SUPERHYDROPHOBIC (PVDF) MEMBRANE INCORPORATED WITH SILICA NANOPARTICLES FOR CARBON DIOXIDE ABSORPTION

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SUPERHYDROPHOBIC (PVDF) MEMBRANE

INCORPORATED WITH SILICA NANOPARTICLES

FOR CARBON DIOXIDE ABSORPTION

by

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LIST OF SYMBOLS

SYMBOL	DESCRIPTION	UNIT
γL	Surface roughness and surface tension of the liquid	-
γSV	Solid/vapor surface tension	-
γLV	Liquid/vapour surface tension	-
γLS	Liquid/solid surface tension	-
θ	The contact angle	°
rw	The roughness factor	-
θw	Wenzel contact angle	-
J	Water permeate flux	$L/m^2\,h$
Δm	Mass of permeate water	L
A	Effective membrane area	m^2
t	Sampling time	s
SR	Salt rejection	%
Cf	Feed concentration	mg/L
Cp	Permeate concentration	mg/L
φ	Porosity	%
V_{oil}	Volume of Oil	m^3
V_{memb}	Volume of Membrane	m^3
R	Rejection	-

LIST OF ABBREVIATIONS

CA	Cellulose Acetate
CO$_2$	Carbon Dioxide
CH$_4$	Methane
DI	Deionized Water
DIPS	Diffusion Induced Phase Separation
FT-IR	Fourier transform infrared spectroscopy
H$_3$PO$_4$	Ortho-Phosphoric Acid
LiCl	Lithium Chloride
MGA	Membrane gas absorption
MMM	Mixed matrix membranes
NIPS	Non-solvent Induced Phase Separation
NMP	N-methyl-2-pyrrolidone
PDMS	Polydimethylsiloxane
PEI	Polyetherimide
PVDF	Polyvinylidene Fluoride
SEM	Scanning Electron Microscopy
SiO$_2$	Silicon dioxide nanoparticles
TIPS	Thermally Induced Phase Separation

SUPERHIDROFOBIK (PVDF) MEMBRAN DIPERBADANKAN DENGAN PARTIKEL SILIKA UNTUK PENYERAPAN KARBON DIOKSIDA

ABSTRAK

Karbon dioksida dipercayai menjadi bahan cemar gas yang utama di atmosfera. Proses gas konvensional seperti penyerapan gas untuk menyerap CO_2 mengalami beberapa batasan termasuk penggunaan tenaga yang tinggi, banjir, berbuih, iringan, menyalurkan, modal dan kos operasi yang tinggi. Membangunkan kaedah dan teknologi baru yang bersaing dengan proses industri konvensional untuk menyinkirkan CO_2 adalah satu topik hangat dalam penyelidikan baru-baru ini. Membran untuk penyerapan gas adalah teknologi penggantian menjanjikan untuk penyingkiran CO_2 untuk mengurangkan isu pemanasan global.

Dalam kajian ini, membran superhidrofobik Polyvinylidene fluoride (PVDF) yang diperbadankan dengan partikel silika telah dicadangkan untuk penyerapan CO_2. Nanopartikel silika digunakan sebagai pengisi untuk meningkatkan CO_2 fluks gas. Struktur membran yg tidak simetri telah disediakan dengan menggunakan kaedah penyongsangan fasa bagi meningkatkan CO_2 gas ditangkap. Kesan nanopartikel Silika memuatkan (0.5-1 % berat) pada membran ciri dan rawatan oleh pengubahsuaian dengan silana telah dikaji. Sampel paling optimum adalah membran dengan 1% berat silika nanopartikel loading, diubah suai oleh silana yang mempamerkan meningkat CO_2 fluks pada kadar aliran penyerap 220 mL/min (0.031 m/s halaju). fluks CO_2 relatif tinggi (3.89×10^{-4} mol/m^{2}s) telah dicapai untuk membran P1.0F, yang hampir dua kali ganda fluks membran PVDF yang jelas nyata. Ini juga membuktikan bahawa membran yang menjalani pengubahsuaian dengan silana akan mempunyai fluks CO_2 yang lebih tinggi, berbanding sampel lain.

SUPERHYDROPHOBIC (PVDF) MEMBRANE INCORPORATED WITH SILICA NANOPARTICLES FOR CARBON DIOXIDE ABSORPTION

ABSTRACT

Carbon dioxide is believed to be the main gaseous contaminant in the atmosphere. Conventional gas processes such as gas absorption for CO_2 capture suffer several limitations including high energy consumption, flooding, foaming, entraining, channeling, high capital and operating costs. Developing new methods and technologies that compete with conventional industrial process for CO_2 capture is a hot topic in recent research. Membrane contactor for gas absorption is a promising replacement technology for removal of CO_2 in order to mitigate the global warming issue.

