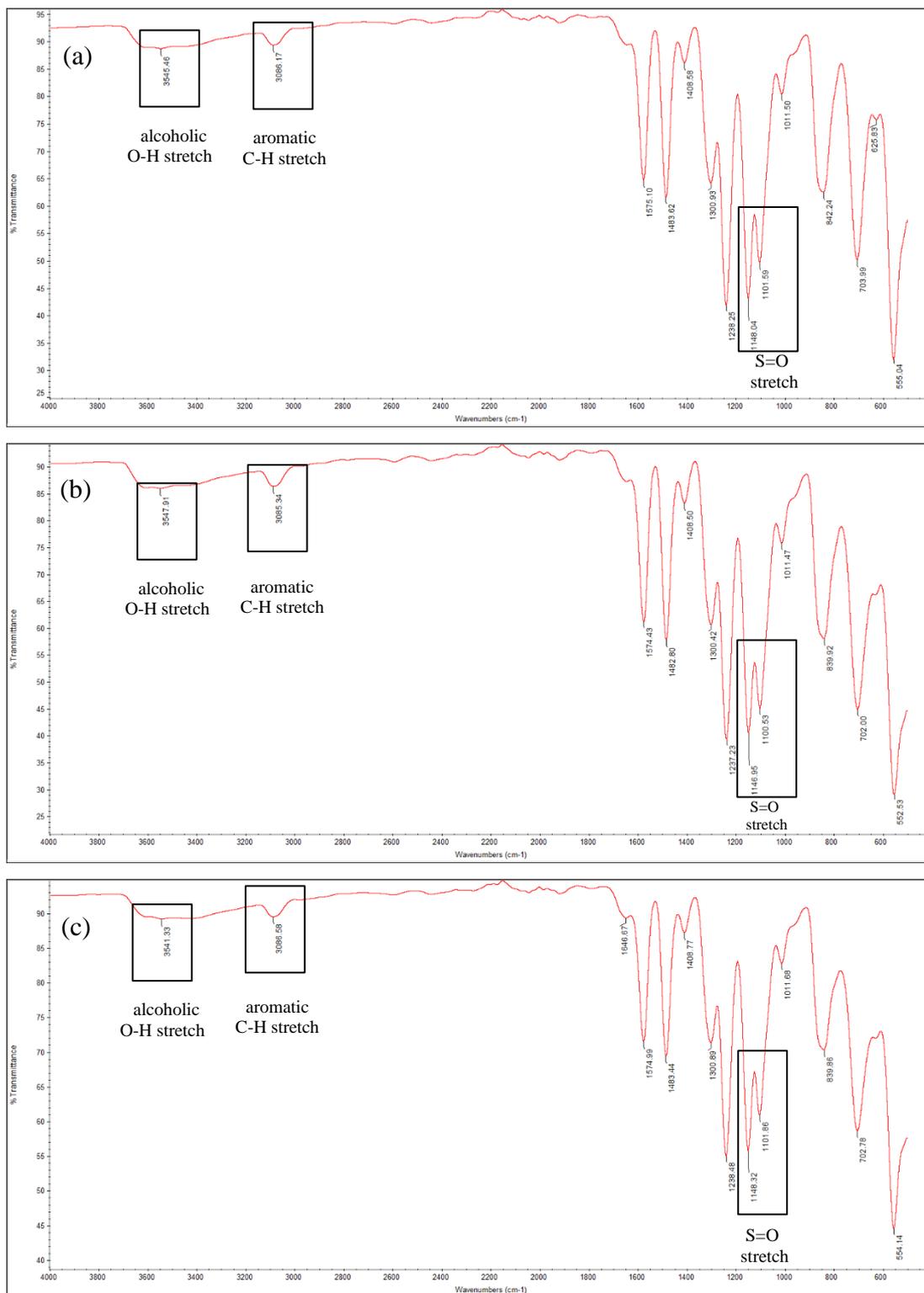


Figure 4.5: FTIR Spectra of Membranes (a) U2, (b) U3, (c) U4

4.1.4 Porosity and Pore Size

The properties of PES membranes with respect to their porosity and pore size are summarized in Table 4.3. All fabricated membranes illustrate considerably high porosity with a minimum value of 85.26 %, whereby the improvement on membrane porosity is insignificant compared to other researches, where the porosity would increase drastically with the addition of TiO₂ additives. In this study, the porosity and pore size of MF (M1) membrane are higher than those for UF membranes. This phenomenon is caused by the higher composition of PVP at 4 wt.% which tends to induce mixture demixing during phase inversion process and to further enhance the phase separation. This situation is in good agreement with the research conducted by Yuan and Li (2008).

The average pore size is directly proportional with the membrane porosity. The calculated pore size of M1 membrane is 2.45 μm , which is in the range of MF membrane. For UF membranes, the pore sizes are between 0.071 μm and 0.091 μm , which are proved to be the membranes with proper UF pore diameters. As the nanoparticles loading increases, the increment of porosity and pore size can be noticed. The presence of TiO₂ tends to weaken the affinity of membrane dope solution when compared with the dope solution without nanoparticles, resulting in an increase of porosity as well as pore size. Therefore, it is suggested that addition of TiO₂ nanoparticles will enhance the pore formation as supported by the SEM cross section micrographs.

