

Preparation and characterization of polyimide membranes in iron wastewater removal by membrane distillation

S S Lee^{1*}, K C Chong^{1**}, S O Lai¹, C H Koo¹, W J Lau², T W Ngu¹ and C H De¹

¹ Lee Kong Chian Faculty of Engineering and Science, Universiti Tunku Abdul Rahman, Jalan Sungai Long, Bandar Sungai Long, 43300 Kajang, Malaysia

² Advanced Membrane Technology Research Centre (AMTEC), Universiti Teknologi Malaysia, 81310 Skudai, Johor, Malaysia

* lsshin@utar.edu.my, ** chongkc@utar.edu.my

Abstract. Polyimide (PI) polymer is a polymeric material with superior thermal, chemical and mechanical properties allowing it to possess the advantages of commercially viable materials to be applied in membrane distillation (MD) process. The PI hollow fiber membranes were fabricated by phase inversion method using N-Methyl-2-pyrrolidone (NMP) as solvent. The effect of feed inlet temperature and polydimethylsiloxane (PDMS) coating concentration on the permeate flux performance were studied. The characteristics test conducted suggest that the membrane possesses dense morphology with tear-drop structure. The results from energy dispersive X-ray (EDX) depicted PDMS solution was successfully coated on the membrane surface. In addition, direct contact membrane distillation experiment in the iron (III) oxide rejection shows that the feed inlet temperature had a positive effect on the permeate flux performance attributed to the higher transmembrane vapor pressure while the rejection rate was found to be consistent at $95.10 \pm 0.15\%$. Besides, the rejection rate of iron (III) oxide for PI hollow fiber membrane coated with PDMS increases from 95.13 to 97.58% with the increase of PDMS coating concentration. This is due to the enhanced surface layer nonetheless further optimization on the concentration is required to improve the permeate flux performance.

1. Introduction

Fresh water supply has been an alarming issue in the 21st century as reported by United Nation [1]. The accelerating industrialization, urbanization as well as population growth increases the need of reliable water supply. Ironically, the rapid growth destroys the balance between the demand and supply of water [2]. As a result, the quality of water is plummeting in some places around the globe. Yang et al. reported that there are more than a billion peoples in this world are unable to access to clean drinking water supply [3]. The water stress and shortage issue are going to upsurge for the years to come. Separation technologies are greatly demanded to remove hazardous inside the water so as to meet the requirements for municipal and industrial purposes. Currently, the commercial membrane separation technologies in wastewater treatment are predominantly pressure driven process such as reverse osmosis (RO), ultra-filtration (UF), nano-filtration (NF) [4].

Membrane distillation (MD) is the emerging technology which is less energy extensive due to thermal driven nature. The concept MD was first introduced in the late 1960s and subsequently being patented in between year 1963 to 1975 by Bodell and Findley, respectively [5]. Despite its early



emergence, membrane distillation was not favoured at that time due to the technical incompetency in achieving comparable performance in terms of vapour permeability and membrane characteristics to pressure driven process [6]. The advancement of polymer industry in early 80s created a huge market for membrane technology in water separation reignite the interest on MD.

The commonly used polymeric materials in MD membrane fabrication are polyethylene (PE), poly(vinylidene fluoride) (PVDF) and polytetrafluoroethylene (PTFE) attributed to their enhanced permeability and hydrophobicity. Polyimide (PI) is the recently interested arising polymeric materials in membrane technology owing to its superior thermal stability, mechanical strength and chemical resistance [7]. The characteristics owned by PI materials allowed it to be effectively applied in MD due to the thermal driven nature of MD in water separation. Lately, several researchers focus performance of the membrane coated with a layer of coating materials such as aerogel (CX) and/or polydimethylsiloxane (PDMS) attributed to its ability to improve the surface defect and permeate flux enhancement in both water and gas separation [8, 9].

In the wastewater rejection research, recent studies found that MD is promising in wastewater rejection with superior rejection rate. Dao et al. reported the rejection rate of more than 99% in MD for aluminium and arsenic wastewater removal [10]. Additionally, Qtaishat et al. focus on the saline waste water removal by DCMD using hydrophilic/hydrophobic polyetherimide membrane [11]. Lately, Zuo et al. investigate the performance of vacuum membrane distillation by using dual-layer hydrophobic/hydrophilic membrane with membrane surface coating for permeate flux enhancement [12].

