

**PREPARATION AND CHARACTERIZATION OF  
SUPERHYDROPHOBIC MEMBRANE FOR DESALINATION  
USING DIRECT CONTACT MEMBRANE DISTILLATION**

**MOHAANEESH A/L NAGARAJAH**

**UNIVERSITI SAINS MALAYSIA**

**2018**

**PREPARATION AND CHARACTERIZATION OF  
SUPERHYDROPHOBIC MEMBRANE FOR DESALINATION  
USING DIRECT CONTACT MEMBRANE DISTILLATION**

**by**

**MOHAANEESH A/L NAGARAJAH**

**Thesis submitted in partial fulfilment of the requirement for the  
degree of Bachelor in Chemical Engineering**

**June 2018**

## **ACKNOWLEDGEMENT**

Firstly, I would like to convey my sincere appreciation to my supervisor, Associate Professor Ir. Dr. Leo Choe Peng for her endless encouragement, guidance and support in this final year project. Her patience and vast knowledge are truly admirable and helpful. I thank her for her assistance throughout the span of my final year thesis completion. She was always willing to sacrifice her time in teaching and correcting me for my study work. Something that I truly value.

I would also extend my sincere gratitude to the final year project coordinator, Associate Professor Dr. Azmier Ahmad for his never ending effort and supervision to assist all the final year students on completing this undertaking. Not forgetting, I also thank my mentors Ms. Norhaziyana Hamzah and Ms. Nor Aini Ahmad who never fail to guide me even with their tight postgraduate schedules. They have been extremely helpful in teaching and sharing valuable information throughout the experiment.

Apart from that, I wish to thank all SCE staffs for their kindness cooperation and helpful hands. Their contributions have provided me a concrete academic and technical platform, which was very helpful when carrying out this study. Indeed their willingness in sharing ideas, knowledge and skills are deeply appreciated.

Last but not least, I would like to express my heartiest gratitude to my beloved parents and dearest friends for their continuous motivation. Their moral support helped me a lot in completing this study. Again, I would like to thank everyone who might have helped me directly or indirectly. Their contributions are very much appreciated. Thank you.

**MOHAANEESH A/L NAGARAJAH**  
**June 2018**

## TABLE OF CONTENT

<b>CHAPTER 1: INTRODUCTION</b>	<b>1</b>
1.1 Solving water crisis using advanced membrane technology principles.	1
1.2 Problem Statement	5
1.3 Objectives	5
1.4 Scope of study	6
1.5 Organization of thesis	7
<b>CHAPTER 2: LITERATURE REVIEW</b>	<b>8</b>
2.1 Hydrophobic Membrane Separation	8
2.2 Hydrophobic Membrane Separation Applications	9
2.2.1 Oil Filtration	9
2.2.2 Membrane Gas Absorption	10
2.3 Membrane Distillation	11
2.3.1 Desalination using membrane distillation	11
2.3.2 Membrane distillation configurations	12
2.4 Membrane Synthesis	14
2.4.1 Phase Inversion Method	14
2.4.2 Electrospinning	16
2.5 Superhydrophobic Membrane	17
2.6 Membrane Characteristics	17
2.6.1 Contact Angle	18
2.6.2 Liquid Entry Pressure (LEP)	19
2.6.3 Membrane porosity and tortuosity	20
2.7 Nanoparticles in polymeric membrane	21
2.8 Mass transfer resistance through membrane distillation	21
2.9 Scanning Electron Microscopy (SEM)	22
<b>CHAPTER 3: MATERIAL AND METHOD</b>	<b>23</b>
3.1 Materials and Chemicals	23
3.2 Equipment and Facilities Required	24
3.3 Membrane preparation	25
3.4 Membrane casting	26
3.5 Direct Contact Membrane Distillation (DCMD)	27
3.6 Contact angle measurements	28
3.7 Membrane surface morphology analysis	28

3.8 Silane solution preparation	29
3.9 Membrane composition analysis	30
3.10 Liquid Entry Pressure (LEP) and porosity calculations	30
<b>Chapter 4: Results and Discussion</b>	<b>32</b>
4.1 Effect on the characteristics of modified and unmodified PVDF membrane	32
4.1.1 Water Contact Angle	32
4.1.2 Fourier Transform Infrared Spectroscopy (FTIR)	38
4.1.3 Liquid Entry Pressure (LEP)	40
4.1.4 Surface Morphology (SEM)	41
4.1.5 Membrane Porosity	47
4.2 Effects of fouling on separation performance of direct contact membrane distillation (DCMD)	48
4.2.1 Membrane distillation of distilled water using varying membrane type.	48
4.2.2 Membrane distillation of salt solution (NaCl) using the PVDF-SiO <sub>2</sub> membrane.	53
4.2.3 Membrane distillation of oily salt (NaCl) solution using the PVDF-SiO <sub>2</sub> membrane.	54
<b>Chapter 5: Conclusion and Recommendation</b>	<b>55</b>
5.1 Conclusion	55
5.2 Recommendations	56
<b>References</b>	<b>57</b>
<b>APPENDIX</b>	<b>60</b>

## LIST OF TABLES

		<b>Page</b>
Table 2.1	Membrane distillation configurations and description	13
Table 2.2	Methods used in phase inversion and description	15
Table 2.3	Membrane polymer with its contact angle and surface	18
Table 2.4	Polymeric membrane liquid entry pressure (LEP) and corresponding pore sizes	20
Table 3.1	List of materials and chemicals	23
Table 3.2	List of equipment and facilities	24
Table 3.3	Table of dope solution preparation criteria	25

## LIST OF FIGURES

		<b>Page</b>
Figure 1.1	Global water demand: Baseline scenario, 2000 and 2050	2
Figure 1.2	Water purification technology and its efficiency	4
Figure 2.1	Membrane diffusion mechanism	8
Figure 2.2	Typical oil filtration configuration. (Sadrzadeh, et al., 2008)	9
Figure 2.3	Typical membrane gas absorption configuration. (Ahmad, et al., 2010)	10
Figure 2.4	Electrospinning process set up (Tamberg, 2014)	16
Figure 3.1	Membrane casting machine	26
Figure 3.2	Direct contact membrane distillation (DCMD) set up	27
Figure 3.3	Rame-Hart Goniometer	28
Figure 3.4	Scanning Electron Microscopy (Hitachi TM3000)	29
Figure 3.5	Thermo Scientific FTIR unit	30
Figure 3.6	Porometer (Porolux 1000)	31
Figure 4.1	Chart of contact angle for Blank-PVDF membrane	34
Figure 4.2	Water droplet image of Blank (a) Unmodified (b) Silane 1:25 (c) Silane 1:50 (d) Silane 1:100 (e) Silane 1:200	34
Figure 4.3	Chart of contact angle for PVDF-TiO <sub>2</sub> -SiO <sub>2</sub> membrane	35
Figure 4.4	Water droplet image of Mixed (a) Unmodified (b) Silane 1:25 (c) Silane 1:50 (d) Silane 1:100 (e) Silane 1:200	35
Figure 4.5	Chart of contact angle for PVDF-TiO <sub>2</sub> membrane	36