Table 4.3: Porosity and Pore Size of Membrane

Membrane	Porosity (%)	Pore Size (μm)
M1	93.10	2.45
U1	85.26	0.071
U2	87.67	0.076
U3	89.26	0.082
U4	89.58	0.091

4.1.5 Pure Water Flux

According to Figure 4.6, it can be seen that the permeability of M1 membrane is the highest compared with UF membranes. This is because higher composition of PVP has been added into the dope solution and PVP additive enhances the pore formation. There is a huge gap between the permeability of MF membrane and UF membrane. This phenomenon is coincided with the porosities and pore sizes of membranes as presented in Table 4.3. As the pore sizes of UF membranes are relatively small, less amount of water is allowed to pass through the membranes.

For UF membranes, the pure water flux is ranging between 668.82 LMH and 768.15 LMH. The increasing trend of permeability can be explained by the addition of TiO₂ nanoparticles from 0 wt.% to 1.0 wt.%. U4 membrane with higher hydrophilicity has higher attraction towards water which allows the water droplets to spread out on the membrane surface and pass through the pore spontaneously. Consequently, increment of TiO₂ nanoparticles causes an increase of macrovoid formation and porosity, leading to an increase of pure water permeability.

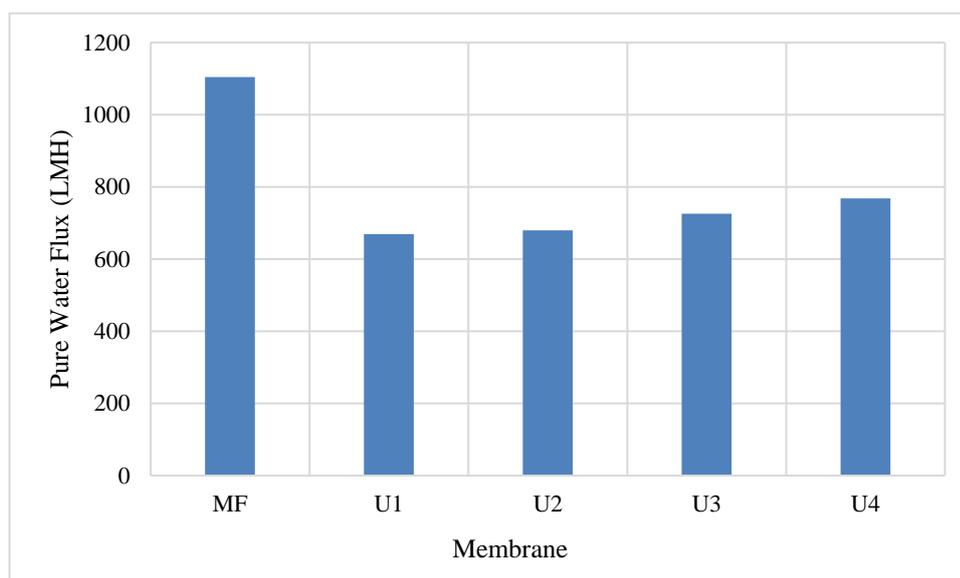


Figure 4.6: Pure Water Flux of Membrane under 1 bar

4.2 Membrane Performance

The permeate flux, oil rejection efficiency and the flux recovery ratio are discussed in this part.

4.2.1 Effect of Pre-treatment on Permeate Flux and Oil Rejection Rate

The permeate flux of pre-treatment, M1 membrane under 2 bar is presented in Figure 4.7. The permeate flux declines drastically from 123.29 LMH to 86.30 LMH at the first ten minutes. The permeate flux continuously reduces to 30.44 LMH throughout the filtration process in a duration of 135 minutes. The reduction of flux can be explained by the occurrence of membrane fouling which requires to undergo a cleaning process.

Besides, when compared with the pure water flux of M1 membrane, the flux decreases from 1104.09 LMH to 30.44 LMH. This phenomenon is caused by the accumulation of oil droplets on the membrane surface, resulting in an addition of transport resistance for water to oil permeate as well as the reduction in permeate flux.

