# Non-solvent Flux Augmentation of an LDPE-Coated Polytetrafluoroethylene Hollow Fiber Membrane for Direct Contact Membrane Distillation

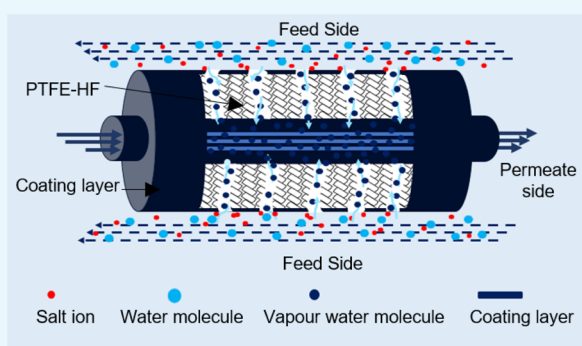Mohamad Razif Mohd Ramli, Abdul Latif Ahmad,* Ebenezer Idowu Oluwasola, and Choe Peng Leo

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**ABSTRACT:** Membrane distillation (MD) is a thermal technology for the desalination process that requires a hydrophobic microporous membrane to ensure that the membrane can maintain the liquid−vapor interface. This work aims to enhance the water permeation flux of the previously coated membrane by modifying the surface of the polytetrafluoroethylene hollow fiber (PTFE HF) membrane with a selected non-solvent such as acetone, cyclohexanone, and ethanol in low-density polyethylene as a polymeric coating solution. However, the modification using acetone and cyclohexanone solvents was unsuccessful because a reduction in membrane hydrophobicity was observed. The modified PTFE HF membrane with ethanol content exhibits high wetting resistance with a high water contact angle, which can withstand pore wetting during the direct contact MD process. Since MD operates under a lower operating temperature range (50−90 °C) compared to the conventional distillation, we herein demonstrated that higher flux could be obtained at 7.26 L m$^{-2}$ h$^{-1}$. Thus, the process is economically feasible because of lower energy consumption. Performance evaluation of the modified PTFE HF membrane showed a high rejection of 99.69% for sodium chloride (NaCl), indicating that the coated membrane preferentially allowed only water vapor to pass through.

Feed Side

PTFE-HF

Coating layer

Permeate side

Feed Side

• Salt ion  • Water molecule  • Vapour water molecule  — Coating layer

## 1. INTRODUCTION

Sustainable access to potable water remains one of the common problems of humanity from time immemorial. The rapidly expanding industrial and technology breakthroughs have significantly increased this burden. This burden will be a continual challenge, especially with the increasing population and increasing water demands for industrial and domestic applications.[1−4] Besides air, water is the most vital resource to survival, followed by food. Unfortunately, our water sources are continually exposed to contamination in the form of chemicals and bio-pollutants. Some of these pollutants do not only limit access to their sustainable uses in terms of quantity and quality as a result of unpleasant changes in their physicochemical properties but they can also become potentially poisonous when consumed at a specific concentration.[5−9]

Consequently, effective and sustainable remediation techniques are continually being researched to obtain potable water for human consumption and other applications. Several water treatment techniques have been reported, including filtration, distillation, chemical precipitation, photocatalysis, membrane, bioremediation, and ion exchange. Direct thermal distillation for water purification is one of the oldest, removing virtually all non-volatile impurities and one of the most expensive water treatment options.[10] The cost limits associated with conven-

tional distillation have necessitated research on alternative techniques for the distillation process. This search gave birth to membrane distillation (MD), which is recognized as a powerful technique to separate arrays of pollutants from contaminated water. It is a highly valued treatment option under investigation for improvement for the past 2 decades, particularly in the recovery of potable water from the scarcely explored but ubiquitous seawater sources, particularly the MD.[11,12] MD, which synergistically combines desalination and filtration processes, has been described as an attractive second-generation water purification technology renowned for the separation of highly saline water that has generated interest in recent times.[4,13,14] The direct contact MD (DCMD) involves two exist streams: hot stream (50−80 °C) on the feed stream (saline water) of the membrane and the cold stream (18−25 °C) at the permeate side under minimum constant differential pressure driving force.[15,16] This principle makes it an option preferable to
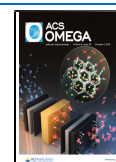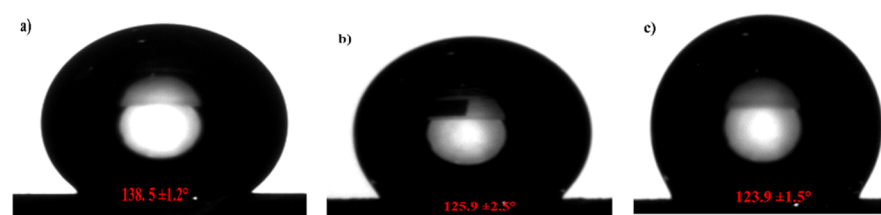
**Figure 1.** Water droplet on the PTFE HF membrane surface obtained from solution coating with (a) ethanol, (b) cyclohexanone, and (c) acetone.

the conventional distillation (CD) and the reverse osmosis (RO) techniques. The technique also benefits from the lower operating temperature and pressure required for its operation compared to the CD and RO, respectively.[1,17,18]

The importance and potential benefits of exploring the MD for seawater remediation and as an effective technique for wastewater treatment have necessitated numerous research efforts to improve the MD concept.[6] The central idea here is to make the fabricated membrane more thermally active to enhance its productivity and energy efficiency.[1,19,20] The use of dense polymeric membranes has been hypothesized to have the ability to increase the flux rate of MD by suppressing the limiting factors associated with the conventional porous membranes.[1,21] The significant limitations of using hydrophobic membranes in the MD process are wetting after prolonged usage and fouling due to continuous accumulation of biofilm, organic, inorganic, and colloidal substances on either the surface of the membrane or in its internal pore structure.[3,22]