Figure 4.6	Water droplet image of PVDF-TiO <sub>2</sub> (a) Unmodified (b) Silane 1:25 (c) Silane 1:50 (d) Silane 1:100 (e) Silane 1:200	36
Figure 4.7	Chart of contact angle for PVDF-SiO <sub>2</sub> membrane	37
Figure 4.8	Water droplet image of PVDF-SiO <sub>2</sub> (a) Unmodified (b) Silane 1:25 (c) Silane 1:50 (d) Silane 1:100 (e) Silane 1:200	37
Figure 4.9	Fourier Transform Infrared Spectroscopy (FTIR) analysis of (a) Blank PVDF (b) PVDF-TiO <sub>2</sub> -SiO <sub>2</sub> (c) PVDF-TiO <sub>2</sub> (d) PVDF-SiO <sub>2</sub> membranes	38
Figure 4.10	LEP of Blank-PVDF, PVDF-TiO <sub>2</sub> -SiO <sub>2</sub> , PVDF-SiO <sub>2</sub> and PVDF-TiO <sub>2</sub> before and after silane grafting	40
Figure 4.11	SEM image for Blank (a) Unmodified (b) Silane 1:50 (c) Silane 1:100 (d) Silane 1:200 membrane of magnification 1.0k	42
Figure 4.12	SEM image for PVDF-TiO <sub>2</sub> -SiO <sub>2</sub> (a) Unmodified (b) Silane 1:50 (c) Silane 1:100 (d) Silane 1:200 membrane of magnification 1.0k	43
Figure 4.13	SEM image for PVDF-TiO <sub>2</sub> (a) Unmodified (b) Silane 1:50 (c) Silane 1:100 (d) Silane 1:200 membrane of magnification 1.0k	44
Figure 4.14	SEM image for PVDF-SiO <sub>2</sub> (a) Unmodified (b) Silane 1:50 (c) Silane 1:100 (d) Silane 1:200 membrane of magnification 1.0k	45



Figure 4.15	SEM image for distilled water fouled PVDF-SiO <sub>2</sub> membrane of magnification 1.0k	46
Figure 4.16	SEM image for distilled salt fouled PVDF-SiO <sub>2</sub> membrane of magnification 1.0k	46
Figure 4.17	SEM image for salt and oil fouled PVDF-SiO <sub>2</sub> membrane of magnification 1.0k	46
Figure 4.18	Chart of membrane porosity volume	48
Figure 4.19	Flux vs Time curve for membrane distillation of distilled water using Blank-PVDF membrane	50
Figure 4.20	Flux vs Time curve for membrane distillation of distilled water using PVDF-TiO <sub>2</sub> -SiO <sub>2</sub> membrane	51
Figure 4.21	Flux vs Time curve for membrane distillation of distilled water using PVDF-TiO <sub>2</sub> membrane	52
Figure 4.22	Flux vs Time curve for membrane distillation of distilled water using PVDF-SiO <sub>2</sub> membrane	53
Figure 4.23	Flux vs Time curve for membrane distillation of salt solution (NaCl) using PVDF-SiO <sub>2</sub> membrane	54
Figure 4.24	Flux vs Time curve for membrane distillation of oily salt water using PVDF-SiO <sub>2</sub> membrane	55

## LIST OF ABBREVIATIONS

AGMD	Air Gap Membrane Distillation
DCMD	Direct Contact Membrane Distillation
FO	Forward Osmosis
FTIR	Fourier Transform Infrared
LEP	Liquid Entry Pressure
MD	Membrane Distillation
NaCl	Sodium Chloride
NMP	N-methyl-pyrrolidone
PP	Polypropylene
PTFE	Polytetrafluoroethylene
PVDF	Polyvinylidene Fluoride
RO	Reverse Osmosis
rpm	Rotation per minute
SEM	Scanning Electron Microscopy
SGMD	Sweep Gas Membrane Distillation
SiO <sub>2</sub>	Silicon Dioxide
TiO <sub>2</sub>	Titanium (IV) Oxide
VMD	Vacuum Membrane Distillation
WHO	World Health Organization

# **PREPARATION AND CHARACTERIZATION OF SUPERHYDROPHOBIC MEMBRANE FOR DESALINATION USING DIRECT CONTACT MEMBRANE DISTILLATION**

## **ABSTRAK**

Air masin adalah air permukaan yang mengandungi pelbagai jenis kekotoran atau bahan pencemar. Air kumbahan juga menyumbang kemasinan yang tinggi ke permukaan air. Oleh itu, rawatan air adalah penting dalam mengekalkan kualiti air. Dalam kajian penyelidikan ini, rawatan air masin dilakukan dengan melakukan penyulingan membran sentuhan langsung (DCMD) yang merupakan proses pemisahan membran termal. Jenis membran poliamilidena fluorida (PVDF) jenis membran superhydrophobik dihasilkan dan diubahsuai dengan penambahan nanopartikel TiO<sub>2</sub> dan SiO<sub>2</sub> untuk meningkatkan kekasaran permukaan membran dan hidrofobisiti. Peyalutan silana juga dilakukan pada membran dengan menggunakan hexadecyltrimethoxysilana. Penyalutan silana dilakukan dengan mengubah nisbah silana dengan isipadu etanol pada 1:25, 1:50, 1: 100 dan 1: 200. Pencirian seperti sudut sentuhan air, tekanan masuk cecair (LEP), pengimbasan mikroskop elektron (SEM), Fourier Transform Spectroscopy Inframerah (FTIR) dan perhitungan keliangan telah dilakukan. Berdasarkan sudut sentuh air, membran PVDF-SiO<sub>2</sub> yang diubahsuai dengan nisbah silana 1:50 meghasilkan sudut sentuhan purata tertinggi berbanding dengan membran yang diubah suai yang lain iaitu 141.6 °. Oleh itu, membran PVDF-SiO<sub>2</sub> (1:50) digunakan untuk melaksanakan penyulingan membrane selanjutnya menggunakan air suling, larutan NaCl dalam kepekatan 1M dan larutan NaCl berminyak. Walaupun membran yang digunakan diubahsuai kepada keadaan hampir superhydrophobik, fenomena pengotoran masih berlaku dengan menganalisis lengkung fluks lawan masa untuk setiap eksperimen penyulingan membran.

