A novel dual-layer bicomponent electrospun nanofibrous membrane for desalination by direct contact membrane distillation

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Abstract

In this study, a bicomponent nanofibrous composite membrane was fabricated by electrospinning and was tested for desalination by direct contact membrane distillation (DCMD). The nanofibrous membrane was composed of a dual-layered structure of poly(vinylidenefluoride-*co*-hexafluoropropylene) (PH) nanofibers and polyacrylonitrile (PAN) microfibers. Morphological characterization showed slightly beaded cylindrical PH nanofibers with porosity of about 90%. The contact angles of PH and PAN nano/microfibers were 150° and 100°, respectively. The nanofibrous membranes were tested by DCMD and a high water flux of 45 and 30 Lm^{-2}h^{-1} was obtained for distilled water and 35 gL^{-1} NaCl solutions as feed, respectively using DL2 membrane (i.e., 25/75 PH/PAN thickness ratio). The present dual-layer membrane showed better flux performance compared to a commercial flat-sheet membrane. The results suggest the potential of the dual-layer nanofibrous membrane for DCMD applications.

Keywords: Membrane distillation; dual-layer; PVDF-*co*-HFP; PAN; electrospinning; nanofiber

1. Introduction

Membrane distillation (MD) is one of the emerging and promising desalination processes for clean water production. MD involves the use of a hydrophobic porous membrane between a hot feed side and a cold permeate side, wherein only water vapour is allowed to pass through the membrane driven by vapour pressure difference [1]. The ideal MD membrane design should be hydrophobic, has high porosity and good pore size distribution, and thin thickness. Several approaches were investigated by different research groups to enhance the properties and performance of MD membranes, which include: (a) incorporation of nanofillers in the polymeric matrix to form a mixed matrix membrane [2]; (b) surface modification by the use of coatings and post-treatments [3]; (c)

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fabrication of dual-layer or triple-layer membranes; (d) synthesis of new materials, and; (e) fabrication of engineered membrane structure with remarkable properties.

In the past two decades, electrospinning of nanofibers has received considerable attention due to its ability to produce ultrafine fibers in nonwoven form with high porosity, high strength-to-weight ratio, and high specific surface area [4]. Recently, a few research groups have reported on the performance of engineered nanofibers for MD application [5]. Most of these studies involved the use of single-layer nanofibers with or without nanoparticle incorporation or surface modification [6, 7]. For instance, Essalhi and Khayet [6] fabricated PVDF nanofibers without any support layer and examined the effect of membrane thickness on direct contact membrane distillation (DCMD) performance. The flux was found to decrease with the increase in membrane thickness. Similarly, Liao et al. [7] prepared PVDF nanofiber membranes with and without heat press treatment. The heat-pressed PVDF nanofiber membrane showed stable permeate flux of about 21 $kgm^{-2}h^{-1}$, which was higher compared to the performance of commercial membranes.

To further enhance the MD flux, one possible approach is to use a dual-layer membrane made of hydrophobic/hydrophilic or superhydrophobic/less hydrophobic layers. Dual-layer membranes have been investigated for MD performance [8] but not in the nanofiber structure. For example, the group of Khayet and Matsuura [9] [10] conducted a series of experiments using dual-layer flat-sheet membranes fabricated by phase inversion. The base polymer used was either polyetherimide (PEI) [9] or polysulfone [10], which were both hydrophilic, and the surface was modified based on the migration of hydrophobic surface modifying macromolecules (SMM). Bonyadi and Chung [11] prepared a dual-layer hollow fiber PVDF/PAN membrane by co-extrusion method incorporating hydrophobic and hydrophilic filler clay nanoparticles. The fabricated dual-layer hollow fiber membrane obtained as high as 55 $kgm^{-2}h^{-1}$ DCMD flux at $90^{o}C$ with 3.5 wt% NaCl as feed.