In this study, Superhydrophobic (PVDF) membrane incorporated with silica nanoparticles were proposed for CO_2 absorption. Silica nanoparticles were used as fillers to improve CO_2 gas flux. The asymmetric membrane structure was prepared using phase inversion method in order to enhance CO_2 captured. The effects of Silica nanoparticles loading (0.5-1 wt%) on the membrane characteristic and treatment by modification with silane were studied. The most optimum sample is the membrane with 1 wt% of Silica nanoparticles loading, modified by silane which exhibit improved CO_2 flux at the absorbent flow rate of 220 mL/min (0.031 m/s velocity). Relatively high CO_2 flux (3.89×10^{-4} mol/m^{2}s) was achieved for the P1.0F membrane, which was almost double the flux of the plain PVDF membrane. This also proved that the membrane that undergoes modification with silane will have higher CO_2 flux, compared to other samples.

CHAPTER 1

INTRODUCTION

1.1   Superhydrophobic Membranes

Membranes are commonly fabricated with great hydrophobicity or hydrophilicity to prohibit or promote the transportation of water, respectively. There are vast applications of hydrophobic membranes such as filtration, gas separation, membrane gas absorption, pervaporation, membrane distillation and more that cannot be attained with hydrophilic membranes. Hydrophobic ceramic membranes are commonly prepared by chemical modification. Besides using different types of chemicals, the membrane surface is roughened to enhance its hydrophobicity. For polymeric membranes, great hydrophobicity can be engineered using per-fluorinated polymers or phase immersion in a dual coagulation bath. Each technique has its advantages and weaknesses (Ahmad et al., 2015). It is also environmentally friendly in that energy consumption is generally very low and few, if any, additives are required. Excellent chemical resistance over a large pH range, hydrolytic stability, high strength and broad agency certifications make these polymers well-suited for membranes used in demanding end-use environments.

The permeation of molecules through a membrane barrier is depends by the concentration gradient, electrical force across the membrane, thermal variation and pressure difference (Reif, 2006). The characteristics of surface membrane are important in membrane separation since the molecules from the inlet (feed) stream will first come into contact with the membrane surface. The selected molecules are then adsorbed onto the membrane surface and desorbed from the membrane barrier into the permeate side (Davis and Davis, 2003). The surfaces of membrane should

have special features to promote and/or prohibit certain molecules to pass through the membrane barrier. There are two common surface features of membrane, either hydrophobic or hydrophilic. The hydrophobic property is also known as the "water repellent". The hydrophobic membrane property prohibiting the surface wettability, while for the hydrophilicity is the "water loving" property, which is will encourage the water spread (Kazunari, 2002; Deyev, 2005; Jun et al., 2008). Water cannot spread on the hydrophobic surface and hence reduces its contact with the surface. Water droplets turned into spherical form on the hydrophobic surface due to low surface energy (Brassard et al., 2012; Jun et al., 2008). However, for the hydrophilic membrane a water droplet will spread on a membrane surface and then be adsorbed into a porous membrane.

The measurement of contact angle is a simple method that is commonly used by researchers to evaluate the surface wettability. Surface wettability is influenced by a few factors such as surface energy of the material, surface roughness and surface tension of the liquid (γL) (Mulder, 2003). The surface energy may encourage or prohibit growth of the surface wettability. As described in Thomas Young's theory, surface energy is a result of the relationship between the cohesion force and the adhesion force on a surface (Gupta et al., 2005; Lawrence, 2004). Once a liquid is dropped on a surface, the droplet spreads out until certain extend due to these forces. The wettability of a liquid droplet resting on a solid surface is illustrated in Figure 1. There are three-phase contact points to explain the force relationship as shown in the figure. The term γSV represents the solid/vapor surface tension, γLV is the liquid/vapour surface tension, γLS is the liquid/solid surface tension and θ is the contact angle. Relationship for the surface tensions among the solid, vapor and liquid can be shown in Young's equation (Eq. (1)) (Jun et al., 2008).

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$$\gamma SV = \gamma LS + \gamma LV \cos\theta \qquad (1)$$
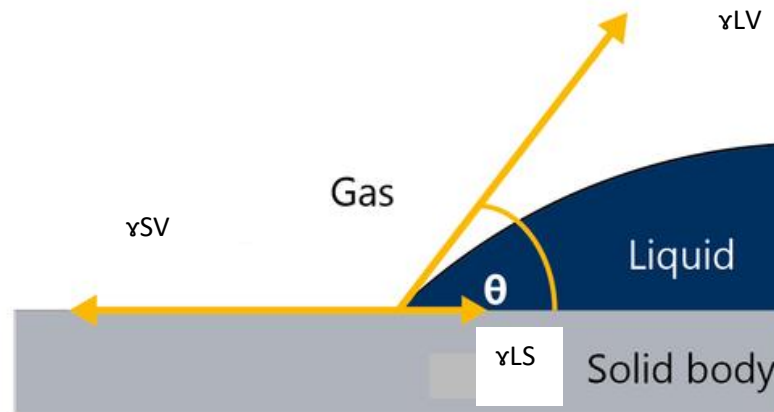
Figure 1.1 Illustration of a liquid droplet resting on a solid surface with contact angle

(Lawrence, 2004)

Once a liquid droplet is placed on a solid surface, the droplet contact angle (θ) will be measured using a goniometer. The liquid contact angle can be used to classify the surface features. For a contact angle less than 90°, the surface is classified as hydrophilic. The droplet tends to spread on the hydrophilic surface due to great surface energy of the membrane surface. If the liquid droplet shows contact angle more than 90° the surface has low surface energy or great hydrophobicity which allows the droplet to roll on the surface. The hydrophobic surface can be further enhanced for superhydrophobic feature that results in the liquid droplet having a contact angle greater than 150°. On the hydrophilic surface, water droplet tends to spread on the surface with contact angle less than 90°. On the hydrophobic and superhydrophobic surface, water droplets form spherical shape to reduce their contact with the surface.