In general, any parameter that improves flux production results in the suppression of delayed wetting and reduced wetting rate in a membrane.[23] Unfortunately, the preferred hydrophobic types of membranes utilized in MD also reduce the membrane's water vapor flux.[22] Therefore, the primary task is to circumvent the mechanisms responsible for the trade-off relationship between water vapor flux and resistance to resistance in MD. Theoretically, some of the factors that influence the type and nature of the surface of a membrane wetting include the interrelationship between wettability and interfacial interactivity, contact angle, surface free energy, surface tension, liquid entry pressure (LEP), adhesion force, mechanisms of membrane wetting, the influence of membrane properties, feed characteristics, and operating conditions (feed concentration and inlet temperature). Therefore, it is necessary to innovate suitable techniques to prevent membrane wetting, thereby improving the use of MD technology in various applications.[24] Most of the time, the desired characteristics of the polymer surface cannot be achieved using the unmodified polymer; therefore, an appropriate modification of the material is typically required.[24]

Several chemical and physical techniques have been used to modify the surface of the membrane to achieve the desired characteristic; such techniques include membrane surface dip coating, membrane surface grafting, vapor deposition of metals, treatment with flame, membrane etching, electric discharge, membrane irradiation, and plasma-ion beam treatment.[1,3,24] Membrane coatings using different materials capable of improving the hydrophobicity and porosity of the membrane is a subject of interest among past and contemporary researchers, including Li et al.,[25] Chen et al.,[12] and Guillen-Burrieza et al.[23]

The surface coating of the membrane is the simplest method to replace various costly techniques and the complex time required to produce superhydrophobic surfaces using a solvent and solvent additive coating method.[12,26−29] The idea of this method is to form a polymeric membrane with a lotus-like microstructure with high hydrophobicity and surface roughness.[31] Based on the research by Erbil et al.,[27] superhydrophobic coating is formed using polypropylene (a simple polymer) and various solvents such as *p*-xylene, methyl ethyl ketone (MEK), cyclohexanone, and isopropyl alcohol at 70 °C by depositing a rough, thin layer on the surface to reportedly yield a gel-like porous coating. They found that xylene and MEK resulted in the highest WCA of 160°. In addition, they also indicated that the concentration of the polymer in the coating solution plays an important role and found that the polymer concentration from 10 to 40 mg/mL increased the WCA by about 26° from 123 to 149°. Feed temperature is one of the operating variables that significantly influences the DCMD process to achieve the highest permeate flux and significantly promotes energy efficiency. The feed temperature is usually set below the boiling point of the feed solution (20−90 °C). Therefore, operational conditions such as feed and permeate temperature and flow rates are the parameters that directly affect membrane performance. The permeate flux increased with the increased temperature of the feed due to a direct correlation between vapor pressure and temperature.[30−32] Many researchers investigate the effect of different feed temperatures on various DCMD modules to determine the efficiency of the permeate flux.[33,34] As the feed temperature increases, the viscosity of the feed solution decreases, and the transmembrane vapor pressure increases due to the heat from the heat loss from the feed stream. Higher output was observed at a feed temperature of 60−70 °C compared to a feed temperature of 40−50 °C.

In our previous study, the surface of commercial polytetrafluoroethylene hollow fiber (PTFE HF) membrane was successfully modified using low-density polyethylene (LDPE) solution coating of different concentrations for DCMD.[2] As a result, the modified commercial PTFE HF membrane at 30 g/L concentration (M-3) satisfies best the four critical parameters considered, which include porosity, contact angle, LEP, and water flux of 60.18 ± 0.10%, 135.14 ± 0.24°, 0.9868 ± 0.02 bar, and 4.12 L m$^{-2}$ h$^{-1}$ at 70 °C, respectively. The present work aims to enhance the water flux of the previously modified membrane by a second coating of (M-3) using non-liquid solvent (acetone, ethanol, and cyclohexanone) and evaluates the effect of feed temperature optimum permeability and efficient salt rejection from a brine solution.

## 2. RESULTS AND DISCUSSION

**2.1. Effect of Non-solvent Additives.** This study investigated the effect of non-solvent additives in a coated PTFE HF membrane coating solution to enhance surface hydrophobicity. The non-solvent additives investigated include ethanol, acetone, and cyclohexanone with a standard boiling point of 78.3, 56, and 155.7 °C, respectively. The formation of a rough LDPE layer on the membrane surface may be attributed
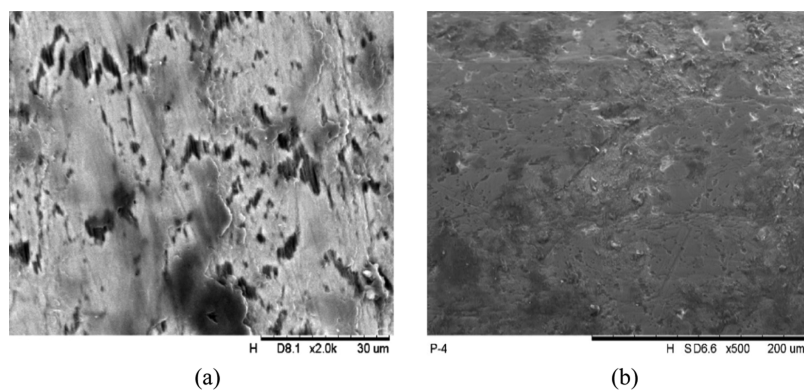
**Figure 2.** SEM images of the PTFE HF membrane coated with (a) cyclohexanone and (b) acetone.