# **PREPARATION AND CHARACTERIZATION OF SUPERHYDROPHOBIC MEMBRANE FOR DESALINATION USING DIRECT CONTACT MEMBRANE DISTILLATION**

## **ABSTRACT**

Saline water is the surface water that contains various types of impurities or contaminants. Wastewater also contributes high salinity to the surface water. Therefore, prior treatment of saline water is crucial in sustaining water quality. In this research study, the treatment of saline water is performed by carrying out direct contact membrane distillation (DCMD) which is a thermally driven membrane separation process. A polyvinylidene fluoride (PVDF) superhydrophobic membrane type is casted and modified with the addition of nanoparticles  $\text{TiO}_2$  and  $\text{SiO}_2$  in order to increase the membrane surface roughness and hydrophobicity. Silane grafting is also done on the membrane by using hexadecyltrimethoxysilane. The silane grafting was done by varying the silane to ethanol volume ratios of 1:25, 1:50, 1:100 and 1:200. Characterization such as water contact angle, liquid entry pressure (LEP), scanning electron microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR) and porosity calculations were done. Based on the water contact angle, modified PVDF- $\text{SiO}_2$  membrane with silane ratio 1:50 stated highest average contact angle compared to the other modified membranes which was  $141.6^\circ$ . Therefore, the PVDF- $\text{SiO}_2$  (1:50) membrane was used to further perform membrane distillation using distilled water, NaCl solution of 1M concentration and oily NaCl solution. Although the membrane used is modified to almost superhydrophobic condition, however, the fouling phenomenon was still observed by plotting the flux against time curves for each membrane distillation experiments

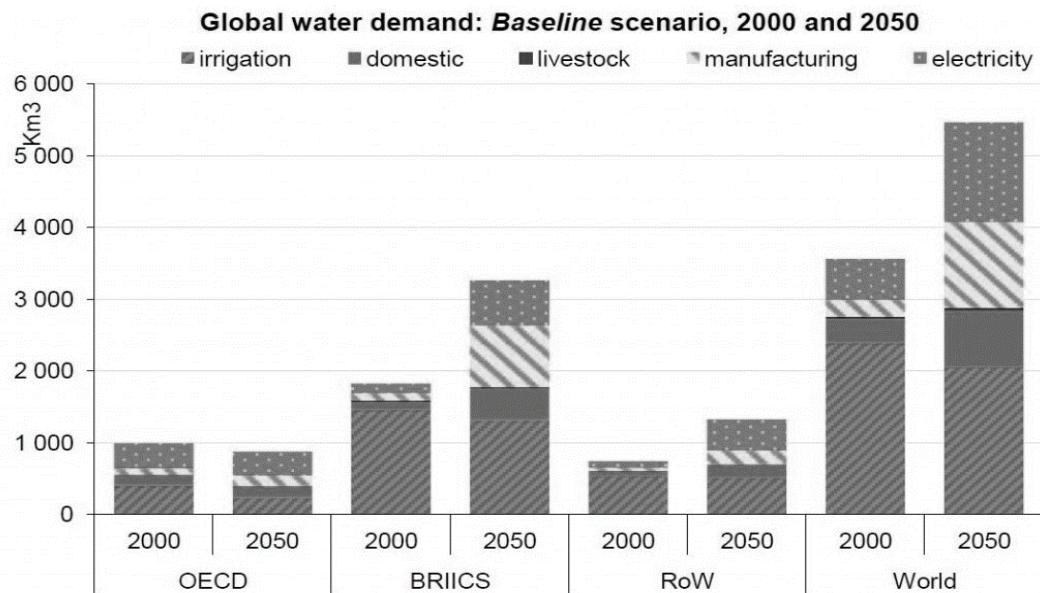
# CHAPTER ONE

## INTRODUCTION

### **1.1 Solving water crisis using advanced membrane technology principles.**

Water is known as the most abundantly existing compound on the Earth's surface and it occurs naturally in liquid, gas and also solid phases. Water covers approximately about 70% of our planet. It is always taken for granted that the water source is plentiful and there will be a continuous supply for drinking, food preparation, agriculture and sanitation. The fact is that, in some countries, fresh water supply are threatened as the demand is higher than its resources as shown in the Figure 1.1. Only 3% of the world's water is fresh water and two-thirds of it exists as frozen glaciers or otherwise unable for our use.

Clean water is vital for life, but majority from the developed world do not think much about the water they use. Millions of people die each year, especially children, due to various kind of preventable diseases caused by lack of access to clean water and proper sanitation. Every minute a newborn baby dies from infection caused by a lack of clean water and unclean environment (WHO, 2015). Due to these life concerning issues, water purification systems are given more attention to improve the lifestyle of human beings.



Note :BRIICS = Brazil, Russia, India, Indonesia, China and South Africa; RoW = rest of the world  
Source: *Environmental Outlook Baseline*; output from IMAGE suite of models.

Figure 1.1: Global water demand: Baseline scenario, 2000 and 2050

Globally, there are various types of water purification methods being practised. Water purification can be subdivided into chemical, biological and chemical methods. The chemical method for water purification includes water chlorination and fluoridation. The chlorination method is used to kill disease-causing pathogens such as viruses, protozoans and bacteria that are usually present in the water storages and streams. Biological methods also have been implemented in purifying water. Microorganisms are used to digest wastewater anaerobically and aerobically as the water treatment. The physical water treatment is the most common and effective way used to treat water for daily uses. Physical methods include screening, bag filtration, membrane filtration, multimedia filtration and a lot more. These processes are done to treat water physically which is one of the developing methods lately. Till date, there are more researches are being conducted worldwide in enhancing water treating and purification.

Physical methods for water treatments are dominated by the processes that involve a membrane as a barrier for mass transfer between desired components. These membrane-involving processes include membrane distillation (MD), reverse osmosis (RO), forward osmosis (FO) and etc. The reverse osmosis (RO) process is dependent on the osmotic pressure of the treated water. Reverse osmosis (RO) membrane properties greatly affect the water productivity and energy costs in the reverse osmosis desalination process (Li & Wang, 2010). On the other hand, the forward osmosis (FO) process has been used commonly to treat industrial wastewaters, to concentrate leachate and to treat liquid foods in the food industry. Lately, the forward osmosis (FO) is being evaluated for desalination applications to produce potable drinking water from seawater (Cath, et al., 2006). Membrane distillation (MD) is one of the emerging non-isothermal membrane separation processes. However, for the membrane distillation (MD) process, the driving force for the mass transfer is due to thermal energy and the vapor pressure gradient which is generated by the temperature difference across the hydrophobic membrane (Alkudhiri, et al., 2012). A vapour-liquid equilibrium is achieved for the separation of components in the feed.