Evaluation of the surface wettability using Young's theory is limited to smooth and homogenous surface. Because surface roughness also affects the liquid

contact angle, modification of Young's equation to include the surface roughness factor is required. In Wenzel's equation (Eq. (2)), the measured contact angle is corrected to Wenzel's contact angle, θw (Jun et al., 2008).

$$\cos \theta w = rw \cos \theta \qquad (2)$$

The roughness factor, rw is a ratio of the actual area of a rough surface to the area of the solid surface. The value of rw is always larger than 1 for rough surface because rw = 1 for flat and homogeneous surface. For rough surface, the apparent Wenzel contact angle (θw) is larger than the contact angle, θ. On the other hand, great roughness on hydrophilic surface not only reduces the Wenzel contact angle (θw) but also improves the degree of surface wettability. Young's equation and Wenzel's equation can be combined into Eq. (3) to determine the surface wettability on rough surface (Jun et al., 2008).

$$\gamma SV = \gamma LS + \gamma LV \cos \theta w \qquad (3)$$

1.2   Polyvinylidene Fluoride

Polyvinylidene fluoride (PVDF) membrane has been widely used in microfiltration, ultrafiltration and recently being explored as potential material for membrane fabrication. This is due to its outstanding properties such as high mechanical strength, good chemical resistance, and good thermal and oxidative stability with high hydrophobicity as compared to others polymeric material. The hydrophobicity of PVDF may not be high as compared to Polypropylene (PP) or Polytetrafluoroethylene (PTFE) but remained as the best option of membrane

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material because PVDF is soluble in common organic solvent and it has greater strength, wear resistance and creep resistance than PTFE.

1.3   Hydrophobic Silica Nanoparticles

Hydrophobic silica nanoparticle is one of the best material that can be used to cooperated with PVDF due to it has hydrophobic groups which normally alkyl or polydimethylsiloxane chemically bonded to the surface of the particles. Hydrophobic silica nanoparticle with the properties of water resistant prevents liquids from permeating the rough texture when this particle is applied to the surface of membrane. It is commonly used in the fabrication of polyester resins, plastic manufacturing and industry of cosmetic. Due to the hydrophobic properties, incorporation of hydrophobic silica with polymeric membrane receives high attention in recent years.

1.4 CO_2 Separation from Biogas using Membrane

The energy demand from combustion of fossil fuel has increased tremendously over the year. However, the combustion of fossil fuel creates negative impact to the environment as the release of greenhouse gases causes the increase of global temperature. There is necessity to develop an alternative sustainable and renewable energy source to fulfil the energy demand besides reducing the environmental impact of energy industry.

Biogas is mainly composed of methane (CH_4) and carbon dioxide (CO_2) with trace amount of hydrogen sulphide (H_2S), ammonia (NH_3), hydrogen (H_2), nitrogen (N_2), oxygen (O_2) and steam. Biogas can be used directly to generate power but large

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volume of CO_2 reduces the heating value of the gas, increasing compression and transportation costs and limiting economic feasibility to uses that occur at the point of production.

The separation of biogas not only recovered CO_2 but it is to purify CH_4 to give an add-on value for biogas. Traditional processes such as physical absorption, reactive absorption and solid bed absorption are employed throughout the world. Although these processes posses many advantages such as high separation performance and throughput, they suffer from problems associated with high capital and operational costs and high environmental impacts that have led researchers to find more efficient and environmental friendly process. Membrane-based separation involves the use of membrane as a thin barrier between miscible fluids to separate mixture.

For separation of gas, membrane separation has advantages compared to the conventional processes as listed below:

- It has high flexibility cost effective

- There is no phase change or chemical additives

- Simplicity in concept and operation

- Can be carried out more efficiently

- Very high selectivity

- Lower energy consumption

1.5   Problem Statement

The combustion of fossil fuel creates negative impact to the environment as the release of greenhouse gases causes the increase of global temperature. However, energy demand from combustion of fossil fuel has increased tremendously over the

year. It's well known that carbon dioxide is a greenhouse gas. Thus, the synthesis of superhydrophobic Polyvinylidene Fluoride (PVDF) membrane incorporated with silica nanoparticles can be the solution for the removal of greenhouse gases.

The application and importance of silica nanoparticles with polymer is well known. However, the effects of silica loading on the properties of superhydrophobic Polyvinylidene Fluoride (PVDF) membrane are still unclear.