In the present study, a novel dual-layer bicomponent nanofibrous membrane was fabricated using electrospinning and tested for DCMD performance. The nanofibrous membrane was made up of two layers of different nanofiber matrix: poly(vinylidene fluoride-*co*-hexafluoropropylene) (PVDF-*co*-HFP) (facing the feed) and polyacrylonitrile (PAN) (facing the permeate) electrospun fibers. To our knowledge, this is the first report of dual-layer membrane utilizing bicomponent nanofiber structures. The nanofiber membrane boasts of high porosity and interconnected pore structures, and high hydrophobicity that are essential for an MD membrane. Our objective was to investigate the effect of thickness ratio of the two components of the dual-layer nanofibrous membrane on the DCMD flux and salt rejection performance.

2. Experimental

2.1. Electrospinning

Two different polymer solutions were prepared for electrospinning. The first solution consisted of 15 wt% PVDF-*co*-HFP (M_w = 455,000 gmol^{-1}, Sigma) (referred herein as PH), which was dissolved in a solvent system composed of N,N dimethylformamide (DMF, Sigma) and acetone (Scharlau) (8:2 by wt%, respectively) by overnight stirring at room temperature. A small amount of lithium chloride (Sigma) was added to the PH solution to improve its electrospinnability. The second solution consisted of 8 wt% PAN (M_w = 150,000 gmol^{-1}, Sigma) dissolved in DMF at 55°C and was stirred overnight.

Electrospinning was carried out using the set-up shown in **Fig. S1**. To fabricate dual-layer membranes, PAN nanofibers were first electrospun directly to the rotating drum collector covered with an aluminium foil, followed by electrospinning of PH nanofibers on top of the PAN membrane. PH and PAN nanofibers were electrospun at an applied voltage of 20 kV and 16 kV, respectively. Other parameters were kept the same for both PH and PAN: tip-to-collector distance = 15 cm; feed flow rate = 1 mlh^{-1}; chamber humidity = 30-36%; chamber temperature = 23-28°C, and; drum speed = 700 rpm. The nozzle (21G, inner diameter = 510 µm) kept on oscillating laterally controlled by LabVIEW program for a distance of 200 mm. Dual-layer membranes with different thickness ratios of PH and PAN layers for a total thickness of 80 µm were fabricated. The thickness of the different membrane layers were controlled by manipulating the electrospinning time duration between 1.5 to 6 h. Neat single-layer PH nanofibers were also fabricated. After electrospinning, the fabricated nanofibers were dried in an oven at 60°C for 48 h to remove the residual solvents.

2.2. Characterization and measurements

The surface morphology and cross-sectional images of the samples were characterized by scanning electron microscopy (SEM, Zeiss Supra 55VP, Carl Zeiss AG). SEM imaging was operated at 10-15 kV, and different image magnifications at different areas were obtained for each sample. The fiber size and pore size distributions were obtained by image analysis of the SEM images using ImageJ software (NIH). Contact angle (CA) measurements were carried out using an optical tensiometer (Theta Lite 100) equipped with image processing software. Equal sizes of sample membranes were placed on a platform and droplets of 5-7 µL volume were dropped carefully on the membrane surface. A real-time camera captures the image of the droplet and the CA is estimated. At least 3 measurements were taken for each membrane sample and the average value is reported here. Membrane porosity, defined as the volume of pores divided by the total volume of the membrane was measured via a gravimetric method [12]. Equal sizes of (2 cm x 2 cm) membrane samples were immersed in ethanol (Scharlau). The weight of the samples was measured before and after saturation of ethanol, and the membrane porosity was calculated following **Eq. S1**. To evaluate the membrane wetting resistance, liquid entry pressure (LEP) measurements were carried out using a home-made

LEP measurement apparatus (**Fig. S2**). The measurement of LEP is described in Supporting Information.