The hydrophobicity of the membrane plays a very essential role in the membrane distillation process (MD). The hydrophobic nature of the membrane prevents wetting of the surface of the membrane that can cause penetration of the water due to surface tensions when the transmembrane pressure exceeds the liquid entry pressure (LEP) of the membrane. The type of hydrophobic membrane used can vary in type such as polytetrafluoroethylene (PTFE), polypropylene (PP) or polyvinylidene fluoride (PVDF) depending on the type of feed used for separation purposes (Alkudhiri, et al., 2012).

Though the membrane distillation (MD) process is advantageous in terms of lower energy costs (usage of heat waste), reduced vapour space and lower operating pressure than pressure-driven process such as reverse osmosis (RO), the membrane distillation (MD) has its drawbacks like membrane fouling and wetting (Onsekizoglu, p. 2000). Recent development to overcome this problem is by performing modification on the hydrophobic membrane to achieve superhydrophobicity properties.

	Distillation	Reverse Osmosis	Deioization	Electro-deaionization	Filtration	Ultrafiltration (UF)	Adsorption	Ultraviolet (UV) Oxidation	Combination UV/UF
Inorganic ions	Excellent	Good	Excellent	Excellent	Poor	Poor	Poor	Poor	Poor
Dissolved gasses	Good	Poor	Excellent	Excellent	Poor	Poor	Good	Poor	Poor
Organics	Good	Good	Poor	Poor	Poor	Poor	Excellent	Excellent	Excellent
Particles	Excellent	Excellent	Poor	Poor	Excellent	Excellent	Poor	Poor	Excellent
Bacteria	Excellent	Excellent	Poor	Poor	Excellent	Excellent	Poor	Excellent	Excellent
Pyrogens	Excellent	Excellent	Poor	Poor	Poor	Excellent	Good	Poor	Excellent
Nucleases	Poor	Poor	Poor	Poor	Poor	Good	Good	Poor	Excellent

●	Excellent
●	Good
●	Poor

Figure 1.2: Water purification technology and its efficiency



## **1.2 Problem Statement**

Seawater is the most abundantly occurring water source in our planet. However seawater cannot be used for drinking purposes due to its high concentration of dissolved sodium chloride (NaCl). A separation process has to be carried out in order to produce drinkable water by using membrane distillation process.

The hydrophobic membrane possesses a very high tendency of fouling. Besides, it also becomes wetted when the membrane is used in a membrane distillation process for a very long period. The wetting of the membrane can then lead to the leakage of dissolved solutes into the permeate side and causing the separation to be inefficient.

In this research, hypothetically the membrane distillation works better using the modified superhydrophobic membrane than the unmodified hydrophobic membrane. Thus by running the membrane distillation (MD) using superhydrophobic membrane, it is important to know which feed water type is more suitable to be used in the direct contact membrane distillation (DCMD).

## **1.3 Objectives**

The main objectives of this study are:

- i. To synthesis superhydrophobic PVDF membrane to reduce membrane fouling in membrane distillation by the addition of different combinations of TiO<sub>2</sub> and SiO<sub>2</sub> nanoparticles.
- ii. To study and compare the characteristics of an unmodified PVDF hydrophobic membrane and a modified superhydrophobic membrane.
- iii. To compare the performance of membrane distillation (MD) by varying the type of feed used in the hot stream.

#### **1.4 Scope of study**

In this study, polyvinylidene fluoride (PVDF) membrane is synthesized by phase inversion method by using ethanol and distilled water as coagulation bath. The parameters that are being manipulated in this study are the type of membrane used for membrane distillation, component of the feed water in the hot feed (distilled water, salt solution and oily salt solution). The membrane type is varied with different combinations of nanoparticles ( $\text{TiO}_2$  and  $\text{SiO}_2$ ) being added into the polymer dope solution and then silane grafted with hexadecyltrimethoxysilane of different volume ratios (1:25, 1:50, 1:100 and 1:200) for 30 minutes. Besides, the characteristics of the membrane such as the water contact angle, liquid entry pressure, composition of the membrane, porosity and morphology of the membrane was analysed using a goniometer, porometer, Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) respectively.

## **1.5 Organization of thesis**

This thesis consists of five main chapters and each chapter contributes to the sequence of this study. The following are the contents for each chapter in this study:

**CHAPTER 1** introduces the importance of water purification using membrane technology, problem statement of the study, research objectives, scope of study and organization of thesis.

**CHAPTER 2** discusses the literature review of this study, which includes the membrane technology and synthesis, an insight into membrane distillation process, review on the characteristics of a superhydrophobic membrane upon modification. It also explains the techniques used to produce a flat sheet membrane.

**CHAPTER 3** includes the materials and apparatus required for this study and describes the methodology in running this experiment. It also discusses the steps carried out in performing the characterization studies on the membrane. Furthermore, it highlights on the precautions need to be taken in handling the equipment.

**CHAPTER 4** covers the experimental results and discussion of the data obtained. Further discussion and critical assessment on the membrane distillation is provided in this chapter.

**CHAPTER 5** concludes all the findings achieved in this research study. Recommendations and suggestions for future studies regarding this research topic are included in this final chapter.

## CHAPTER TWO

### LITERATURE REVIEW

#### 2.1 Hydrophobic Membrane Separation

A hydrophobic membrane is a non-wetting semi-selective barrier or interface between two phases which can exist as liquid or in gas phase. A typical membrane will be impermeable to specific substances or molecules depending on its physical or chemical properties. The membrane is a medium for mass and heat transfer to occur. For the mass transfer to occur between the two phases, certain factors need to be considered as the driving force such as the pressure ( $\Delta P$ ), temperature ( $\Delta T$ ), concentration ( $\Delta C$ ) or electric potential ( $\Delta E$ ) gradient. The membrane separation process can be classified based on the driving forces, type of membrane, size of retained material and its application. Membrane separation is an alternative to distillation as it utilizes lesser heat and more efficient compared to distillation. Membrane separation is advantageous for its features like compactness, minimal footprint for large membrane surface area, ease of casting and preparing as well as simple and modular operational design. However, there are certain limitations in using a membrane that hinders its performance such as fouling, low mass transfer, high cost for regular maintenance and poor cleaning ability.