1.6   Research Objective

1. Synthesis and characterize the superhydrophobic Polyvinylidene Fluoride (PVDF) membrane incorporated with silica nanoparticles.
2. Study the effects of silica loading on the properties of Polyvinylidene Fluoride (PVDF)/SiO_2 membrane post-treated with hydrophobic membrane.

1.7   Research Scope

For this research, synthesis of superhydrophobic Polyvinylidene Fluoride (PVDF) will be varying with different composition of material and filler. These membranes then will undergo several test that we call as characterization to determine the properties of that particular membrane. For example, the contact angle of water droplet was measured to determine membrane hydrophobicity by using a goniometer (Ramé - Hart Instruments Co.). The other test is to determine the pore size and pore size distribution of the membranes. It was done by using porometer (Porolux 1000, IB-FT GmbH, Germany). Next is, the membrane will undergoes performance for the gas absorption.

CHAPTER 2

LITERATURE REVIEW

2.1 Superhydrophobic Membrane Technology for Membrane Gas Absorption

In this modern day, the continual increase in atmospheric concentration of carbon dioxide (CO_2) is considered to be one of the most causes of global warming. This increase is attributed to both anthropogenic and natural emissions including fires, ocean temperature oscillations and volcanoes. However, CO_2 emission due to the industrial-associated activities such as iron and steel production, gas flaring, cement, combustion of fossil fuels in power plants and chemical processes are believed to primarily contribute to increment of CO_2 emission level (Herzog et al., 2000; Luis et al., 2012). From another point of view, the sustained growth of energy consumption all over the world and the obligation to supply energy sources, are directly correlated with the accumulation of greenhouse gases particularly CO_2 in the atmosphere and consequently global climate change (Ghoniem, 2011). Thus, it has been predicted that CO_2 atmospheric concentration will reach a value two times higher than the current one at the year 2050 (Favre, 2011). In this case, CO_2 removal from various pollutant sources has gained considerable attention. It has been implemented by developing several techniques such as physical and chemical absorption, use of cryogenic processes, adsorption of the gas using molecular sieves, solid adsorption, column absorption (Mansourizadeh et al., 2010; Mansourizadeh et al., 2014).

It is well known that biogas is rich with CO_2 gas content. Biogas production has been globally promoted due to the need of renewable energy. Federal Land

Development Authority (FELDA) and Sime Darby Plantation Sdn. Bhd. have initiated the generation of biogas as well that is located in Malaysia. This is due to oil palm industry produced a huge amount of biomass wastes that contribute about 85.5 % of the total biomass (Khan et al., 2010). Sime Darby Plantation is collaborating with Tenaga Nasional Berhad to develop 6 potential biogas plants (Ching 2014). Meanwhile, FELDA is currently having 12 biogas trapping plants (Adnan and Sarif, 2012). Besides methane (CH_4), the biogas contains up to 60 % of carbon dioxide (CO_2) (Ryckebosch et al., 2011). The presence of the CO_2 will cause fuel gas efficiency to significantly reduced (Zhao et al., 2014). Among all the gas purification methods that have been listed above, membrane gas absorption (MGA) is the most appropriate technology for biogas upgrading as it requires a low pressure in CO_2 separation. MGA also shows other advantages such as small foot-print, easy scale-up and flexible modularity. More importantly, MGA exhibits the excellent mass transfer properties because it integrates the benefits of chemical absorption and membrane process (Zhang and Wang, 2014).

The morphology of PVDF membranes for MGA was further improve by several methods has been introduced. Besides changing the polymer concentration (Ghasem et al., 2012), non-solvent additives such as LiCl, acetone, phosphoric acid, glycerine, polyethylene glycol were added into the polymer solution to engineer porous structure for the high CO_2 flux (Mansourizadeh and Ismail, 2010). The non-solvent induced phase separation (NIPS) method was also introduced to improve membrane hydrophobicity (Ahmad et al., 2012). In addition, surface modification was used to create near superhydrophobic PVDF membrane (Rahbari-Sisakht et al., 2012; Ahmad et al., 2013). In recent research, the membrane researchers continued to develop PVDF mixed matrix membranes (MMM) for MGA even though MMM

was originally developed to surpass Robeson plot during gas separation (Kang et al., 2015; Kang et al., 2016). This is because the incorporation of inorganic fillers in PVDF membranes resulted in great hydrophobicity, porosity and mechanical stability for other applications. New method has been introduced the hydrophobic clay particles (Cloisite 15A) and the fluorinated silica into polymer matrix during the fabrication of dual layer PVDF hollow fiber membranes (Edwie et al., 2012). They reported on the significant improvement of surface hydrophobicity and permeability for membrane distillation. Rezaei et al. (2015) later reported the use of hydrophobic montmorillonite in the preparation of hydrophobic PVDF membrane for CO_2 removal. They concluded that the CO_2 flux was greatly improved, 54 % and 82 % higher than the flux of MMMs with Cloisite 15A and PVDF membrane respectively.