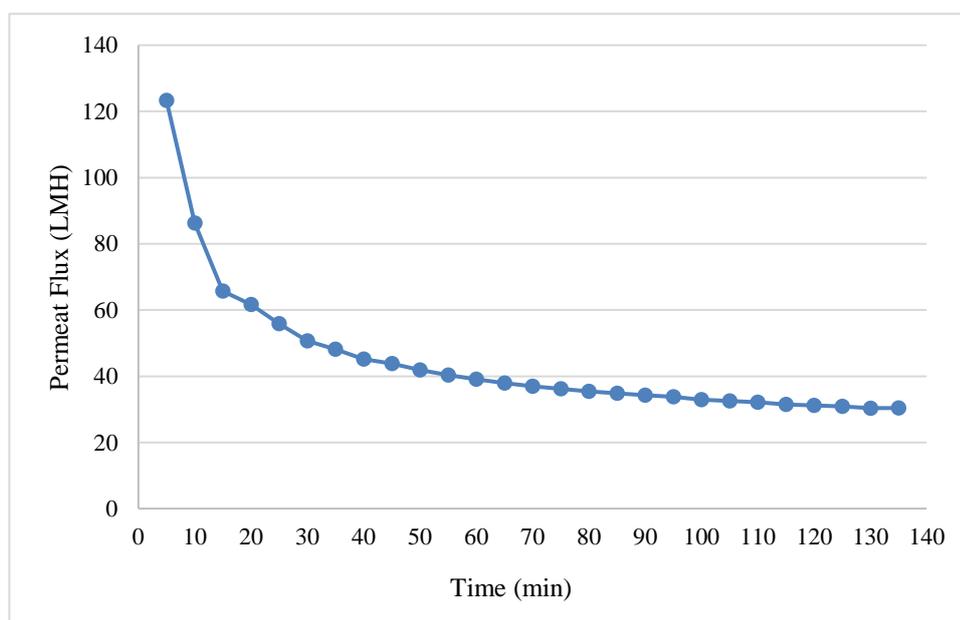


Figure 4.7: Permeate Flux of M1 Membrane against Time under 2 bar

For the oil rejection, the initial oil concentration of the synthetic produced water is 556.33 mg/L, whereas the oil content of wastewater after MF process is 265.11 mg/L as shown in Table 4.4. Therefore, the calculated oil removal rate is only 52.35 %.

Table 4.4: Oil Removal Analysis on M1 Membrane

Oil Concentration (mg/L)		Oil Removal (%)
Feed Solution	MF Permeate	
556.33	265.11	52.35

4.2.2 Effect of TiO₂ Concentration and Transmembrane Pressure on Permeate Flux

Figure 4.9 illustrates the permeate flux of ultrafiltration membranes under different pressure. All line graphs exhibit the similar trends with microfiltration membrane as depicted in Figure 4.8, whereby the permeate flux continuously declines with time. It is found that the permeate flux increases with the addition of TiO₂ nanoparticles from U1 to U4 membranes. This phenomenon can be explained by the improved hydrophilic properties after adding TiO₂ additives. Therefore, greater amount of permeate is allowed to pass through the membrane.

Based on Figure 4.8, for U1 membrane without TiO₂ additive, the permeate flux increases from 45.66 LMH at a transmembrane pressure of 3 bar to 50.23 LMH at a transmembrane pressure of 6 bar. Meanwhile, for U4 membrane with 1.0 wt.% TiO₂ nanoparticle, the permeate flux also raises from 46.80 LMH at 3 bar to 55.25 LMH at 6 bar. The bar graphs indicate that higher pressure exerts higher force that allow more wastewater to flow through respective membrane, leading to an increase of permeate flux with greater pressure.

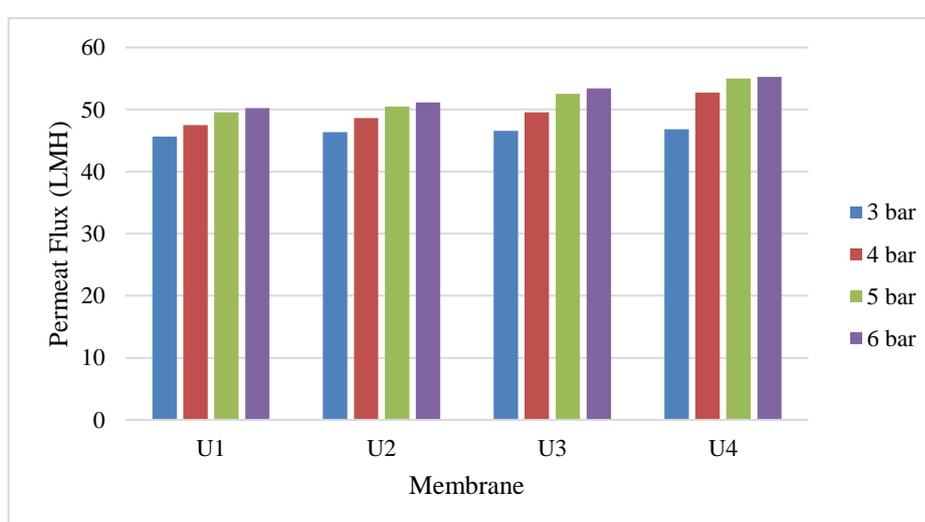


Figure 4.8: Permeate Flux of U1, U2, U3, U4 Membranes at 90 minutes under Different Transmembrane Pressures