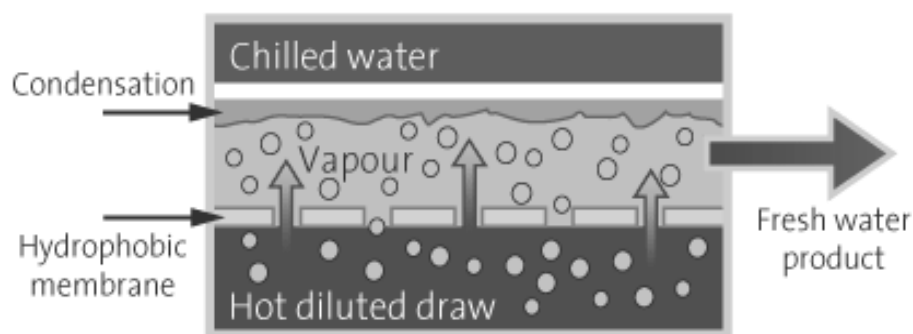


Figure 2.1: Membrane diffusion mechanism

## 2.2 Hydrophobic Membrane Separation Applications

### 2.2.1 Oil Filtration

In traditional methods, unwanted oil separation from water is done via gravity settlement (API separator), flow through packed beds and air flotation. However the efficiency of separating coalescence is dependent to the droplet size distribution and wettability of the media by dispersed phase (Mohammadi, et al., 2003). The membrane technology as shown in Figure 2.2 is a cost saving and effective alternative method in oil separation. It is more advantageous as it can be run continuously, lower energy cost and there is no degradation due to heating. In the membrane separation module, a crossflow configuration is used for better mixing and contact. The operating conditions of the system such as the flow rate, temperature and pressure plays its role in determining the efficiency (Sadrzadeh, et al., 2008).

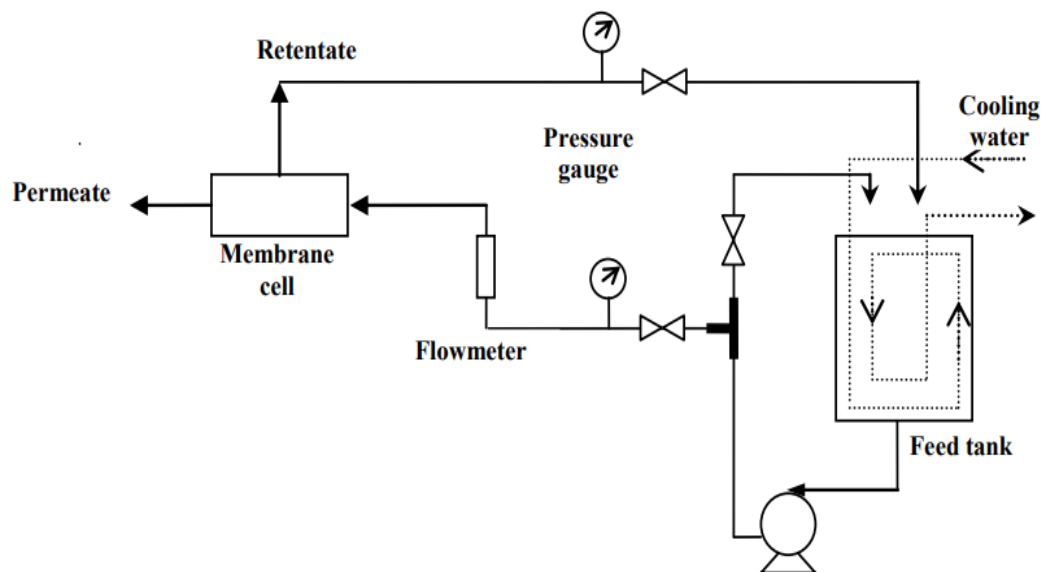


Figure 2.2: Typical oil filtration configuration. (Sadrzadeh, et al., 2008)

## 2.2.2 Membrane Gas Absorption

The membrane gas absorption technology designed as shown in Figure 2.2 is used in capturing gases such as carbon dioxide from flue gas that are usually produced in power plants. This technology was developed to overcome the drawbacks in using the conventional absorption processes like the bubble columns, packed towers, venture scrubbers and sieve trays. A microporous hydrophobic membrane is used in this capturing process. The flue gas is passed along a side of the membrane and the selective component which is needed to be removed will diffuse through the pores of the membrane and the purified gas will be the retentate (Ahmad, et al., 2010).

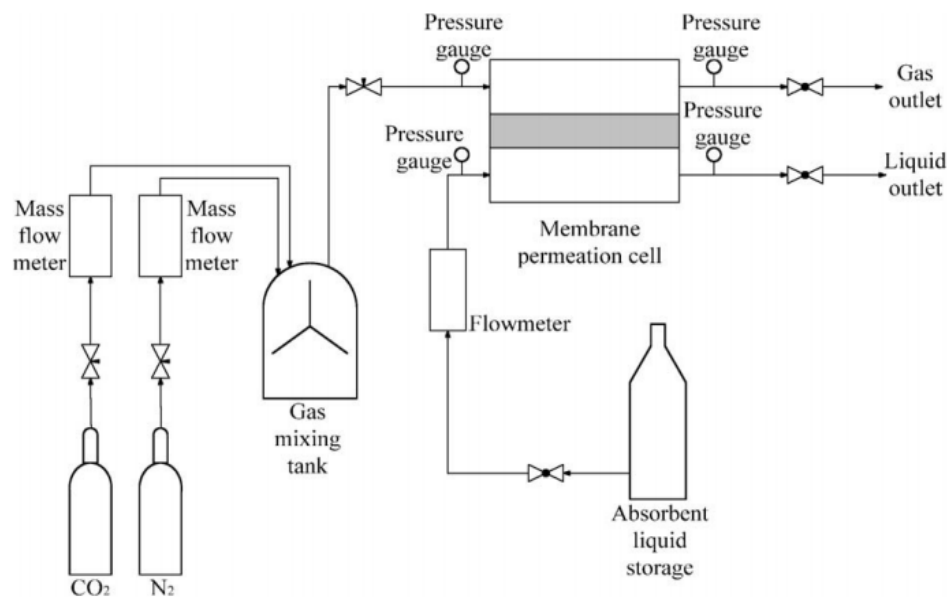


Figure 2.3: Typical membrane gas absorption configuration. (Ahmad, et al., 2010)

## 2.3 Membrane Distillation

### 2.3.1 Desalination using membrane distillation

Membrane distillation (MD) is a growing technology that are being used conventionally for separation processes such as for wastewater management, water purification, heavy metal removal and for concentrating purposes in food or pharmaceutical industries. Membrane distillation (MD) is one of the emerging non-isothermal membrane separation process that depends on thermal energy as the driving force for the vapour through a non-wetted porous hydrophobic membrane (Khayet & Matsuura, 2011). The membrane distillation is more advantageous than other conventional separation processes such as the reverse osmosis or forward osmosis in certain aspects as (Lawson, 1997):

- 100% (theoretical) rejection of ion, macromolecules, colloids, cells and non-volatiles.
- Lower operating temperatures than conventional distillation.
- Lower operating pressure than conventional pressure-driven membrane processes.
- Reduced chemical interaction between membrane and process solutions.
- Less demanding membrane mechanical properties requirements.