to the interfacial interaction between the solvent and non-solvent.[25] This is because the non-solvent and the solvent diffuse into each other, decreasing the tension and partitioning of the initially smooth interface into numerous curves. Eventually, the curved interface was broken, and the solvent was brought into contact with the non-solvent. Thus, the separation of the microphases occurred due to the precipitation of the LDPE polymeric solution onto the HF membrane of the PTFE. Therefore, the curved interface was further divided into smaller interfaces, which gave rise to the fine nanostructure of the micro-papillae and formed a superhydrophobic surface. The impact on the wettability of non-solvent additives was evaluated via water contact angle (WCA). Figure 1a−c shows the images of the water droplet on the resulted surface, which indicates that the surface WCA was found at 138.5,125.9, and 123.2° for ethanol, cyclohexanone, and acetone, respectively. The WCA was increased by 3° by adding ethanol; from our previous work, it was observed that the WCA of the modified PTFE HF membrane was found at 135.14° (a mixture of LDPE and xylene).

In contrast, the addition of acetone and cyclohexanone caused a reduction in WCA. The increment of WCA by adding non-solvent additives (ethanol) as a hard precipitator in a polymeric solution accelerates phase separation, enhances the coagulation process, and thus results in a membrane with uniform structure compared to the soft precipitator non-solvent.[35−37] The instability of coating solution contributes to low WCA of cyclohexanone and acetone content due to its curve shape before reaching the solidification step.

Figure 2a,b shows the SEM images of the PTFE HF membrane coated by cyclohexanone and acetone. There was a significant cracking of the coated layer on the PTFE HF membrane when acetone and cyclohexanone were used. In addition, while using cyclohexanone as the non-solvent, there was blockage of some of the modified PTFE HF membrane surface pores, and large cracks were also found, which offsets the benefit of the rough surface.

Rapid solidification is required to obtain high WCA on the surface; therefore, the surface characteristics of the coating layer on the PTFE HF membrane was affected by the boiling point of the non-solvent. Thus, selecting a non-solvent additive with a low boiling point is vital to obtain a coated layer's rough surface and to induce a high solidification rate. Therefore, the relatively higher boiling point of cyclohexanone compared to ethanol and acetone causes a longer evaporation time, which is undesirable for the desired superhydrophobic surface of the PTFE HF membrane. However, although the boiling point of acetone is

lower than that of ethanol, a hydrophobic surface is expected using acetone as a non-solvent, but the additional role of ethanol as a hard precipitator could aid the nucleation and crystallization rates on the membrane surface[38] compared to acetone, which also offers a similar mechanism, resulting in low porosity.[12] Therefore, cyclohexanone and acetone as non-solvent additives in the coating solution were not considered for further investigation due to reduced surface hydrophobicity of the membrane by sensile drop contact angles with water and decreased porosity of the membrane which could affect the membrane flux.

**2.2. Effect Ethanol Concentrations.** The effect of ethanol concentration in the coating solution was investigated as non-solvent additives due to its capability to enhance phase separation. To determine the effect of surface hydrophobicity, the ethanol concentration was varied from 10 to 50% (v/v), designated as E-1 to E-5. Figure 3 shows that the surface WCA
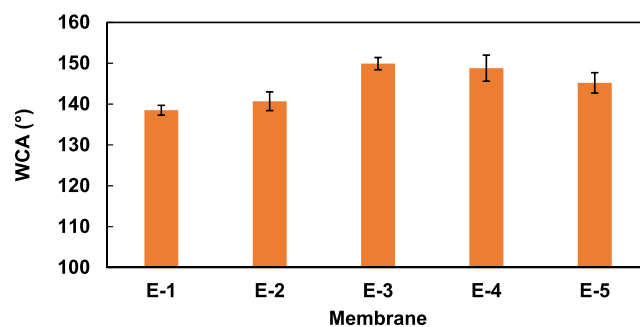


**Figure 3.** Effect of ethanol content.

was proportionally increased with the increasing ethanol concentration in the coating solution. The result indicates that a maximum WCA of 149.9 ± 1.5° was achieved at 30% (v/v) ethanol, which is very close to the superhydrophobic WCA of ∼ 150°.[41] The high hydrophobicity obtained is due to the increased rate of precipitation in the coating solution used, forming a micro-structure and nanostructure of LDPE on the coated surface of the PTFE HF membrane. The WCA value had dropped at high concentrations of ethanol for E-4 and E-5 at 148.8 ± 3.2° and 145.2 ± 2.5°, respectively, due to the heterogeneous coating and excess heterogeneity formed on the coated surface. The coating solution's solidification rate had failed to reach the membrane's surface due to the instability of the coating solution at high non-solvent content.