In this work, PI hollow fiber membranes were fabricated by dry-jet wet phase inversion spinning method to evaluate the performance of PI membrane on the iron (III) oxide synthesized wastewater rejection. Subsequently, the membranes were coated by different concentration of PDMS solution to investigate the effect of the surface coating on the permeate flux and rejection rate of iron (III) oxide using direct contact membrane distillation system.

2. Materials and method

2.1. Membrane dope solution preparation

In this study, PI hollow fibre membranes were fabricated with 12 wt% of polyimide and 88 wt% of N-methyl-2-pyrrolidone (NMP). PI was purchase in flake form from Alfa Aesar, USA and NMP was acquired from Sigma Aldrich, USA. Polydimethylsiloxane (PDMS) used as coating materials that applied on the membrane surface and hexane used as solvent for coating solution preparation were both obtained from Sigma Aldrich, USA. The iron (III) oxide used to fabricate the laboratory synthesized wastewater was obtained from Sigma Aldrich, USA.

Prior to the dope solution preparation, PI flakes was dried in vacuum oven at 70°C for 24 h to remove the moisture content. Then, the dope solution was prepared by dissolving PI flakes in the NMP solution and stirred thoroughly to produce a homogeneous solution. Then, the solution was degassed to remove potential air bubbles produced during mixing and stirring. The presence of bubble will reduce the quality of membrane formed.

The PI hollow fibre membranes were fabricated using dry-jet wet phase inversion spinning method as depicted in figure 1 where the spinning parameter used in this study was tabulated in table 1. The dope solution was firstly poured into the storage tank before spinning. The dope solution was forced through the spinneret by gear pump while the bore fluid flows through the annulus to solidify the membrane. The nascent hollow fibre membranes enter the coagulation bath where the solvent exchange occurs. The hollow fibre membranes were collected by winding drum and later the membranes were stored in pure water for two days in order to completely removing the residue solvent. Lastly, the membrane was dried at room temperature for two days before usage.

PDMS coating solution was used in this study to improve the membrane surface structure as depicted by Zulhairun *et al* [13]. The concentrations of the coating solution were at 3, 5 and 10 wt% respectively. The PDMS coating solution was prepared by mixing the PDMS solution with hexane solvent at

predetermined volume to acquire the desired solution concentration. The solution was stirred by mechanical stirrer for 2 h in order to obtain a homogeneous solution.

Dip coating method was engaged in this work where the PI hollow fibre membranes were immersed in a conical flask for ten minutes and this procedure was repeated five times to attain a good coating surface. Lastly, the membrane was dried in a vacuum oven at 70°C for 24 h before usage. The pristine PI hollow fibre membrane used in this study was labelled as PI whereas the PI hollow fibre membrane with PDMS coating concentrations of 3, 5 and 10 wt% were marked as PI-3, PI-5 and PI-10, respectively, for ease of reference.

Table 1. Spinning parameter of hollow fibre membrane.

Spinning parameter	Value
Bore fluid type	Distilled water
Bore fluid temperature (°C)	25
Bore fluid flow rate (mL/min)	1.0
External coagulant type	Tap water
External coagulant temperature (°C)	25
Spinneret dimension OD/ID (mm/mm)	0.6/0.3
Air gap distance (cm)	30
Room relative humidity (%)	55 ± 5