Nonselective membranes have been widely studied in the past, but Gomez-Coma et al. (2016) reported on the PVDF membrane filled with ionic liquid [emim][EtSO$_4$] recently. The gas selective ionic liquid enhanced the CO_2 flux of the modified membrane up to 45 % in comparison to the neat PVDF membrane. In Ahmad et al. (2017) work, the incorporation of porous fillers with CO_2 affinity into PVDF membrane is proposed to improve membrane properties for MGA. SAPO-34 appealed as an interesting candidate as its small pores (0.38 nm) are near to the molecular size of various gas species in biogas. SAPO-34 has been successfully incorporated into various polymeric matrix for CO_2 separation (Junaidi et al., 2014; Rabiee et al., 2015; Dan et al., 2014). The sorption isotherms of different gases on SAPO-34 zeolite confirmed on its stronger affinity toward CO_2 compared to the other gases such as CH_4 and N_2 (Li et al., 2004; Rabiee et al., 2015). Besides that, polyhedral oligomeric silsesquioxanes (POSS) with monoscopic cage is selected for

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the creation of additional CO_2 pathway. The well-defined nanometer-sized structure of the cubic silsesquioxane unit possesses the high surface area and controlled porosity for CO_2 diffusion. The intrinsic cavity of POSS contributed to a higher CO_2 gas permeability through the polymeric membranes blended with POSS (Li and Chung, 2010; Ríos-Dominguez et al., 2006). On top of that, the silsesquioxane units can be modified with different reactive or non-reactive organic groups at the tetravalent Si atoms during POSS synthesis. The functional groups such as amine and silanol can further promote CO_2 capture (Dibenedetto et al., 2002).

In this work, the incorporation of silica nanoparticles filler with different loading into PVDF membrane is proposed to improve membrane properties for MGA. Not only that, the modification with silane for the membrane also has been studied in this work. The PVDF incorporated with hydrophobic silica nanoparticle could give the result of hydrophobic membrane. However, the hydrophobicity of membrane is not enough to be superhydrophobic membrane. Thus, modification is take place to increase the hydrophobicity of the membrane. Silica nanoparticles appealed as an interesting candidate as its size is about 5-15 nm. Non-solvent additives such as LiCl, acetone, phosphoric acid were added into the polymer solution to engineer porous structure for the high CO_2 flux in this study (Mansourizadeh and Ismail, 2010).

2.2   Superhydrophobic Membrane Prepared via Electronspining Fillers

Efome et al. (2015) studied that the effects of superhydrophobic SiO_2 nanoparticles on the performance of PVDF flat sheet membranes for vacuum membrane distillation. For materials, two different molecular weights: Kynar® 740 and Kynar® HSV 900 of Poly(vinylidene fluoride) (PVDF) polymer were supplied.

Dimethyl acetamide (DMAc, > 99 %) used as solvent was supplied by Sigma Aldrich Inc., St. Louis, MO and Superhydrophobic silica nanoparticles (purity: ≥ 99.8, particle size: 10–20 nm, surface area: 100–140 m^2/g), surfaces modified with single layer organic chains were supplied by SkySpring Nanomaterials Inc. (Houston, TX). Butan-1-ol (> 99.8 %) was from Sigma Aldrich Inc., St. Louis, MO.

Then, dope solution was prepared by mixing PVDF (15 wt%), DMAc (83.75 wt%) and water (1.25 wt%) together at a stirrer rotation of 180 rpm and 50 °C for 72 h to ensure complete polymer dissolution and solution homogeneity. The solution was then allowed to de-gas for 24 h at room temperature. The required amount of nanoparticles was then added to the required quantity of dope solution and the suspension was stirred at 100 rpm for 2 h to yield the dope solution with expected final wt% (1, 2, 4, 6, 7, 8, and 10) of nanoparticles. Hereafter "nanoparticle concentration" means the nanoparticle concentration in the dope. The compositions for the respective concentrations are listed in Table 2.1. (Efome et al., 2015)

Table 2.1

Composition of the dope solution for flat-sheet composite membrane preparation.

Membrane	Dope solution concentration			Nanoparticles concentration in the dope suspension[a]
Code	PVDF (wt.%)	DMAc (wt.%)	Water (wt.%)	SiO$_2$ (wt.%)
MS-0	15	83.75	1.25	0.0
MS-1	15	83.75	1.25	1.0
MS-2	15	83.75	1.25	2.0
MS-4	15	83.75	1.25	4.0
MS-6	15	83.75	1.25	6.0
MS-7	15	83.75	1.25	7.0
MS-8	15	83.75	1.25	8.0
MS-10	15	83.75	1.25	10.0

The dope solution containing the nanoparticle at the desired wt% was then cast on a glass plate using a casting bar (0.25 mm thickness) at a speed of approximately 7 cm/s. The plate was then exposed to air for 10-15 s, followed by immersion into deionised water at ambient temperature. Upon completion of phase inversion, the solidified polymer sheet was peeled off the plate, transferred into fresh deionised water at ambient temperature and kept there for 24 h. Thereafter, the sheet was allowed to dry at room temperature for 24 h. The dried membranes were then subjected to characterization. (Efome et al., 2015)