These phenomena occurred especially for a curve-shaped membrane, which leads to low WCA. In addition, the higher
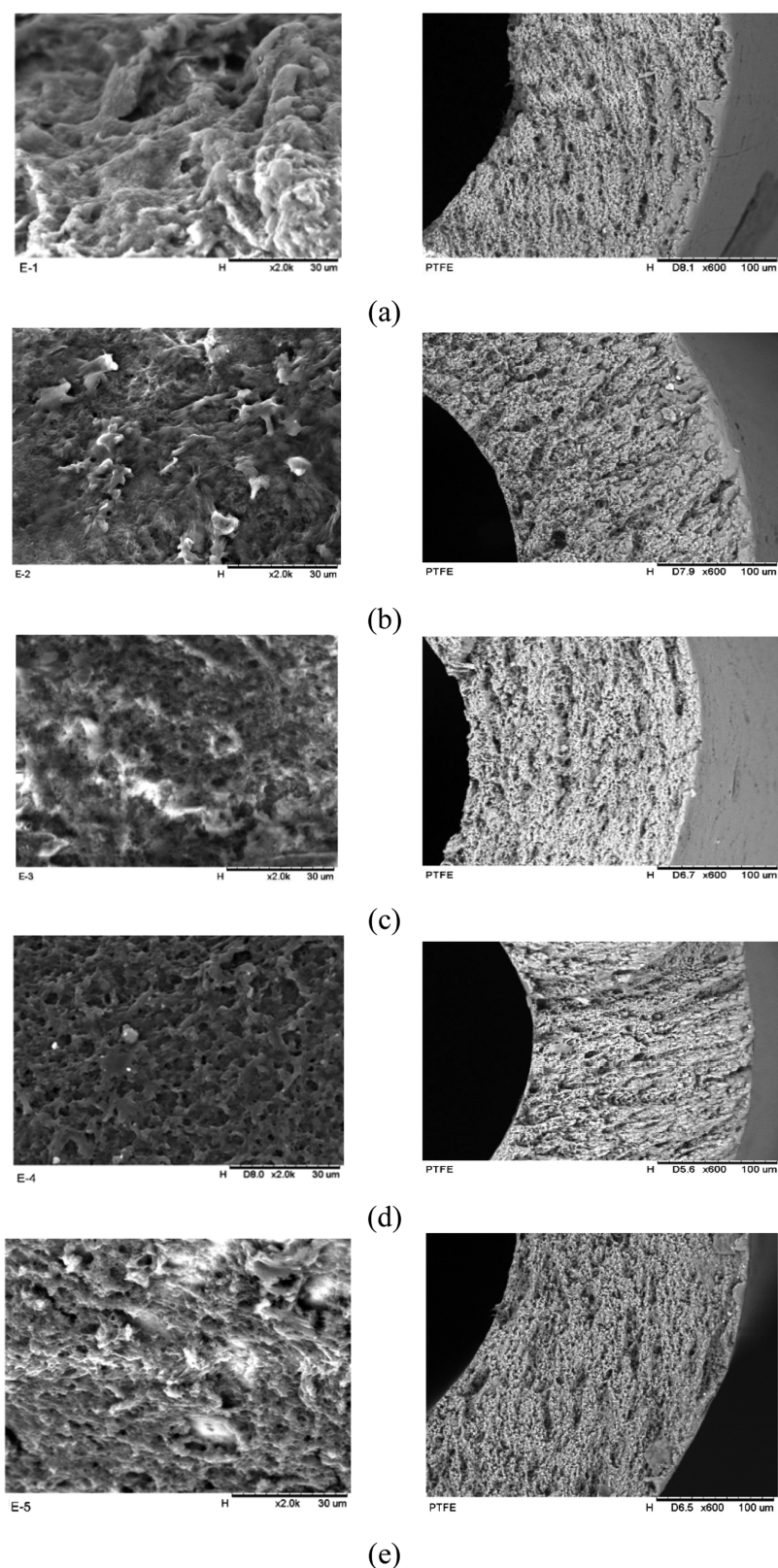
**Figure 4.** SEM image of the surface and cross section of (a) E-1, (b) E-2, (c) E-3, (d) E-4, and (e) E-5.

concentration of ethanol formed a large polymer floc due to the poor solubility of LDPE in the coating solution, contributing to poor dispersion of the coated layer on the PTFE HF membrane. According to Chen et al.,[39] formations of large floc were observed in the polyvinyl chloride solution at higher ethanol content, more than 56.5% (v/v). Based on a study by Li et al.,[25] the interfacial interaction between the solvent and the non-solvent could promote the formation of the rough surface layer on the membrane. The roughness of the membrane surface also confirmed this observation after the non-solvent treatment.

Therefore, the optimum concentration of non-solvent additives in the coating solution is critical to considering obtaining a non-wetted membrane.

**2.3. Morphology of the PTFE HF Membrane.** Modification of the PTFE HF membrane by adding a non-solvent in the coating solution can contribute to the change in surface morphology. Nevertheless, the SEM imaging test was conducted to examine the effect of ethanol content on the morphology of the membrane. Figure 4a−e shows E-1 to E-5. It can be noticed that each membrane image exhibited a different surface morphology and thickness. The result showed that the thickness of the coating layer was in the range of 8.94−36.1 $\mu$m when the concentration of ethanol content increased from 10 to 50% (v/v). The coating thickness for E-1 and E-2 was 36.1 and 20.9 $\mu$m, respectively, which increased its resistance during the performance test. Although the WCA of the membrane achieved hydrophobic property, it nonetheless showed a relatively low porosity. The porosity of membrane E-1 to E-5 was 48.96 ± 0.43%, 54.21 ± 0.78%, 61.11 ± 0.80%, 61.59 ± 0.45%, and 61.43 ± 0.78%, respectively. These lowered porosity results (less than 60%) are attributable to the membrane pore blockage by the coating layer. It is important to point out that the thickness of the coated layer is in proportion to the viscosity of the coating solution.

A lower ethanol content of 10−20% (v/v) resulted in a higher viscosity of the polymer concentration, resulting in a non-uniform crystalline structure deposited on the PTFE HF membrane. Based on the surface of the membrane, the non-solvent and solvent diffuse into each other and formed two microscopic phases: the LDPE-rich phase and the LDPE-poor phase, partitioned into numerous curved ones. The volatility of ethanol was higher than that of the polymer−solvent (LDPE) as a factor microphase separation took place on the PTFE HF membrane surface due to precipitation of LDPE in the coating solution. Meanwhile, the fast solidification occurs before the scattering of the coated layer to form the micro- and nanostructure of LDPE, which was responsible for the increasing hydrophobic layer on the membrane surface.