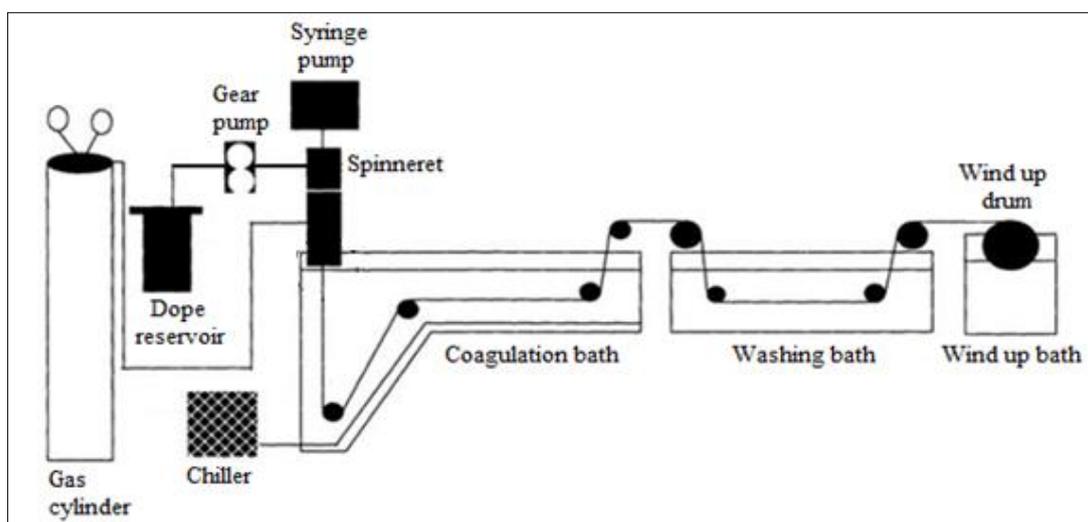


Figure 1. Schematic diagram of dry-jet wet phase inversion spinning method [14].

2.2. Membrane characterization

The membrane morphology was observed with scanning electron microscope (SEM) (Hitachi, Japan). Prior to the characterization, pre-treatment was undergone where the membranes were cryogenically cracked using liquid nitrogen. The membrane samples were then fixed to the sample holder using carbon tape and subsequently sputtered with gold by a sputter coater (Emitech, United Kingdom).

The membrane porosity in this work was measured using the gravitational method. The dry weight of the membrane was first measured by an electronic weight balance (AND, Japan). Later, the membrane was wetted by being immersed into 2-butanol to fully fill up the membrane pores. The membrane was then

dried at room temperature to eliminate excess alcohol on the surface of the membrane before the wet weight was measured. The membrane porosity can be calculated by the following equation.

$$\text{Porosity, } \epsilon = \frac{(W_w - W_d)}{\frac{\rho_a}{(W_w - W_d)} + \frac{W_d}{\rho_b}} \quad (2.1)$$

where W_w is the weight of wet membrane (g), W_d is the weight of dry membrane (g), ρ_a is the density of PI polymer (g/cm^3) and ρ_b is the density of 2-butanol (g/cm^3).

In this work, liquid entry pressure was determined by the method similar to Khayet and Matsuura [4]. Five hollow fiber membranes with an average length of 23 cm were attached to a tubular module by applying epoxy adhesive. Distilled water was flow into the lumen of the membrane with the aid of compressed nitrogen gas. The pressure of the gas was increased in the stepwise rate of 0.5 bar until first distilled water droplet was seen, i.e. the liquid entry pressure of the membrane.

2.3. Membrane distillation experiment

In this work, direct contact membrane distillation (DCMD) was utilized to remove iron (III) oxide synthesized wastewater where the experiment setup was schematically shown in figure 2 which is similar to the work reported by Chong *et al* [15]. Ten hollow fiber membranes with average length of 23 cm were inserted into the cylindrical tubular membrane module. Both ends of the module were sealed up with epoxy glue. The feed and permeate were in cross-flow pattern in the membrane module. The feed solution flow along the lumen side of the membrane while the permeate solution flow along the shell side. Two booster pumps were used to re-circulate the feed and permeate solution.

The laboratory synthesized feed solution was similar the wastewater from mining industry (1.0 wt% Fe_2O_3). The solution was heated to the temperature ranging from 40 to 55°C on an electrical heating plate (LMS, Japan). Concurrently, the permeate solution was cooled to 18°C by electrical chiller (Eyela, Japan) before being pumped into the shell side of the membranes. Water rotameter (Blue White, USA) was used to measure the flow rate of feed and permeate. Meanwhile, the flow rates were regulated by needle valve (Swagelok, USA). The quality of permeate was monitored by an electronic conductivity meter (4520 by Jenway, United Kingdom). The weight of the permeate obtained was measured using an electronic weight balance (AND, Japan) with data logger (AND, Japan).