For characterization of membrane, liquid entry pressure of water (LEP_w) measurements was tested. LEP_w of the membranes was measured using the setup shown in Figure 2.1, and the following approach (Drioli et al., 2015). A static liquid reservoir was installed with a membrane sample of surface area 0.00131 m^2 and filled with 200 ml of deionised water at ambient temperature. Compressed nitrogen from a cylinder was used to apply pressure on the liquid and a regulator was used to control the increment at 2 psi per 10 min until water dripped off continuously from the cell outlet. A pressure gauge connected on the line displayed the operating pressure. For each membrane, three samples were analysed and the average was reported. The pressure at which water was seen dripping off the cell was noted as the LEP_w.
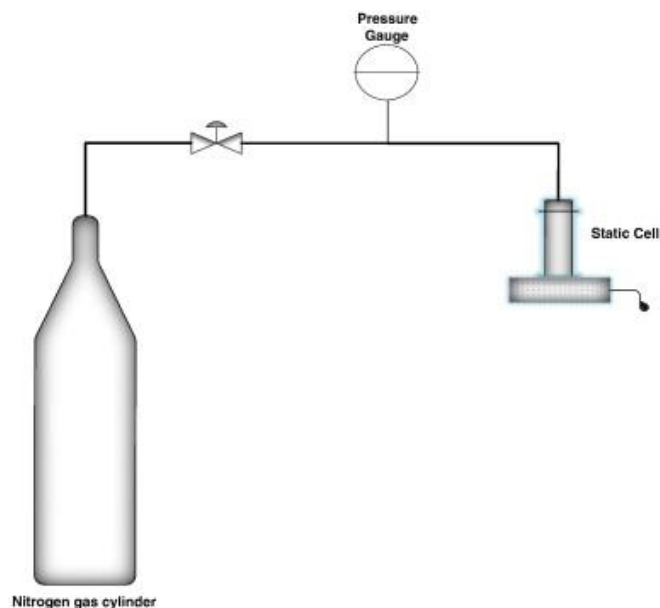
Figure 2.1 Schematic diagram of the experimental LEPw set-up. (Efome et al., 2015)

Tijing et al. (2016) studied about Superhydrophobic nanofiber membrane containing carbon nanotubes for high-performance direct contact membrane distillation. For materials, Polyvinylidene fluoride-co-hexafluoropropylene or PcH (Sigma-Aldrich, Mw = 455,000 g/mol), lithium chloride (powder, Sigma), N,N dimethylformamide (DMF, 99.8 % anhydrous, Aldrich), and acetone (analytical grade, Scharlau) were used as received. Multiwalled carbon nanotubes (referred generally herein as CNTs) (diameter ⩽ 8 nm, length ~ 10-30 μm, specific surface area ~ 500 m^2/g) were purchased from Cheap Tubes, Inc., USA and were used as received.

For the synthesis of membrane two solutions were prepared for electrospinning; one was neat PcH solution and the other one contained 1-5 wt% CNTs w.r.t. to the amount of PcH. Neat 20 wt% PcH solution was prepared by dissolving a certain amount of PcH pellets in DMF/acetone (80/20 by wt%) solvent solution by overnight stirring at room temperature. Table 2.2 shows the contents of the different dope solutions and their respective codes used in this paper. To prepare

the CNT/PcH solution, CNTs were first dispersed in a certain amount of DMF for at least 1 h by bath sonication (Soniclean). After sonication, the CNT/DMF solution was mixed with a neat 15 wt% PcH solution by rapidly stirring overnight at room temperature. Before electrospinning, the CNT/PcH solution was sonicated again for 30 min to disperse the CNTs. (Tijing et al., 2016)

Table 2.2 Dope compositions used for electrospinning in the present study

Dope/membrane code	[a]PcH (wt%)	DMF (wt%)	Acetone (wt%)	[b]CNT (wt%)
PcH	20	64	16	0
1CNT	15	68	17	1
3CNT	15	68	17	3
5CNT	15	68	17	5

[a] Polyvinylidene fluoride-co-hexafluoropropylene
[b] Amount of CNTs added to dope solution w.r.t. to the total weight of PcH.

Figure 2.2 shows a schematic layout of the DCMD system used in the present study. The produced membranes were placed in a home-made module, and sealed tightly. Both feed and permeate streams had identical flow channels with dimensions (L × W × H): 77 mm × 26 mm × 3 mm. The effective surface area of the membrane was 20 cm^2. The feed and permeate streams were both cycled through the MD cell each at 400 mL/h forming a counter flow set-up. The feed stream was composed of either DI water, 35 g/L or 70 g/L NaCl aqueous solutions, while DI water with an initial conductivity of < 5 µS/cm was used in the permeate stream. The inlet temperatures at the feed and permeate streams were maintained at 60 ± 1 °C and 20 ± 1 °C, respectively. The permeate flux was calculated according to Eq. 1, which is based from the change in weight through time of the water at the permeate tank as automatically measured by a digital balance (PGW 4502e, Adam) connected to a

personal computer. The conductivity of the feed and permeate solutions was monitored throughout the test using a portable conductivity meter (HQ40d, Hach). Salt rejection performance of DCMD was then calculated using (2), which is based from the measurements of the initial and final electrical conductivities to get the concentrations of the feed and permeate solutions. The DCMD performance of the nanofibrous membranes were compared to a commercial flat-sheet PVDF membrane (GVHP, Millipore). (Tijing et al., 2016)

$$J = \frac{\Delta m}{A \times \Delta t}$$

(4)