**2.4. PTFE HF Membrane Wetting Resistance.** The assessment of the resistance of the membrane to wetting was performed using LEP. A membrane with high LEP value that can prevent wetting of the membrane for the MD process is desired. The values of LEP for the modified PTFE HF membrane are shown in Figure 5. It can be observed that the LEP value for membranes E-1 to E-5 ranges from 1.188 to 1.364 bar, with the least LEP value higher than the value of 0.9868 bar obtained for the coated PTFE membrane but without non-solvent additives. To achieve a high LEP value, membrane modification should meet several characteristics, including a high WCA, minimum
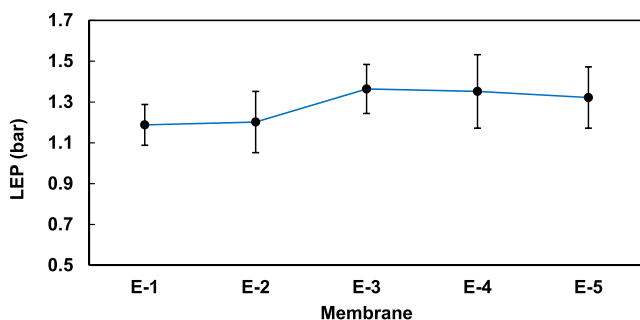
surface energy, high surface tension for the feed solution, and optimum pore size. The LEP values of E-3 were the highest among other modified membranes at 1.364 ± 0.12 bar. In addition, it achieved maximum WCA at an optimum concentration of ethanol content in the polymer solution, and the gas permeability test yielded a pore size close to 0.21 ± 0.003 $\mu$m. Researchers recommended a pore size between 0.2 and 1.0 $\mu$m in most MDs.[40] However, the reduction in pore size may reduce the surface porosity of the membrane while increasing the tortuosity, leading to a lower permeation flux.[41] To prevent wettability, the pore size of the membrane must be optimal.

These results reveal that coating the PTFE HF membrane with additional non-solvent additives can enhance the hydrophobic properties of the PTFE HF membrane. The minimum applied pressure to water before it penetrates membrane micropores is defined by its LEP value. The relationship as defined by the Laplace equation is as shown below[42−44]

$$LEP > \Delta P_{interface} = P_{liquid} - P_{vapor} = \frac{-2\beta\gamma L \cos\theta}{r_{max}}$$

where $\beta$ is the pore geometric factor, $\gamma$ is the liquid surface tension, $\theta$ is the contact angle of liquid (water), and $r_{max}$ is the maximum pore size among pore size distribution. $\Delta P_{interface}$, $P_{liquid}$, and $P_{vapor}$ are the pressure gradient applied at the interface, the pressure process liquid, and the water vapor pressure within the pores, respectively. According to the Laplace equation, if the LEP value is higher than the value of the transmembrane pressure ($\Delta P_{interface}$) means that the wetting resistance was high and it would not affect the quality of water flux during the MD test. Additionally, when the pore structure remains unchanged, with optimal pore size and high surface hydrophobics, the LEP value of the membrane increases.

Furthermore, Cassie Baxter (CB) explained this phenomenon by the equation listed below[45]

$$\cos\theta_{CB} = rf_s \cos\theta_Y - f_v = f_s[r \cos\theta_Y + 1] - 1$$

where $\theta_{CB}$ and $\theta_Y$ are the contact angles of water on a rough and original smooth surface. $f_s$ and $f_v$ are the area fractions of the solid and vapor, respectively. $r$ is the combining roughness effect. According to the CB described from the equation, the rough solid surface's wettability resistance will increase with respect to the smooth surface. This indicates that the surface becomes more hydrophobic and has a higher LEP value with increased surface roughness ($r$). Thus, roughness is another crucial parameter for the MD process as rough surfaces offer a higher adhesion tendency for fouling.[46] Since E-3 shows higher WCA, LEP value, and an acceptable percentage of porosity, E-3 was chosen to compare the roughness between the PTFE HF membrane coated with and without ethanol content in the polymer solution by atomic force microscope (AFM). Figure 6a,b shows the AFM images to relate the surface roughness to the contact angle. The surface roughness parameters of the PTFE HF membrane were determined by a scan size of 12.5 $\mu$m × 12.5 $\mu$m. These membranes present the rough lumpy aggregates from the surface and clearly can be observed as bright high peaks.

Meanwhile, the dark regions show that the pores were depressed on the surface. In terms of roughness, E-3 (ethanol content) from Figure 6b has the highest surface roughness ($R_a = 0.488$ $\mu$m) compared to without ethanol ($R_a = 0.168$ $\mu$m). The high roughness value of the E-3 membrane corresponding to the highest contact angle among the treated membranes could be