2.3. DCMD test

DCMD experiments in a counter-flow set-up (**Fig. 1**) were carried out with constant inlet temperatures at the feed and permeate sides of 60±0.5 and 20±0.5 ˚C, respectively. First, distilled water (DW) was used as feed and then followed by 35 gL^{-1} NaCl solution. The initial electrical conductivities of DW and NaCl solution were maintained at <5 µS/cm and 62,000 µS/cm, respectively. The feed and permeate circulation rates were maintained at 400 ml min^{-1} and 200 ml min^{-1}, respectively. The MD cell had a dimension of 77 mm x 26 mm x 3 mm (L x W x H) with an effective membrane area of 20 cm^2. The electrical conductivity of the solutions were constantly monitored using a portable conductivity meter (HQ40d, Hach), and the change in weight of the permeate solution was automatically recorded through a data acquisition system attached to the digital balance (PGW 4502e, Adam) throughout the duration of the test. A commercialized PTFE flat-sheet membrane (GE, with polypropylene support layer) was used for comparison.

3. Results and discussion

Figure 2 shows the surface and cross-sectional morphologies of the electrospun nano/micro fibers and their respective fiber diameter distribution. There are two kinds of dual-layer membranes that were fabricated: 50/50 PH-PAN and 25/75 PH-PAN referred herein as DL1 and DL2 membranes, respectively. The 25/75 PH-PAN membrane signifies 25% PH to 75% PAN layer by thickness. During electrospinning, nanofibers are ejected from the tip of a nozzle as high voltage is applied. The solidified nanofibers attach to the rotating collector in a random, non-woven manner. The continuous overlapping of the nanofibers forming layers upon layers of fibers results to interconnected pores throughout the depth of the membrane. **Table 1** shows the characteristics of the commercial and fabricated samples. The electrospun PH nanofibers showed a diameter in the range of 125 – 325 nm with an average of 210 nm (**Fig. 2a**). The PAN nanofibers on the other hand showed diameters from 1-3.5 µm (**Fig. 2b**). The PH nanofibers showed cylindrical structure with some bead formation on the fiber surfaces. The beads are attributed to the lower PH concentration as also observed by other researchers [13]. The PAN nanofibers showed bigger fiber sizes and had more interconnecting nodes. The PTFE flat-sheet membrane (**Fig. S3**) was an expanded type showing submicron fiber sizes with many flat densed areas. One can see the differences in structure between PTFE surface (**Fig. S3a**) and the PH surface (**Fig. 2a**), wherein the PH showed highly porous structure with interconnecting pore structures. The support layer of PTFE membrane was made of polypropylene (**Fig. S3b**) with micron-sized diameters and very large pore sizes. By gravimetric method [12], the PH nanofibers were found to have around 90% porosity, which was much higher than that of the commercial PTFE membrane

(70% porosity). Of note is that the neat single-layer PH nanofibers have similar properties as with the PH of dual-layer membranes.

The highly porous nature of the nanofiber membranes can be clearly seen in **Fig. 2c**, showing interconnecting pores through the depth of the membrane. Similarly, the dual-layer membranes also showed interconnecting pores, but two distinct layers of differently-sized bicomponent fibers with highly porous structure can be clearly identified in **Fig. 2d**. The top PH nanofibers showed a superhydrophobic property (CA = 150°), which was higher compared to the commercial PTFE flat-sheet membrane (~124°) (**Fig. 3**). The higher hydrophobicity of PH nanofibers is attributed to the increased surface roughness due to overlapping nanofiber layers, which results in less contact area for the solid fiber and water leading to higher CA [14]. Moreover, the presence of some beads-on-string has added to the roughness of the membrane [15], thus enhancing its hydrophobicity. PAN nanofibers showed less hydrophobic behaviour at 100°. The nanofibrous mats had a thickness of 80-82 μm.