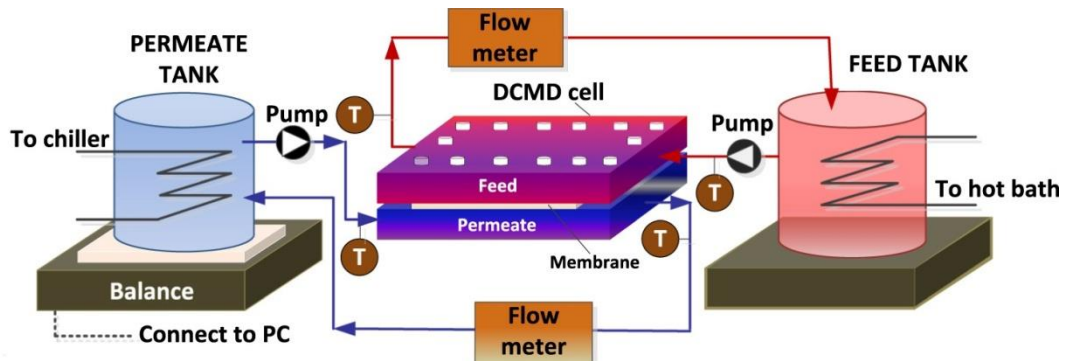$$SR = \frac{Cf\text{-}Cp}{Cf} \times 100$$

(5)

Figure 2.2 Direct contact membrane distillation system.

In the above equations, *J*, Δm, *A*, *t*, *SR*, *Cf*, and *Cp* represent the water permeate flux (L/m^2 h or LMH), mass of permeate water (L), effective membrane area (m^2), sampling time (s), salt rejection (%), feed concentration (mg/L), and permeate concentration (mg/L), respectively.

2.3 Superhydrophobic Membrane Prepared via Phase Inversion

The addition of non-solvents (acetone and phosphoric acid (H_3PO_4)) into polymer with phase inversion using water only resulted in PVDF membrane with water contact angle of 83.8 ° ± 1.3 as reported others (Hou et al., 2014; Hou et al., 2012). The fabrication of PVDF membrane using a mixture of non-solvents and dual bath coagulation lead to the greater hydrophobicity as compared to literature Table 2.3 (Hou et al., 2014; Kuo et al., 2008; Ahmad and Ramli, 2013). The double soft coagulation baths had been applied by Ahmad and Ramli (2013) in the preparation of neat hydrophobic PVDF membrane with a water contact angle of 127.2 °. The first bath contained pure ethanol while the second bath contained 80 wt% of NMP in water. Ethanol was the poor and non-solvent coagulation solution which delayed the demixing process to form porous surface morphology. The hydrophobicity improvement was completely achieved using the second coagulation containing 80 wt% of NMP in water in their work. The inversed double coagulation bath was applied in (Ahmad et al., 2017) work. The first coagulation bath contained 80 wt% of NMP in water while pure ethanol was used in the second bath. The combination of non-solvent added into dope polymer and inverse double coagulation bath improved the membrane contact up to 137.5° ± 1.8. In contrast, another additive has been added which the LiCl in this work. The first coagulation bath contained pure ethanol and distilled water at room temperature was used in the second bath. The combination of non-solvent added into dope polymer and double coagulation bath improved the membrane contact.

Table 2.3 Comparison of the surface hydrophobicity of P1.0-F membrane to the PVDF membranes reported in literature

| Solvent | Additives | Solvent/bath | Contact angle (°) | Pore size | | Roughness | | References |
				Mean (nm)	Maximum (nm)	Rq (um)	Ra (um)	
DMAc	Acetone + H_3PO_4	Water	83.8 ± 1.3	216.5	482.7	0.2853	0.2185	Hou et al., 2014
NMP	-	Ethanol and water	138 ± 1	-	-	-	-	Kuo et al., 2008
NMP	-	Ethanol and 80 wt% of NMP in water	127.2	30–70	35	0.376	0.293	Ahmad and Ramli, 2013
NMP	Acetone + H_3PO_4	80 wt% of NMP in water and ethanol	137.5 ± 1.8	2770	3047	0.621	0.532	Ahmad et al., 2017
NMP	Acetone + $H_3PO_{4\ +}$ LiCl	Ethanol and water	-	-	-	-	-	This work

CHAPTER 3

METHODOLOGY

3.1 Materials

Polyvinylidene Fluoride (PVDF) powder (Solef$^®$ PVDF) was supplied by Solvay Solexis (France). N-methyl-2-pyrrolidone (NMP) (purity > 99.5 %), ortho-phosphoric acid (H_3PO_4) (purity > 85 %) and ethanol (purity > 99.9 %) were purchased from Merck (Darmstadt, Germany). Silicon dioxide (SiO_2) nanoparticles in the size range of 5 - 15 nm (TEM), 99.5 % trace metals basis were acquired from Sigma-Aldrich (St. Louis. MO). (Heptadecafluoro-1,1,2,2-tetrahydrodecyl) triethoxysilane from Gelest, Inc (Morrisville, PA). Lithium Chloride (LiCl) for analysis EMSURE® ACS, Reag. Ph Eur. 5 wt% of acetone (for analysis, Merck).