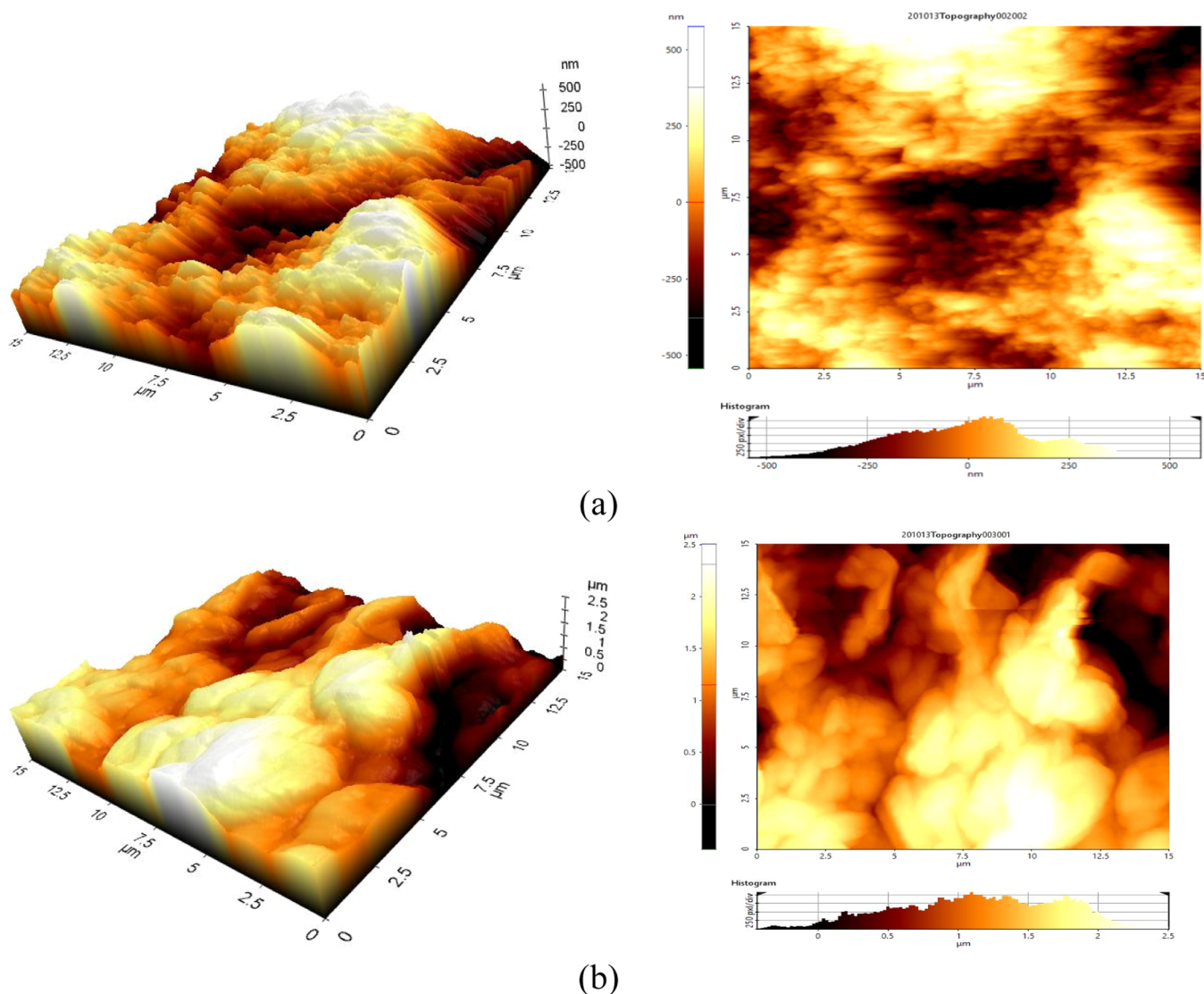**Figure 5.** LEP of the modified membrane.

(a)



(b)

**Figure 6.** AFM images of (a) coating without ethanol content and (b) coating with ethanol content in a polymer solution.

responsible for surface hydrophobicity enhancement. A similar conclusion was reached by Giljean et al.[47] and Razmjou et al.,[48] indicating that the surface roughness of a membrane is proportional to its WCA and inversely to the surface energy and could also prevent membrane wetting, as demonstrated in the present finding.

**2.5. Performance of the Membrane in DCMD.**
*2.5.1. Effect of Temperature.* The modified PTFE HF membrane was tested in the DCMD experiment in which sodium chloride was introduced in the feed solution with increasing feed temperature. Feed temperature is one of the parameters that has been widely investigated to determine the MD process's success in achieving the highest permeate flux.[49] In general, the exponential increase in water permeation flux can be obtained by increasing the temperature of the feed solution.[50] E-3 was chosen for the wettability study, where feed temperature was varied from 60 to 80 °C at 10 °C increments to remove salt (synthetic sodium chloride). In this experiment, the wettability test was operated for 6 h. Figure 7 shows the water permeation flux profile versus different temperatures at a constant distillate temperature of 20 °C. The fluxes of the PTFE HF membrane exhibited higher permeation flux with an increase in the feed
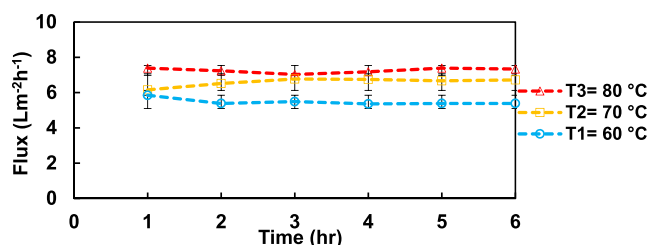


**Figure 7.** Water flux for the PTFE HF membrane at different feed temperatures.

temperature. A highest permeate flux of NaCl ($7.26 \, \text{L m}^{-2} \, \text{h}^{-1}$) was obtained at the higher feed temperature of T3 compared to T1 and T2 with fluxes of 5.48 and $6.48 \, \text{L m}^{-2} \, \text{h}^{-1}$, respectively. A similar trend was observed by El-Abbassi et al.,[51] where a higher vapor pressure reportedly gave a higher water flux due to an increase in the feed temperature. However, there seem to be no significant change in permeate flux between 60 and 80 °C due to the fact that the PTFE HF membrane evaluated has a minimum porosity value of a 61.11 ± 0.80% and also possess a near-superhydrophobic characteristic at 149.9 ± 1.5° WCA. In general, a large evaporation surface leads to increased porosity.