Nevertheless, the slow progress of membrane distillation is due to the high energy consumption with respect to RO, membrane wetting, low flux and limited research on module designing and developments. The type of membrane to be used in the membrane distillation is the hydrophobic (non-wetting) microporous membrane. These includes membranes that are made of polytetrafluoroethylene (PTFE), polypropylene (PP) or polyvinylidene fluoride (PVDF). The general characteristic of

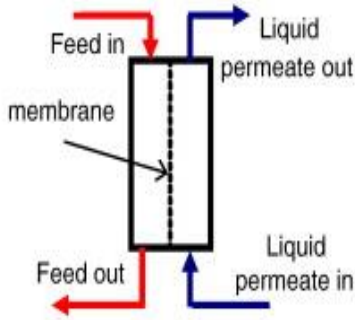
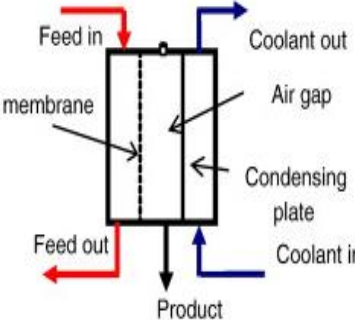
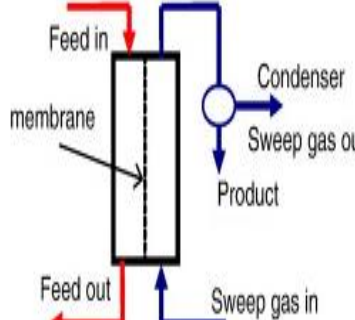
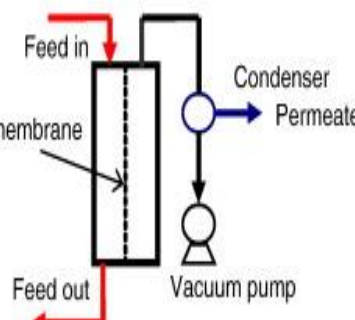
the membrane used should be low resistance to mass transfer and low heat conductivity. Besides, the membrane should be able to withstand high temperatures as the feed used is fed into the system at high temperatures. In carrying out the membrane distillation, variety of membrane modules can be used such as the plate and frame module, hollow fibre, tubular membrane and spiral wound membrane module (Alkhudhiri, et al., 2012).

### 2.3.2 Membrane distillation configurations

In a typical membrane distillation module, a microporous hydrophobic membrane is used as a barrier that divides the hot feed stream from the cold stream in order to create temperature gradient across the membrane. This phenomenon causes a vapour-liquid interface at the surface of the hydrophobic membrane. On the other side, the cold permeate forms a transmembrane vapour pressure gradient as the driving force of membrane distillation. There are four possible membrane distillation configurations which are; Direct Contact Membrane Distillation (DCMD), Air Gap Membrane Distillation (AGMD), Sweeping Gas Membrane Distillation (SGMD) and Vacuum Membrane Distillation (VMD) (Drioli, et al., 2015).



Table 2.1: Membrane distillation configurations and description. (Drioli, et al., 2015)

Configuration	Description
 <p style="text-align: center;">DCMD</p>	<p>The cold side of the membrane distillation carries cold liquid having lower temperature than the feed side that causes the condensing of the fluid in the permeate side. Liquid in the both sides of the membrane is in direct contact with the hydrophobic membrane.</p>
 <p style="text-align: center;">AGMD</p>	<p>Cold surface condenses the vapour that derived from the separation across the hydrophobic membrane. It is effective as it minimizes heat losses by having a stagnant air gap within the membrane and the condensation surface.</p>
 <p style="text-align: center;">SGMD</p>	<p>Cold inert gas at the permeate side for sweeping and carrying the vapour from the membrane and then to a condenser outside to condense the vapour carried away. This configuration has a relatively low conductive heat loss.</p>
 <p style="text-align: center;">VMD</p>	<p>Driving force induced by creating a vacuum condition at the permeate side. The applied vacuum pressure is lower than the equilibrium vapor pressure, hence, condensation takes place out of the membrane module.</p>

## 2.4 Membrane Synthesis

Usually in the application of Membrane Distillation (MD), the type of membrane used is the polymeric type instead of using any ceramic which are more costly and expensive. Besides that, a polymeric type of membrane has a lower thermal conductivity thus lesser heat lost through the membrane matrix. The most common type of polymeric membranes used include polyvinylidene fluoride (PVDF), polyethylene (PE), polypropylene (PP), and polytetrafluoroethylene (PTFE) membranes. Usually, the method used in fabricating a membrane is the Phase Inversion method. Apart from this method, stretching method can also be used to synthesis the membrane, however, these membranes are not feasible to be used in membrane distillation as water vapor will condense within the multiple layers of membrane which will cause ballooning and affects the performance.

### 2.4.1 Phase Inversion Method

The phase inversion method is one of the base method in preparing the membrane from the dope solution (homogeneous solution). The phase inversion involves the change in phase from one form to another (usually liquid to solid phase) by manipulating factors that will change the solubility of the dope solution (polymer). Phase inversion process can be divided into four basic techniques namely; vapor induced phase separation (VIPS), precipitation by controlled solvent evaporation, thermally induced phase separation (TIPS), and immersion precipitation (Eykens, et al., 2017).

Table 2.2: Methods used in phase inversion and description. (Eykens, et al., 2017).

Phase inversion technique	Description
Vapor induced phase separation (VIPS)	The polymer-solvent mixture casted on the film will be placed in an atmosphere that contains vapor of non-solvent saturated. Since the concentration of non-solvent in the vapor is higher than that in the casting solution, it will take up the non-solvent from the vapor phase that results in a porous membrane.
Precipitation by controlled solvent evaporation	The casting solution is prepared with dissolved solvent and non-solvent together. The solvent then evaporated off the casting solution due to its high volatility compared to the non-solvent. As result, the amount of non-solvent will be more than solvent in the casting solution which eventually leads to precipitation of membrane.
Thermally induced phase separation (TIPS)	The mixture dope solution is cooled down to achieve phase separation. This is induced by evaporating the solvent from the polymer solution. Often used in preparing membrane for microfiltration.
Immersion Precipitation	The polymer plus solvent (dope solution) that had been casted on a support or glass plate is submerged in a coagulation bath containing non-solvent. This immersion causes solvent-nonsolvent exchange and finally forms a solid membrane structure.