The permeate flux of the membranes, J , was determined using equation (2.2) [16],

$$J = \frac{\Delta W}{A \Delta t} \quad (2.2)$$

where J is the permeate flux ($\text{kg/m}^2 \cdot \text{hr}$), ΔW is the difference between the initial and final permeate weight (kg), A is the effective surface area of the membrane (m^2), and Δt is the sampling time (hr). On the other hand, equation (2.3) was used to calculate the rejection of iron (III) oxide, R (%) [16].

$$R = \frac{C_f - C_p}{C_f} \quad (2.3)$$

where C_f and C_p are the iron (III) oxide concentration (ppm) in the feed and permeate solution, respectively.

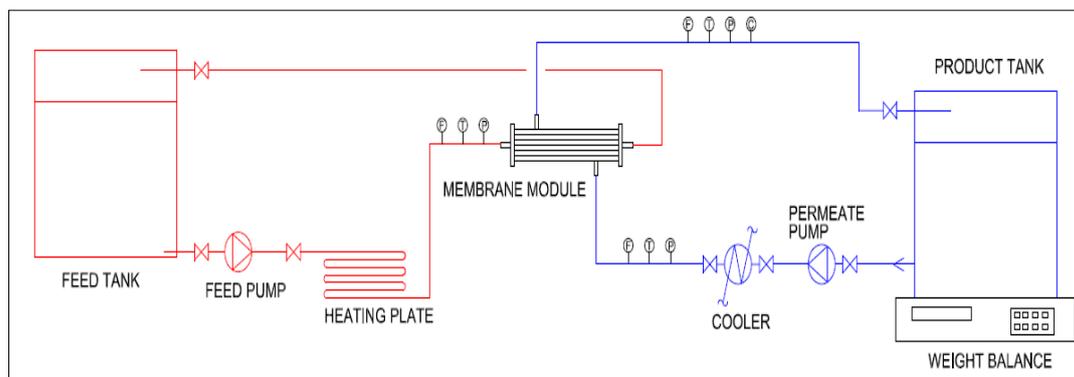


Figure 2. Schematic diagram of DCMD setup [14].

3. Results and discussions

3.1. Membrane morphology

The SEM images of the as-spun hollow fibre membrane morphology were as shown in figure 3. The hollow fibre membrane fabricated with 12 wt% of PI and 88 wt% of NMP illustrated a dense membrane structure extending from the inner to the outer structure. The formation of the dense membrane structure found in the hollow fibre membranes was attributed to the high viscosity of the membrane dope solution (4285 cP) which lead to the delay in formation of membrane structure during phase inversion. It is noteworthy to mention that the membrane illustrated tear-drop like microvoids extended from the middle of the cross section to the inner and outer layer. This phenomenon was due to the used of NMP as strong solvent encourage rapid phase inversion but restricted by the high viscosity of the dope solution which similar to the reported in literature study [5].

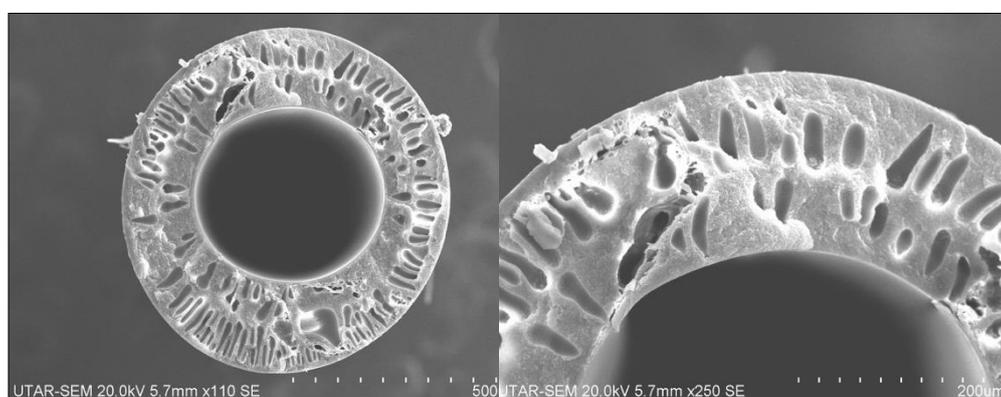


Figure 3. Membrane morphology.