High porosity results in poor mechanical resistance, which tends to compress or crack the pressurized membrane, reducing the performance of the MD.

The modified PTFE HF membrane's fluxes influenced by feed temperature conform to the Antoine equation relationship between vapor pressure and temperature.[52] At a constant feed rate and feed concentration, increasing the temperature could increase the driving force to allow water vapor to pass through the membrane. These results confirmed that the mass transfer via the hydrophobic micropore membrane was close to the vapor pressure difference between the permeate and the distillate sides of the membrane. Conversely, maintaining the permeate temperature at 20 °C, which is lower than the feed temperature, is an effective practice to prevent vapor pressure drop across the membrane and help obtain higher permeate flux. Besides, it is worth mentioning that enhancement of surface hydrophobicity for the modified E-3 membrane at an optimum concentration of ethanol content in the polymer solution effectively improves the membrane flux.

*2.5.2. Rejection.* As shown in Figure 8, all the membranes maintained a consistent high value of 99% sodium chloride
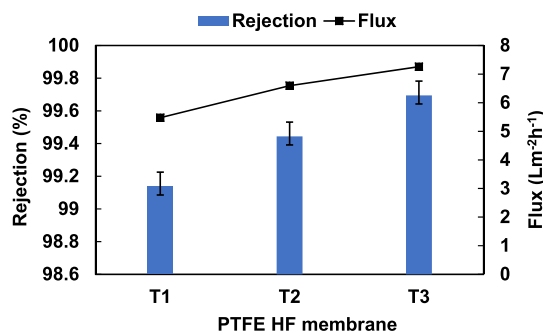


**Figure 8.** NaCl rejection of the PTFE HF membrane.

(NaCl) removal within the operating temperature range. It was observed that the PTFE HF membrane had a better rejection of 99.69% at a temperature of 80 °C compared to 99.44 and 99.14% at temperatures 70 and 60 °C, respectively. The rejection of NaCl with a lower value of conductivity at the permeate side of 59.21 $\mu$S compared to the initial conductivity of 19.4 mS shows that the ethanol content in the polymeric solution-coated PTFE HF membrane only permitted water vapor to be transported across via the hydrophobic microporous membrane. Besides, higher wetting resistance of membrane pores successfully promotes separation processes of salt ion, whereby only water vapor allows it to be transported and condensed at the permeate side. Several essential characteristics suitable for the DCMD membrane process can be enhanced by modifying the PTFE HF membrane via non-solvent addition in the polymeric solution. The modified membrane effectively created a rough surface which affects the heat transfer, which especially undergoes laminar flow.[53] The research by Liu et al.[54] and He et al.[55] found that effective gas and vapor adsorption properties by the membrane could be achieved by high hydrophobicity and surface area. In addition, activated diffusion occurs when water content salt ion comes in contact with the modified PTFE HF membrane's surface, where they will only allow the vapor to pass through. As mentioned above, the conductivity was reduced at the permeate tank during the DCMD experiment. Thus, microporous hydrophobic membrane is the fundamental principle to serve as a barrier that

separates hot and cold sides.[56] From the experimental result, the increase of WCA, LEP value, surface roughness, and acceptable range of porosity from the characterization of the PTFE HF membrane has contributed to better permeation and enhance the membrane to maintain the liquid–vapor interface. Based on the above discussion, an optimum concentration of ethanol content in polymeric solution to coat the PTFE HF membrane successfully enhanced the membrane permeation flux and increased the percentage of salt rejection. A 6 h DCMD process stability test conducted on the PTFE HF membrane using a synthetic brine solution showed only a slight reduction in its WCA from the initial value of 149.9 ± 1.5° to 138.2 ± 2.3°. This result indicates the efficiency of the coating layer in the enhancement and maintained the stability of the membranes' hydrophobicity after prolonged operation.

## 3. CONCLUSIONS

In conclusion, the second coating solution for the PTFE HF membrane was shown to successfully enhance the properties and improve the DCMD process flux compared to our earlier study. A non-solvent additive (ethanol, acetone, and cyclohexanone) in the polymeric LDPE coating solution achieved WCA values of 138.5, 125.9, and 123.2° for ethanol, cyclohexanone, and acetone, respectively. It has been demonstrated that the proposed hydrophobic coating of the HF PTFE membrane through the inclusion of the non-solvent (ethanol) in the polymer solution was effective in the DCMD process. The coated PTFE HF membrane's unique characteristics such as high wetting resistance and LEP, the rough surface at 149.9 ± 1.5°, 1.364 ± 0.12 bar, and 0.488 $\mu$m, respectively, proved satisfactorily for the MD process. Furthermore, we have demonstrated that a modified membrane can successfully act as a barrier to salt with a high rejection of salt ions (above 99%) at the permeate side with a low conductivity value. Since MD is a membrane-based technique that utilizes low-grade heat, we have demonstrated an optimum feed temperature at 80 °C (below the temperature of the feed solution), directly impacting the DCMD performance, resulting in high water permeation flux at 7.26 L m$^{-2}$ h$^{-1}$. The light reduction in the WCA of the membrane surface after being operated for 6 h indicates that the modified membrane could be operated under a long-term operation of DCMD. The coating layer on the PTFE HF membrane enhanced the membrane's stability and maintained its hydrophobicity, potentially having a longer lifetime. However, it is in our opinion that the surface of a modified membrane can withstand a harsh operating environment if a superhydrophobic surface with a WCA larger than 160° can be obtained.