## 2.4.2 Electrospinning

The electrospinning method produces a special class of nanomaterials with unique properties in the membrane technology which is also referred to nanofibers. The porosity of an electrospun membrane reaches up to about 80% with high surface roughness and results in high flux and the membrane is more stable thermally. Besides that, the membrane tends to have greater strength to weight ratio. The electrospinneret used in producing the nanofibers contains a metallic syringe, high voltage power supply and a collector. Polymer solution is contained in the syringe to be pumped out at the tip of the needle tip by the aid of a syringe pump. At the tip of the needle, the polymer exposes to the electric field produced. Once the Coulomb forces overcome the surface tension, the fibre is formed and deposited randomly on the collector (Eykens, et al., 2017).

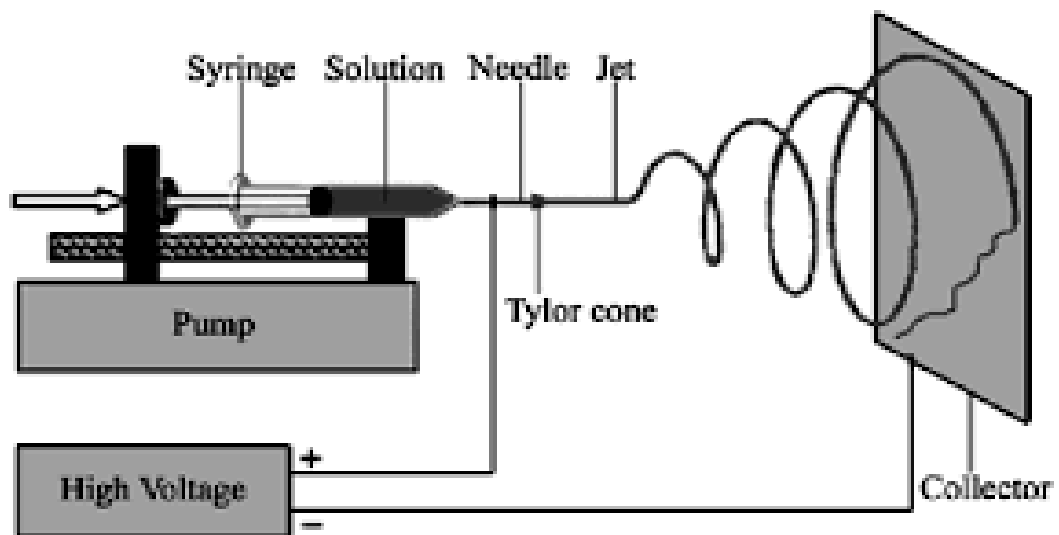


Figure 2.4: Electrospinning process set up (Tamberg, 2014)

## **2.5 Superhydrophobic Membrane**

A superhydrophobic membrane is the membrane that has been modified or altered either physically, chemically or both. This modification in producing a superhydrophobic is done to curb with the problems faced in membrane distillation or other membrane related flaws. Superhydrophobicity can be achieved by roughening of the membrane surface by a low temperature hydrothermal process (Macedonio, 2010). The characteristics of a superhydrophobic varies significantly from the conventional membrane before prior modifications made. Firstly is the water contact angles. The inclination or angle recorded when a drop of water placed on the superhydrophobic membrane is more than  $150^\circ$ . This property of membranes justifies that the wetting of membrane is reduced in superhydrophobic membrane.

## **2.6 Membrane Characteristics**

The hydrophobic membrane plays the major role in repelling water away from the surface. The conventional hydrophobic membrane used is the polyvinylidene fluoride (PVDF) membrane. In order for the membrane to perform effectively during membrane distillation, it should have certain characteristics that has to be considered such as the contact angle, liquid entry pressure (LEP), porosity and tortuosity. These characteristics are used to measure the performance of the membrane used in membrane distillation. Membranes consist of wide variety of building blocks with either inorganic or organic substances. The characteristic of a typical membrane is due to the membrane chemistry which can undergo further reversible and irreversible changes as result of exposure to various feeds, fouling or cleaning (Bernstein, et al., 2013).

### 2.6.1 Contact Angle

The contact angle is the angle measured on the surface of a membrane where the liquid/vapor interface is exposed to the membrane. The contact angle varies depending on the surface free energies between the liquid, solid and surrounding vapor. Contact angle is measured using a goniometer by sessile drop method (Zhang, et al., 2013). A tiny liquid droplet rests stationary on a flat surface. The hydrophobicity of a membrane is measured using the contact angle as one of the criteria whereby the hydrophobicity is greater with the increasing contact angle (Al-Amoudi, et al., 2008). A blank or unmodified hydrophobic membrane often results in a contact angle with a range between 90°-150° whereas a typical modified or superhydrophobic membrane will have a contact angle higher than 150° (Tomaszewska, 1996). Contact angle of a liquid droplet on a membrane changes with the addition of nanoparticles such as silica or activated carbon nanotubes. However, (Ghasemian, et al., 2017), says that the contact angle is not a function of surface chemistry alone but also depends on the surface roughness of the membrane.

Table 2.3: Membrane polymer with its contact angle and surface energy. (Ahmad, et al., 2015)

Polymer	Water contact angle, $\theta_w$ (°)	Surface energy, $\gamma_s$ ( $10^3$ N/m)
Polyethylene (PE)	99-94	33.2
Polypropylene (PP)	95	30.0
Polysulfone (PSf)	69-74	41.0
Polyamide (PA)	53-57	35.9
Polytetrafluoroethylene (PTFE)	114	19.1
Polyvinylidene fluoride (PVDF)	85	30.3

### 2.6.2 Liquid Entry Pressure (LEP)

The liquid entry pressure (LEP) is the minimum hydrostatic pressure required on the feed solution to overcome the hydrophobic forces of the membrane which then penetrates into the membrane pores (Drioli, et al., 2015). This term is also referred as the pore entry pressure. The liquid entry pressure (LEP) depends on the membrane characteristics and diminishes the chance for membrane pore wetting during membrane distillation. In other words, the LEP depends on the pore size (Zhang, et al., 2013). It is important to monitor the flow rate when running the membrane distillation as it could lead to pressure higher than the LEP if the flow rate is too high (Izquierdo-Gil, et al., 2008). However, the presence of surfactants or organic solvents can lead to reduced surface tension and thus causes membrane wetting. LEP can be calculated using the Laplace-Young equation:

$$LEP_w = \frac{B\gamma_L \cos \theta}{d_{max}} \quad (2.1)$$

Whereby  $B$  in the equation denotes the geometric factor,  $\gamma_L$  is the liquid surface tension,  $d_{max}$  is the maximum pore size and  $\theta$  is the liquid/solid contact angle. From the equation derived, membranes that has a high contact angle, small pore size, low surface energy and high surface tension for the feed solution will yield high LEP value (Alkudhiri, et al., 2012).