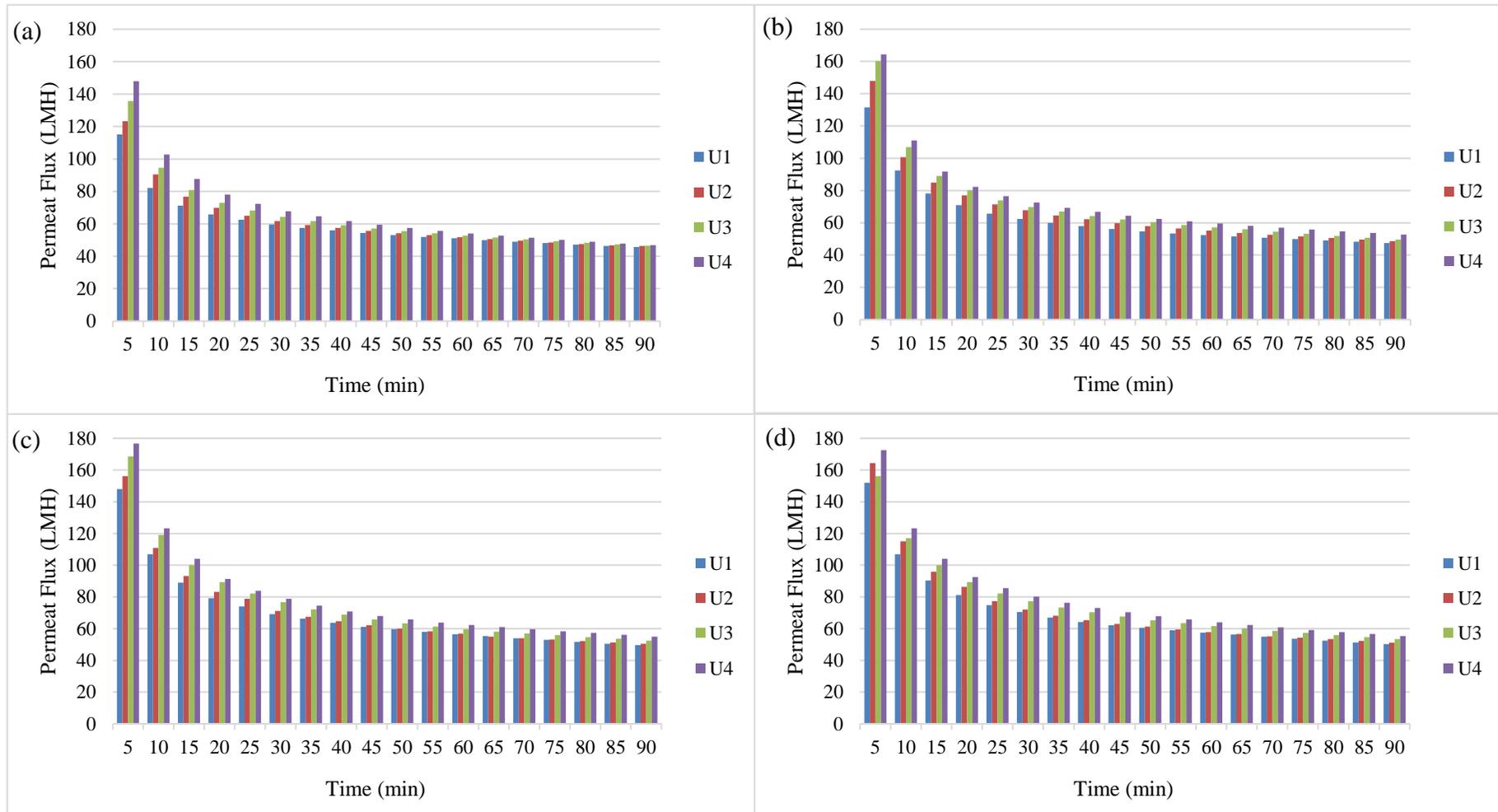


Figure 4.9: Permeate Flux of U1, U2, U3 and U4 Membranes against Time under Different Pressures (a) 3 bar, (b) 4 bar, (c) 5 bar, (d) 6 bar

4.2.3 Effect of TiO₂ Concentration and Transmembrane Pressure on Oil Rejection Rate

The oil rejection rate of each membrane under different pressure is presented in Figure 4.10. At the transmembrane pressure of 3 bar, the oil removal rate exhibits a relatively constant trend but the oil removal rate increases slightly from 89.24 % for U1 to 95.71 % for U4. The overall oil rejection which is the rejection rate for combined MF and UF processes thereby increases from 94.87 % for U1 to 97.96 % for U4. The slight improvement is attributed to the enhanced hydrophilicity coupled with the increase in pore diameter upon increment of highly hydrophilic additive (Ong et al., 2013).

However, at the transmembrane pressure of 4 bar, the line graph shows an opposite trend when compared with the trend at the transmembrane pressure of 3 bar. The oil removal rate declines from 92.64 % for U1 to 85.94 % for U4. Hence, the overall oil rejection rate also decreases from 96.49 % for U1 to 93.30 % for U4. The main reason contributed to this abnormal phenomenon is human error. The solvent layer containing oil droplets was not completely evaporated, whereby the measurement of oil concentration might not only include residual oil but also the solvent.

At the transmembrane pressures of 5 bar and 6 bar, both of the oil removal trends are similar with the increasing trend at 3 bar. The oil removal rate of UF membranes and the overall oil rejection rates increases with the addition of TiO₂ nanoparticles. It is observed that most of the membranes illustrate the promising oil rejection performances, where at least 82.34 % oil rejection can be achieved. The highest overall oil removal rate can reach as high as 97.96 %.

By comparing the oil removal rate for different transmembrane pressures, the oil rejection is slightly reduced from 3 bar to 6 bar. This phenomenon is coincided with the research conducted by Masoudnia et al. (2014), where it is mainly caused by membrane fouling issue and the cake resistance decreases with an increase of transmembrane pressure. More oil droplets can pass through the membrane with high pressure without blocking by membranes, leading to a decline in oil rejection rate.

By considering the permeate flux and oil rejection, it is evidenced that PES membrane prepared by 1.0 wt.% additive is the optimum membrane to be used in UF process at the transmembrane pressure of 3 bar due to moderate permeate flux and excellent oil removal greater than 97 %.