The membrane characteristics of the as-spun PI membrane in this study were tabulated in table 2. The diameter of the hollow fibre membranes was recorded between the range of 390 to 420 μm whereas the thickness of the membranes was found to be 170 to 185 μm . The PDMS coating concentration had a positive effect on the membrane thickness where the higher the membrane coating concentration, the higher the thickness of the membrane attributed to the increase of PDMS content in the coating solution. EDX elemental analysis performed on the membrane surface was tabulated in table 3. The EDX result suggested that the membrane was coated by the PDMS solution attributed to the presence of silicon element which was not presence in the pristine PI membrane. The presence of the silicon trace element on PI-3, PI-5 and PI-10, respectively, was due to the silanol group contained in PDMS where the results was well agreed with the literature study [8].

Table 2. Characteristic of as-spun membrane.

Membrane	Inner diameter (μm)	Thickness (μm)
PI	390 ± 20	170 ± 10
PI-3	410 ± 23	174 ± 16
PI-5	420 ± 18	179 ± 11
PI-10	410 ± 21	185 ± 14

Table 3. EDX elemental analysis of surface coating.

Membrane	Composition (At%)			
	Carbon	Oxygen	Nitrogen	Silicon
PI	72.08	14.35	13.57	Not detected
PI-3	71.86	13.28	12.14	2.72
PI-5	71.39	13.12	11.36	4.13
PI-10	70.67	9.87	10.72	8.74

3.2. Effect of feed temperature in iron (III) oxide removal

Figure 4(a) illustrates the permeate flux performance of as-spun PI hollow fibre membrane on iron (III) oxide synthesized wastewater with respect to different feed inlet temperature where the permeate inlet temperature was set at 18°C , while feed inlet and permeate inlet flow rate were both set at 0.3 l/min . The results illustrated the feed inlet temperature possesses positive effect on the permeate flux performance where the flux increase from 10.20 to $11.65 \text{ kg/m}^2\cdot\text{hr}$ with the feed inlet temperature increase from 50 to 60°C . This phenomenon was identical to the report by Khayet and Matsuura where the higher the feed temperature, the higher the vapor pressure difference between the feed and the permeate stream induced higher transmembrane pressure which eventually lead to higher permeate flux performance [4]. As shown in figure 4(b), the rejection rate of the iron (III) oxide was found to be consistent at $95.10 \pm 0.15\%$ for all the feed inlet temperature indicating the membrane possess good rejection rate.

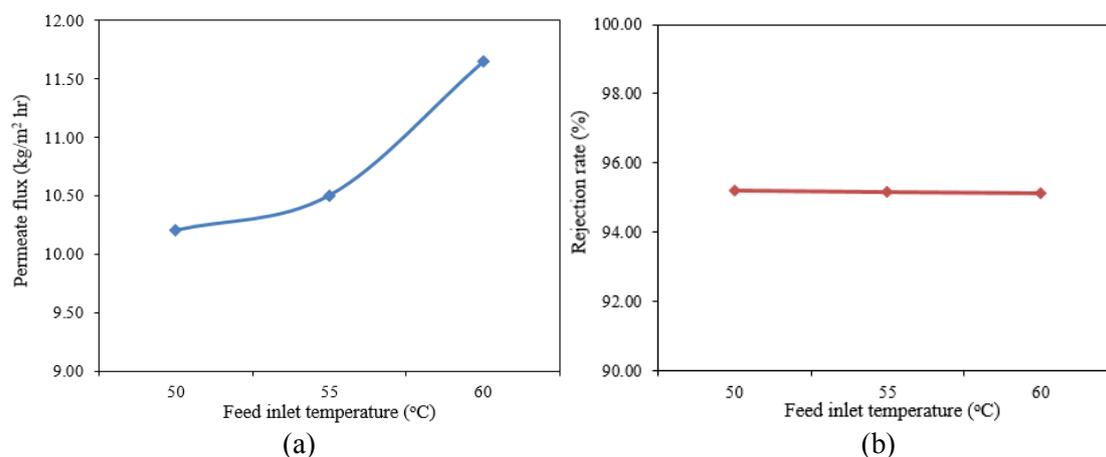


Figure 4. Performance of iron (III) oxide rejection by PI membrane operated at different feed inlet temperature (a) permeate flux, (b) rejection rate.