3.2 Synthesis of Membrane

The membranes were synthesized according to (Hamzah and Leo, 2016) with some modifications. Polyvinylidene Fluoride (PVDF) powder was dried (Figure 3.1) at 60 ^{o}C for 24 hours in the oven to remove the moisture content. The dried Polyvinylidene Fluoride (PVDF) powder was mixed with solvent and non-solvent according to Table 3.1. For blank membrane, polymer was dissolved in solvent for 24 hours at 40-50 °C until homogenous. The polymer was slowly added in small amount to prevent lump. For mixed membrane, the mixture of solvent and non solvent has been prepared. Add filler (powder form) into the mixture and was continuously stirred (Figure 3.2) for 30-60 minutes and undergoes sonication for 30 minutes. Next, 5 wt% of polymer was added and continuously stirred until dissolve and undergoes sonication for 30 minutes. Add the remaining polymer and

continuously stirred until homogenous and degassed to remove bubbles for 24 hours.

The function of non solvent is to enhance the membrane properties. The porosity and

pore size can be increased by adding the non solvent.

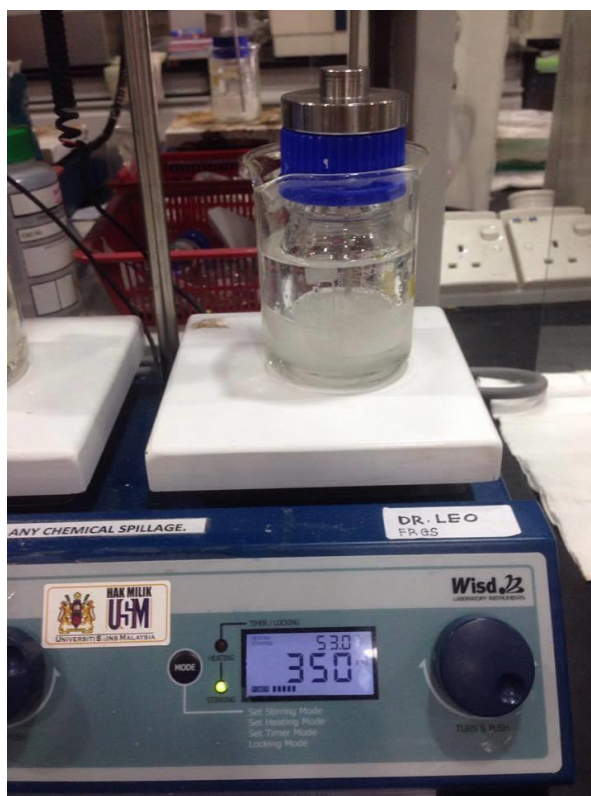Figure 3.1 Drying oven (Memmert, Germany)

Figure 3.2 Magnetic stirrer

The mixture then was cast on a glass plate of 400 µm casting gap (Elcometer 4340 automatic) (Figure 3.3 and 3.4) at room temperature. The cast film was immersed into the first coagulant bath (slow bath) in ethanol (Figure 3.5) for 1 hour to prevent the rapid mixing and to enhance surface roughness to improve membrane hydrophobicity. The cast film was then immersed into second coagulant bath (Figure 3.5) of distilled water for 24 hours to removed residual chemicals. The wet membrane then was dried in ambient temperature (Figure 3.6) for 72 h in order to get a dry flat-sheet porous membrane.

Figure 3.3 Casting machine (Elcometer 4340 automatic)

Figure 3.4 Cast film ready for casting process (Elcometer 4340 automatic).

Figure 3.5 The cast film was immersed into the first and second coagulant bath.

Figure 3.6 Wet membrane then was dried in ambient temperature.

For silane modification, silane was mixed with ethanol at a ratio of 1 mL : 50 mL and the mixture was stirred for 30 min. The Silicon dioxide, nanopowders were added into the silane for 5 min and separated by filtration. The pre-treated Silicon dioxide nanopowder later rinsed with ethanol to remove silane residue. The pre-treated TiO_2 nanoparticles were then dried in the oven at 50 ℃ for 24 h before being used as the filler of P-pre membrane. In the preparation of P-post membrane, the Polyvinylidene Fluoride (PVDF) membrane blended with unmodified TiO_2 produced was immersed (Figure 3.7) in the silane solution for 5 min. The membrane was rinsed with ethanol and dried in the oven before being used.