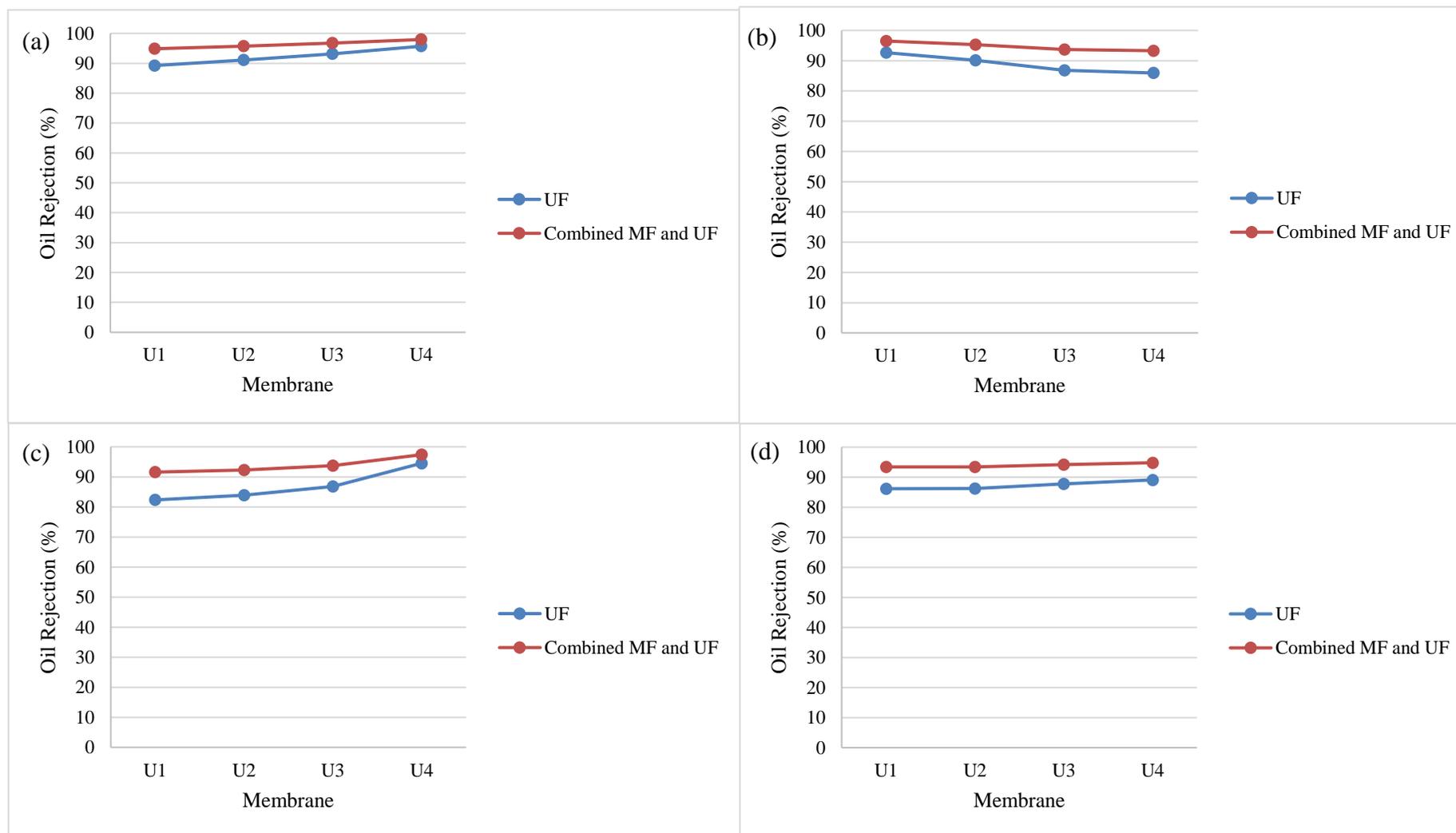


Figure 4.10: Oil Rejection of U1, U2, U3 and U4 Membranes under Different Pressures (a) 3 bar, (b) 4 bar, (c) 5 bar, (d) 6 bar

The appearances of oily wastewater at different stages are depicted in Figure 4.11. The feed solution is in relatively dark brown colour, indicating greater quantity of oil droplets and impurities. After the pre-treatment process, the colour has changed to pale brown due to removal of 52.35 % of oil. The final permeate after UF process is as clear as water, and the transparency increases. Therefore, the appearance of the wastewater is in accordance with the oil rejection.