3.3. Effect of PDMS coating concentration in iron (III) oxide removal

Figure 5(a) shows the permeate flux performance of as-spun PI hollow fiber membrane on iron (III) oxide synthesized wastewater with respect to different PDMS surface coating concentration where the feed inlet temperature was set at 60°C, permeate inlet temperature was set at 18°C, feed inlet and permeate inlet flow rate were both set at 0.3 l/min. The results illustrated the PDMS surface coating concentration possesses negative effect on the permeate flux performance where the flux decrease from 11.65 to 6.56 kg/m².hr with the PDMS concentration increase from 0 to 10 wt%. The reduction of the permeate flux across the membrane resulted from the increase of PDMS coating concentration was attributed to the increase of surface layer thickness which lead to the increase of mass transfer resistance and hence reduces the amount of water vapor to diffuse across the membrane. However, as shown in figure 5(b), it is noteworthy to mention that the rejection rate of the iron (III) oxide increases consistently from 95.13 to 97.58% with the increase of PDMS coating concentration showing the additional layer of coating on the surface restricted the iron (III) oxide particle to move across the membrane. The result suggested that further optimization of the PDMS concentration is required in order to obtain a good permeate flux and rejection rate for the iron (III) oxide rejection.

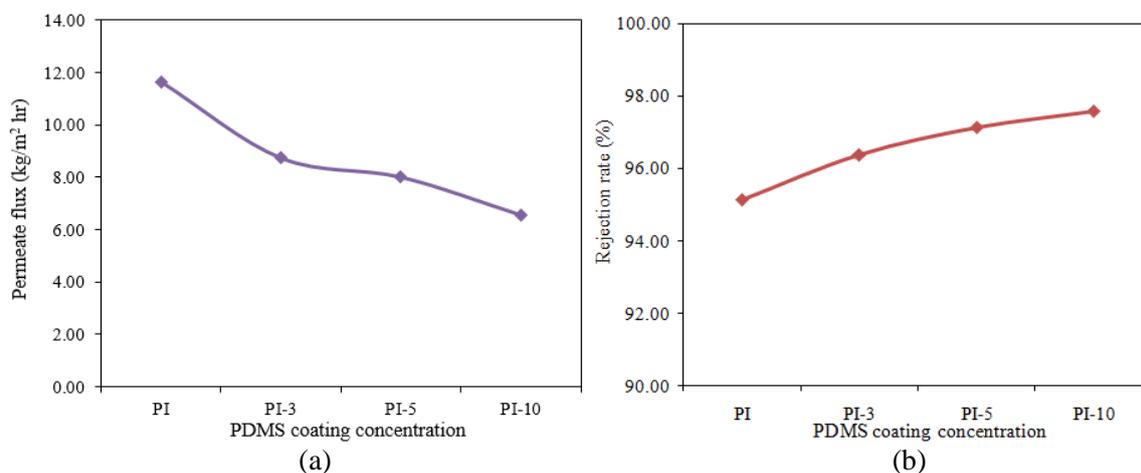


Figure 5. Performance of iron (III) oxide rejection by PI membrane at different PDMS coating concentration (a) permeate flux, (b) rejection rate.

4. Conclusions

In this work, PI membrane was successfully fabricated by dry-jet wet phase inversion spinning method in laboratory scale with the PDMS coating concentration at 3, 5 and 10 wt%, respectively. The hollow fibre membranes were characterized in terms of morphology, thickness and elementally analysed on the coating quality. The membrane morphology obtained from this work was generally dense membrane with tear-drop like structure due to rapid phase inversion of the solvent in highly viscous dope solution. The direct contact membrane distillation experimental study showing the permeate flux performance increase with the increment of feed inlet temperature which was induced by the increase of transmembrane vapor pressure. On the other hand, the PI hollow fibre membrane with high PDMS coating concentration illustrated a drop in permeate flux performance but improved rejection rate of iron (III) oxide. The findings from this study suggested that the PI hollow fibre membrane coated with PDMS possesses the potential to be used in the iron (III) oxide wastewater rejection subjected to the further optimization of the concentration in our future works.