## 4. MATERIALS AND METHODS

**4.1. Membrane and Chemicals.** A PTFE-HF membrane (OD/ID: 0.8/0.5 $\mu$m) of 0.2 $\mu$m pore was supplied by PLC Solution (Malaysia). The PTFE HF membrane is hydrophobic and has been selected as the substrate as it allows surface modification through LDPE via indirect coating from our previous work.[2] Xylene (>98.5% of the mixture isomers + ethyl benzene base, France) as a solvent, ethanol, acetone, and cyclohexanone were purchased from Sigma-Aldrich (St. Louis, MO, USA) to be used as non-solvent additives, while sodium chloride (NaCl) as a feed solution was supplied from Merck Sdn. Bhd.

**4.2. Preparation of the Non-solvent Additive Coating Solution.** The optimum concentration of the coating solution

(30 g/L) from the previous work was further studied to enhance the surface hydrophobicity of the PTFE HF membrane by adding non-solvent additives (ethanol, acetone, and cyclohexanone). The percentage volume of ethanol, acetone, and cyclohexanone was fixed at 10% (v/v) and slowly added to the polymeric solution (mixture of LDPE and xylene) below the non-solvent boiling point by controlling the circulated water at the same temperature. The above steps varied from 10% (v/v) to 50% (v/v) to study the effect on membrane wettability. The PTFE HF membrane was coated and dried at room temperature in a vacuum oven.

## 4.3. Membrane Characterization and Performance Test.

The hollow fiber-modified membrane was characterized by wetting properties, surface morphology, surface roughness, LEP, and porosity. In addition, the effect of the preparation parameters was assessed in terms of hydrophobicity.

### 4.3.1. Water Contact Angle.
The membrane wettability was measured with goniometer equipment, Rame-Hart 250-FI USA, based on the sessile drop method at ambient temperatures ($24 \pm 1$ °C). The PTFE HF membrane was placed on top of a platform, and DI water (2 $\mu$L) was dropped on the membrane surface using a microsyringe. The digital image was analyzed by determining the average values of WCA to minimize experimental errors. This step was repeated at five different positions for each sample.

### 4.3.2. Scanning Electron Microscopy.
The surface morphology of each modified membrane was examined by scanning electron microscopy (SEM) using table-top SEM, HITACHI (TM3000), Japan, to analyze the flat and curved surface of the modified PTFE HF membrane. The modified membranes were immersed into liquid nitrogen, $N_2$, and then cracked to obtain a brittle and clean[57] fracture to measure the coating thickness of the membranes. The membrane was initially coated with gold using a Quorum SC7620 sputter-coater (USA).[58]

### 4.3.3. Surface Roughness.
AFM (Model XE 100, Park System) was used to analyze the topographic map of the membrane surface via the non-contact mode at room temperature. The membrane samples with a dimension of 5 $\mu$m × 5 $\mu$m were fixed on a magnetic holder. All AFM images were observed using XEI software to determine the roughness parameter, $R_a$.

### 4.3.4. Liquid Entry Pressure.
LEP is defined by the minimum TMP at which the first drop of the feed solution enters the pore by overcoming the forces of the PTFE HF membrane. The membrane was equipped with water inserted in the lumen shell side in a stainless steel tubular module. The value of LEP was analyzed using PMI software.

### 4.3.5. Membrane Porosity.
Porosity measurement ($\varepsilon$) of the modified membrane was determined by the gravimetric method mentioned in our previous publication;[2] three PTFE HF membranes were cut into 3 cm long pieces for each measurement to reduce the error and immersed in Porefil for 24 h. Then, the total porosity was averaged for three fibers and was calculated according to eq 1

$$\varepsilon(\%) = \frac{[(W_w - W_d/\rho_w)] - \pi r^2 h_f}{[(W_w - W_d/\rho_w)] - \pi r^2 h_f + W_d/\rho_p} \times 100\% \quad (1)$$

where $W_w$ and $W_d$ are the weight of the wet and dry membranes (g), $\rho_w$ represents the density of Porefil (1.78 g/cm$^3$), r is the inner radius (cm), $h_f$ is the length of the fiber (3 cm), and $\rho_p$ is the polymer density (2.2 g/cm$^3$).

### 4.3.6. Pore Size Distribution.
The size of the membrane pores was estimated using a capillary flow porometer POROLUX

1000 and a gas flow/liquid displacement method (Benelux Scientific, Germany). First, Porefil was used to moisten the membrane samples measuring 5 cm in length completely. The samples were then connected to the instrument, where tests were performed using the "dry/wet" procedure, and pore sizes were calculated using PMI software.

### 4.3.7. Direct Contact Membrane Distillation.
The experimental DCMD study was conducted to determine the separation performance for modified membranes at different feed temperatures. In this experiment, 35 g/L of sodium chloride (NaCl)-simulated seawater was used as a feeding solution. The temperature of the hot feed varied from 60 to 80 °C, and the cold permeate side was set at 20 °C. The permeation flux (L m$^{-2}$ h$^{-1}$) and salt rejection (%) of the membrane by MD were calculated from the following equations, respectively

$$J = \frac{\Delta V}{A \Delta t} \quad (2)$$

$$R(\%) = \left[ 1 - \frac{C_p}{C_f} \right] \times 100 \quad (3)$$

where $J$ denotes the permeate flux (L m$^{-2}$ h$^{-1}$), $\Delta V$ is the permeate volume (L), $A$ is the membrane surface area (m$^2$), $\Delta t$ is the time interval (h), $R$ is the rejection coefficient (%), and $C_p$ and $C_f$ are the feed's concentration and permeate solution (g L$^{-1}$), respectively.

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**Notes**

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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