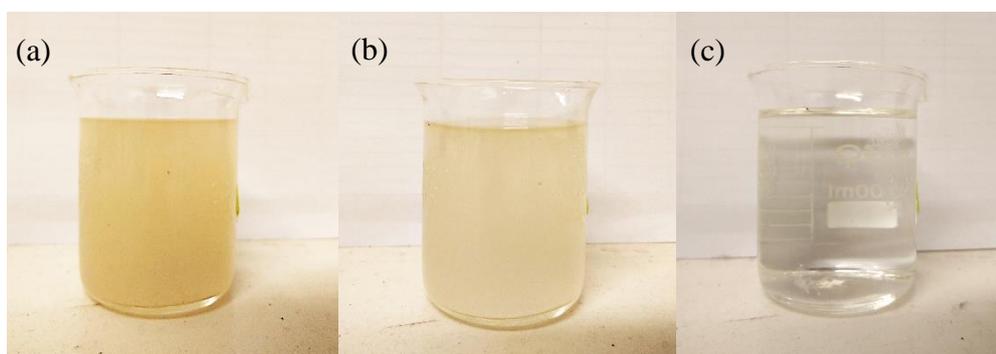


Figure 4.11: Appearance of Oily Wastewater (a) Feed Solution, (b) Permeate after MF Process, (c) Permeate after UF Process

4.2.4 Effect of Membrane Cleaning on Flux Recovery Ratio (FRR)

The recovery ratio of the fouled M1 membrane after cleaning by NaOH solution with different concentration and immersing duration is shown in Figure 4.12. It is noticeable that most of the flux recovery ratio are generally low as the best recovery result of 52.18 % is just slightly higher than 50 % after cleaning with 1.0 M NaOH solution. For the basic aqueous solution at a lower concentration of 0.1 M, the flux recovery ratio is lower than 20 %. According to Figure 4.12, the recovery performances exhibit similar trends between each other. It can be concluded that the flux recovery ratio increases with prolonged immersing duration and higher concentration of NaOH solution.

The results from membrane cleaning are coincided with the research conducted by Masoudnia et al. (2014), which reported that the recovery after washing by NaOH solution is low because the basic solution is not effective in removal of oil droplets within the membrane pores. By employing NaOH solution as the cleaning agent, the oil droplets deposited on the surface of the membrane can be eliminated and the cake layer formed on the surface reduced slightly. However, the irreversible fouling cannot be easily treated by NaOH solution but intense chemical or thermal treatment should

be applied. Therefore, this finding suggested that the cleaned M1 membranes are not suitable to be reused as NaOH solution is not sufficient to remove all the foulants and to let the fouled membranes recovered back to the original pure water flux.

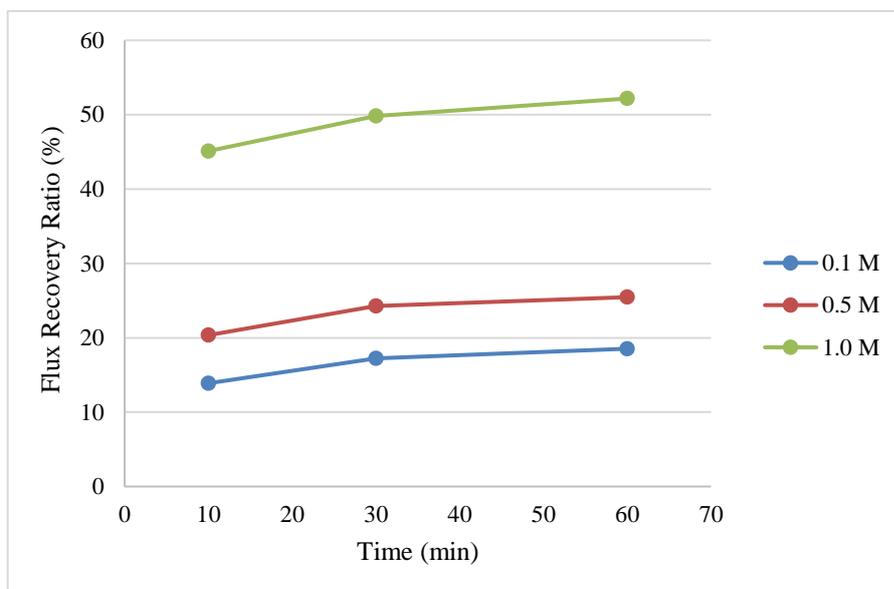


Figure 4.12: Flux Recover Ratios of M1 Membrane After Cleaning with Different Concentrations of NaOH Solution

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Throughout the research, the treatment of synthetic produced water using hybrid membrane processes was initiated by combining microfiltration as pre-treatment and ultrafiltration with different concentrations of TiO₂ nanoparticles ranging from 0 wt.% to 1.0 wt.%. The fabricated membranes were characterized by SEM, EDX, FTIR and permeability tests. The SEM cross section micrographs showed that all membranes comprised of dense top finger-like layers and porous spongy support layers. U4 membrane surface contained the highest number of white particles with larger size due to the agglomeration of nanoparticles. From the FTIR and EDX analyses, the chemical composition of fabricated membranes was in accordance with the composition of prepared dope solution, but the weight percent of Ti element was slightly different due to the statistical error. The increase in TiO₂ nanoparticles enhance the pore formation, porosity and pure water permeability due to improved hydrophilicity. In terms of membrane performance, the permeate flux of MF and UF membranes declined with time, whereas the permeate flux of UF membrane increased with the increase of TiO₂ nanoparticles and transmembrane pressure. Besides, the oil removal rate after MF process was only 52.35 %, whereas the oil rejection efficiency using UF process was in the range between 82.34 % and 95.71 %. Overall, the oil removal rate using the hybrid membrane processes could achieve as high as 97.96 %. Based on the results, PES membrane incorporated with 1.0 wt.% was found to be the most promising membrane since it exhibited the best separation performance in oil removal at a transmembrane pressure of 3 bar. The best recovery rate (52.18 %) after the membrane cleaning process was achieved using 1.0 M NaOH solution. Nevertheless, individual NaOH solution was proved to be not sufficient to overcome the fouling issue.