Acknowledgement

The authors are grateful to the financial support from Universiti Tunku Abdul Rahman under the UTARRF grant number IPSR/RMC/UTARRF/2017-C1/L08.

References

- [1] Satulu V, Mitu B, Altynov V A, Lizunov N E, Kravets L and Dinescu G 2017 Synthesis and characterization of porous composite membranes with hydrophilic/hydrophobic sides *Thin Solid Films* **630** 92–99
- [2] González D, Fane A G and Wang R 2017 Membrane distillation: Perspectives for sustainable and improved desalination *Renewable and Sustainable Energy Reviews* **80** 238–259
- [3] Yang X, Fane A G and Wang R 2014 *Membrane distillation: Now and future Desalination* John Wiley & Sons, Inc. pp 373–424
- [4] Khayet M and Matsuura T 2011 *Introduction to membrane distillation Membrane Distillation* Amsterdam Elsevier pp 1–16
- [5] Chong K C, Lai S O, Lee K M, Lau W J, Ismail A F and Ooi B S 2014 Characteristic and performance of polyvinylidene fluoride membranes blended with different polymeric additives in direct contact membrane distillation *Desalination and Water Treatment* 1–9
- [6] Hitsov I, Maere T, Sitter K D, Dotremont C and Nopens I 2015 Modelling approaches in membrane distillation: A critical review *Separation and Purification Technology* **142** 48–64
- [7] Khayet M 2011 Membranes and theoretical modeling of membrane distillation: A review *Advances in Colloid and Interface Science* **164(1-2)** 56–88
- [8] Chong K C, Lai S O, Lau W J, Thiam H S, Ismail A F and Zulhairun A K 2016 Fabrication and characterization of polysulfone membranes coated with polydimethylsiloxane for oxygen enrichment *Aerosol Air Quality Research* 1–8
- [9] Magueijo A M, Anderson L G, Fletcher A J and Shilton S J 2013 Polysulfone mixed matrix gas separation hollow fibre membranes filled with polymer and carbon xerogels *Chemical Engineering Science* **92** 13–20.
- [10] Dao T D, Laborie S and Cabassud C 2016 Direct As(III) removal from brackish groundwater by vacuum membrane distillation: Effect of organic matter and salts on membrane fouling *Separation and Purification Technology* **157** 35–44
- [11] Qtaishat M, Rana D, Khayet M and Matsuura T 2009 Preparation and characterization of novel hydrophobic/hydrophilic polyetherimide composite membranes for desalination by direct contact membrane distillation *Journal of Membrane Science* **327(1-2)** 264–273
- [12] Zuo J, Chung T-S, O'Brien G S and Kosar W 2017 Hydrophobic/hydrophilic PVDF/Ultem® dual-layer hollow fiber membranes with enhanced mechanical properties for vacuum membrane distillation *Journal of Membrane Science* **523** 103–110
- [13] Zulhairun A K, Fachrurrazi Z G, Izwanne M and Ismail A F 2015 Asymmetric hollow fiber membrane coated with polydimethylsiloxane–metal organic framework hybrid layer for gas separation *Separation And Purification Technology* **146** 85–93
- [14] Chong K C, Lai S O, Lau W J, Thiam H S, Ismail A F and Roslan R A 2018 Preparation, Characterization and Performance Evaluation of Polysulfone Hollow Fiber Membrane with PEBAX or PDMS Coating for Oxygen Enhancement Process *Polymers* **10** 126

- [15] Chong K C, Lai S O, Lau W J and Ooi B S 2014 Preparation, Characterisation and Performance of Polyvinylidene Fluoride Membrane for Sodium Chloride Rejection in Direct Contact Membrane Distillation *Materials Research Innovation* **18** 359 – 363
- [16] Hou D Y, Wang J, Qu D, Luan Z K and Ren X J 2007 Fabrication and characterization of hydrophobic PVDF hollow fiber membranes for desalination through direct contact membrane distillation *Separation And Purification Technology* **69** 78–86