### 2.6.3 Membrane porosity and tortuosity

The membrane porosity is referred as the void volume fraction of the membrane. Mathematically, it is defined as the volume of the pores divided by the total volume of the membrane. Membranes with higher porosity will have a larger evaporation surface area (Alkudhiri, et al., 2012). The membrane porosity also affects the amount of heat loss by conduction. Higher permeate flux is expected to be obtained when membrane with high porosity is used. In measuring the porosity of the membrane, the density of the polymer is determined by using alcohol which penetrates inside the pores of the membrane and the density of the membrane using pure water which does not enter the pores (Tomaszewska, 1996). The membrane porosity can be determined by the Smolder-Franken equation:

$$\varepsilon = 1 - \frac{\rho_m}{\rho_{pol}} \quad (2.2)$$

Where  $\varepsilon$  is the membrane porosity,  $\rho_m$  is the membrane density and  $\rho_{pol}$  is the density of the polymer material. The membrane tortuosity on the other hand is the average length of the pores compared to the membrane thickness.

Table 2.4: Polymeric membrane liquid entry pressure (LEP) and corresponding pore sizes.

Polymer	Liquid Entry Pressure, LEP (bar)	Pore Size ( $\mu\text{m}$ )	Reference
Polyethylene (PE)	0.50	0.05	(Zuo, et al., 2016)
Polysulfone (PSf)	2.64	0.27	(Tian, et al., 2015)
Polytetrafluoroethylene (PTFE)	2.88	0.45	(Alkudhiri, et al., 2012)
Polyvinylidene fluoride (PVDF)	2.04	0.22	(Alkudhiri, et al., 2012)



## **2.7 Nanoparticles in polymeric membrane**

Introducing nanoparticles into polymeric membrane is known as a hybrid technology as it is beneficial in certain aspects. The main attraction towards the incorporation of nanoparticles in polymeric membrane is because it can enhance the flux and reduce fouling in membrane. The commonly used nanoparticles are oxides such as silica dioxide and zeolites (Kim & Bruggen, 2010). According to (Ng, et al., 2013), the addition of silica nanoparticles will enable the membrane to withstand high temperature, higher selectivity and higher diffusivity. The incorporation of nanoparticles can be done by simply dispersing the nanoparticles in the casting solution. Adding nanomaterials into the polymeric membrane can change the porosity and pore size of the membrane thus results a change in the permeability and solute rejection (Yin & Deng, 2015).

## **2.8 Mass transfer resistance through membrane distillation**

In the membrane distillation processes, hot vapours are carried through the pores of membrane. In this vapour transport, a certain molecular resistance is imposed by the air trapped in the pores besides the physical structure of the pore itself. To curb this challenge, several trials have been made to reduce the resistance such as having both sides of the membranes (feed and permeate) under vacuum to control partial pressure of air in the pores (Cath, et al., 2004). In describing the mass transfer across the membrane, Dusty gas model is used whereby it consist of the Knudsen diffusion, molecular diffusion, surface diffusion and viscous flow. However, the surface diffusion is always neglected in membrane distillation (Srisurichan, et al., 2006). Typically for direct contact membrane distillation, the flux is described by applying

Knudsen-molecular diffusion transition. The mass flux can be represented linearly in a function of vapor pressure across the membrane (Termpiyakul, et al., 2005);

$$J = C(P_1 - P_2) \quad (2.3)$$

Denoting  $J$  as the mass flux,  $C$  as the membrane distillation coefficient and  $P_1$  and  $P_2$  as the partial pressures of the water vapor at separated sides of the membrane.

## **2.9 Scanning Electron Microscopy (SEM)**

The scanning electron microscopy (SEM) is an imaging method used to obtain complete information about the sample morphology and structural properties. Via the imaging of SEM, the surface porosity, pore size and pore distribution can be estimated (Ahmad, et al., 2015). The sample has to be coated with ultra-thin layer of metal by an ion sputtering equipment under vacuum (Ren, et al., 2017). The specimen inside the SEM is stabilized under vacuum conditions and electrically conductive samples are grounded to avoid electrostatic charge accumulation. The imaging of the two-dimensional image is produced by the electrons which have been emitted from an electron source of a heating type or a field emission type are accelerated so as to be formed into a slender electron beam (Todokoro, et al., 1999).

## CHAPTER THREE

### MATERIAL AND METHOD

This chapter covers the overall experimental elements of the research project including the material and chemicals used, equipment utilized for experiments and characterization. Furthermore, this chapter includes the experimental procedure along with the manipulated operating parameters used in this research project. Workplace safety and environmental precautions were designated to ensure a safer and sustainable research environment.

#### 3.1 Materials and Chemicals

The list of materials and chemicals used in this study are shown in Table 3.1:

Table 3.1: List of materials and chemicals.

Chemical	Molecular Formula	Purity (%)	Supplier
N-Methyl-2-pyrrolidone	C <sub>5</sub> H <sub>9</sub> NO	99.5	Merck
Acetone	C <sub>3</sub> H <sub>6</sub> O	99.5	Sigma-Aldrich
Phosphoric acid	H <sub>3</sub> PO <sub>4</sub>	99.5	Merck
Lithium chloride	LiCl	-	Merck
Polyvinylidene fluoride	(C <sub>2</sub> H <sub>2</sub> F <sub>2</sub> ) <sub>n</sub>	-	Solef
Titanium (IV) oxide	TiO <sub>2</sub>	99.5	Sigma-Aldrich
Silicon dioxide	SiO <sub>2</sub>	99.5	Sigma-Aldrich
Ethanol	C <sub>2</sub> H <sub>5</sub> OH	99.5	Merck
Hexadecyltrimethoxysilane	C <sub>19</sub> H <sub>42</sub> O <sub>2</sub> Si	85.0	Sigma-Aldrich

### 3.2 Equipment and Facilities Required

The list of equipment and facilities used in the study are shown in Table 3.2:

Table 3.2: List of equipment and facilities.

Equipment	Model	Usage
Direct Contact Membrane Distillation (DCMD)	Masterflex L/S	To run the direct contact membrane distillation in pilot scale.
Scanning Electron Microscope	Hitachi TM3000	To study the surface morphology of the membrane.
Porometer	Porolux 1000	To measure the liquid entry pressure (LEP) of the membrane samples.
Fourier Transform Infrared Spectroscopy (FTIR)	Nicolet iS10	To analyse the components of the prepared membrane.
Membrane Casting Machine	Elcometer 4340	To evenly cast a flat sheet membrane on the glass plate.
Goniometer	rame-hart instrument	To measure the contact angle of water droplet on membrane surface.