5.2 Recommendations for Future Work

Since the oil rejection rate can be affected by hydrophilicity, the hydrophilic additives should be added into the membrane dope solution. Different types of additives are suggested to be employed and adding higher concentration of TiO₂ nanoparticles are highly recommended to have a significant effect on oil removal and permeate flux.

Besides, different operating parameters for ultrafiltration process such as pH, temperature and initial oil concentration can be practised. Therefore, optimum values for these parameters can be obtained and the proper treatment of synthetic produced water can be identified.

Membrane characterization becomes significant in this study in order to improve the membrane performance. Additional characterization test such as X-ray Diffraction (XRD) can be conducted to determine the presence of TiO₂ nanoparticles in the fabricated membranes.

Moreover, for better analysis on the membrane surface morphology, Field Emission Scanning Election Microscope (FESEM) is encouraged to be employed so that the membrane pore sizes can be easily viewed by greater magnification. Besides, a better understanding on the distribution of nanoparticles on the membrane can be obtained.

In addition, membrane fouling problem is an important issue which has to be solved in order to provide reusable membrane for cost saving purpose. Therefore, other cleaning agents such as acid, surfactant and combination of basic and acid should be used to investigate the flux recovery ratio after membrane cleaning.

Furthermore, for measurement of oil concentration, greater amount of oil permeate should be collected rather than only collecting 100 mL of permeate. This is because analysing greater quantity of oil mixture will provide a more precise result on the oil content. By using greater amount of oil permeate, greater amount of solvent (n-hexane) also has to be used to completely extract out the oil droplets. Therefore, the solvent layer containing oil droplets should be evaporated through rotary evaporator and the n-hexane can be collected and reused, avoiding wastage of solvent and environmental pollution. Alternatively, green and environmental friendly solvent, such as ionic liquid, will be of great interest in future research in oil extraction.

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APPENDICES

APPENDIX A: EDX Results for Section 4.1.2

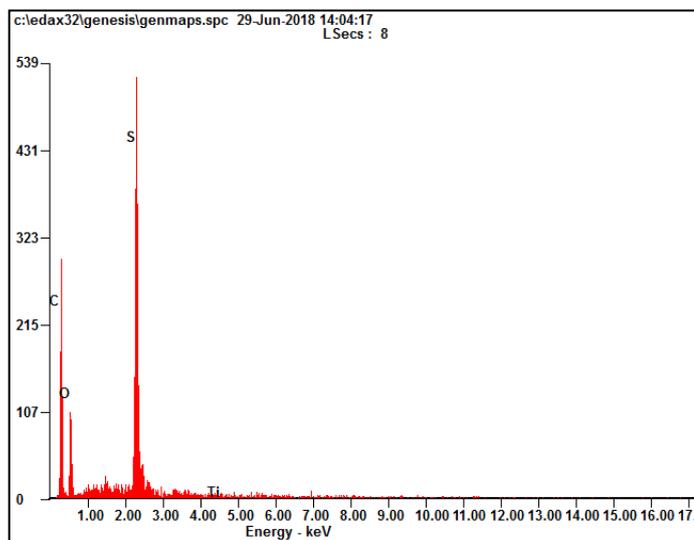


Figure A-1: Intensity of Elements in M1 membrane

Table A-1: Chemical Composition of M1 membrane

<i>Element</i>	<i>Wt%</i>	<i>At%</i>
<i>CK</i>	60.02	72.71
<i>OK</i>	20.09	18.27
<i>SK</i>	19.79	08.98
<i>TiK</i>	00.11	00.03
<i>Matrix</i>	Correction	ZAF

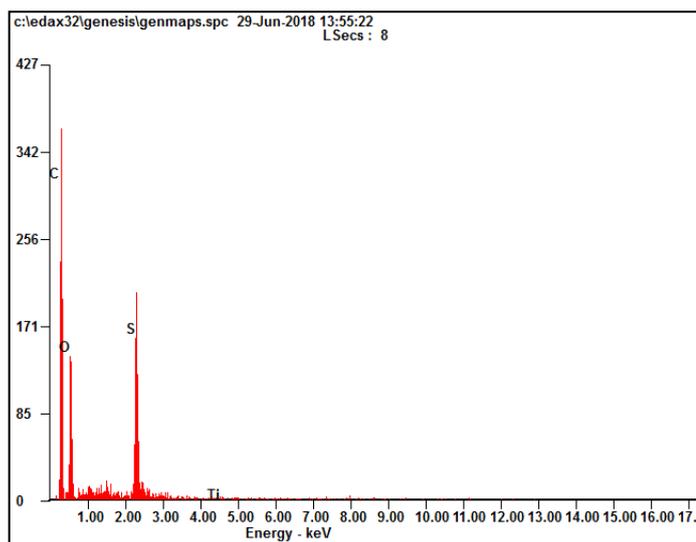


Figure A-2: Intensity of Elements in U1 Membrane

Table A-2: Chemical Composition of U1 Membrane

<i>Element</i>	<i>Wt%</i>	<i>At%</i>
<i>CK</i>	61.16	70.40
<i>OK</i>	29.70	25.66
<i>SK</i>	09.14	03.94
<i>TiK</i>	00.00	00.00
<i>Matrix</i>	Correction	ZAF

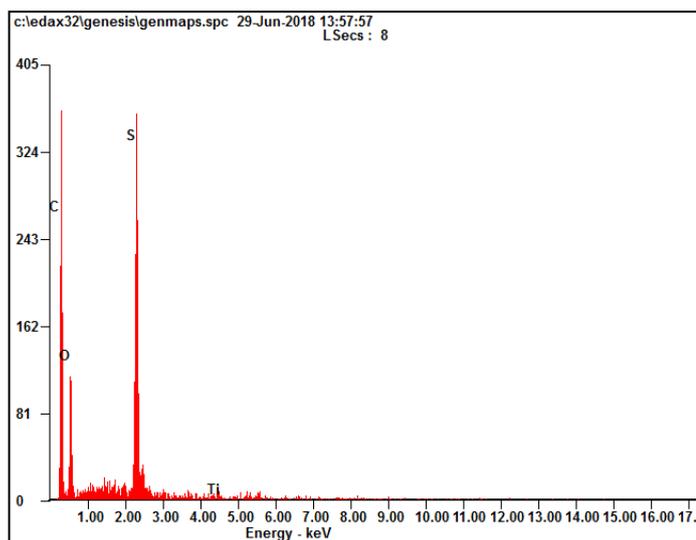


Figure A-3: Intensity of Elements in U2 Membrane

Table A-3: Chemical Composition of U2 Membrane

<i>Element</i>	<i>Wt%</i>	<i>At%</i>
<i>CK</i>	62.08	73.28
<i>OK</i>	22.56	20.00
<i>SK</i>	14.89	06.59
<i>TiK</i>	00.46	00.14
<i>Matrix</i>	Correction	ZAF

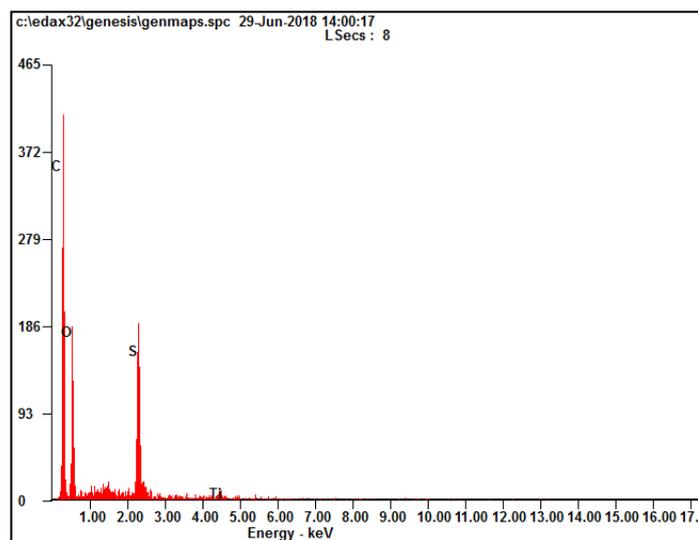


Figure A-4: Intensity of Elements in U3 Membrane

Table A-4: Chemical Composition of U3 Membrane

<i>Element</i>	<i>Wt%</i>	<i>At%</i>
<i>CK</i>	60.19	69.54
<i>OK</i>	30.65	26.59
<i>SK</i>	08.51	03.68
<i>TiK</i>	00.65	00.19
<i>Matrix</i>	Correction	ZAF

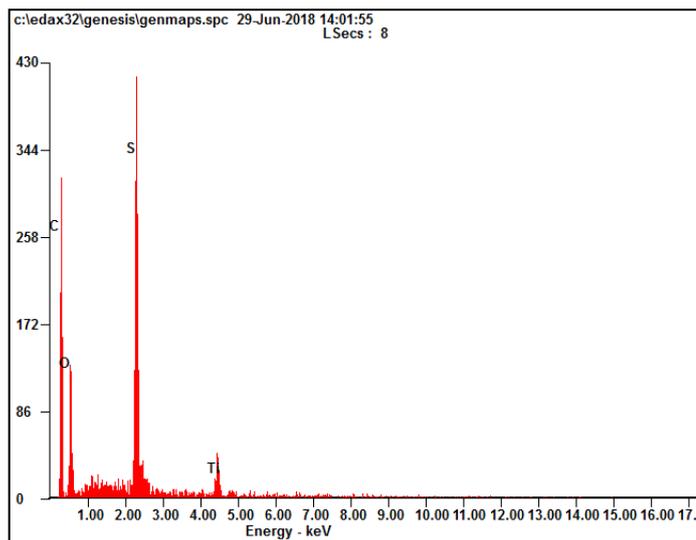


Figure A-5: Intensity of Elements in U4 Membrane

Table A-5: Chemical Composition of U4 Membrane

<i>Element</i>	<i>Wt%</i>	<i>At%</i>
<i>CK</i>	57.05	70.17
<i>OK</i>	22.96	21.20
<i>SK</i>	16.19	07.46
<i>TiK</i>	03.80	01.17
<i>Matrix</i>	Correction	ZAF