LEP measurements were conducted using a home-made LEP set-up. In the present study, the nanofiber membranes showed LEP values of 77-94 kPa while the PTFE commercial membrane was 273 kPa. This difference in values could be explained by checking the surface properties of the membranes. Though nanofiber membranes have higher surface hydrophobicity, the average surface pore size of the PH membrane was also much higher than that of the PTFE membrane. Through image analysis, the average surface pore size of the PH nanofiber was found to be 1 μm, while based from the manufacturer's data, the PTFE membrane had an average pore size of 0.22 μm. The high LEP of PTFE membrane is mainly attributed to its small average pore size and smaller surface area for penetration (many densed areas) as observed on its morphological structure in **Fig. S3a**.

Figures 4a and 4b show the permeate fluxes of the neat PH and dual-layer nanofibrous membranes in comparison with a commercial flat-sheet PTFE membrane. DW and 35 gL^{-1} NaCl solutions were used as feed. In **Fig. 4a**, stable permeate fluxes were observed for both PTFE and DL2 membranes for over 3 h of DCMD test using DW as feed. The dual-layer DL2 showed higher flux (45 LMH) compared to that of PTFE membrane (28 LMH). Both dual-layer membranes (DL1 and DL2) showed much better flux performances compared to neat PH and PTFE membranes (**Fig. 4b**). Similar flux trend results as follow were observed for DW and 3.5 wt% NaCl feed solutions: DL2>DL1>15PH≥PTFE. The highest flux was observed for DL2 (25/75 PH-PAN) membrane obtaining a flux of 45 LMH using DW and 30 LMH using NaCl solution (Fig. 5b). These results are much higher compared to the reported results in the literature [12] [16]. The improvement in flux performance for dual-layer membranes is attributed to: a) increased top surface hydrophobicity, thereby decreasing the potential wetting of the membrane; b) higher porosity of the top surface which increases the available surface area for evaporation; c) and the structure of thinner more hydrophobic surface layer (i.e., PH) (DL2) and thicker less hydrophobic layer (i.e., PAN), which decreases the mass transfer resistance [17]. The salt rejection of neat PH was 99.4%, while the dual-layer

membranes were >98.50% and the PTFE membrane was 99.9%. The present results suggest that a thinner more hydrophobic and high porosity layer would result to better DCMD flux. Furthermore, the results here show the potential and competency of the dual-layer nanofibrous membrane for DCMD applications.

4. Conclusion

In this study, dual-layer nanofibrous membranes made of PVDF-*co*-HFP and PAN layers have been fabricated by electrospinning. The PVDF-*co*-HFP nanofibers showed highly porous structure (~90% porosity) with interconnecting pores. The formation of rough surface due to overlapping nanofibers and the presence of beads-on-string have improved the hydrophobicity of the membrane up to a contact angle of 150°. The paired PAN layer had micron-sized fibers and lower contact angle of 100°. Through DCMD tests, the dual-layer PVDF-co-HFP/PAN with 25/75 thickness ratio showed the highest permeate flux of 30 LMH using 35 gL^{-1} NaCl feed solution. Further optimization of the membranes needs to be carried out by altering the different electrospinning parameters to improve the DCMD flux performance and salt rejection.

Acknowledgements

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Figure captions

Figure 1. Schematic illustration of the DCMD set-up.

Figure 2. SEM images of the dual-layer nanofibrous membranes: (a) PVDF-HFP nanofibers (top layer), (b) PAN nanofibers (bottom layer), and cross-sectional view of (c) neat PH nanofibers and (d) dual-layer PH-PAN nanofibers.

Figure 3. Contact angle measurements of the PTFE and electrospun nanofiber membranes.

Figure 4. (a) Continuous DCMD test of the 25/75 dual layer membrane (DL2) and commercialized flat-sheet membrane in DW water as feed, and (b) final flux values of the different MD membranes for both DW and 35 gL^{-1} NaCl solution as feed (feed: inlet temperature = 60˚C, flow rate = 400 ml min^{-1}; permeate: inlet temperature = 20˚C, flow rate = 200 ml min^{-1}).

Table caption

Table 1. Characteristics of the electrospun nanofibrous membranes and the commercial flat-sheet membrane.
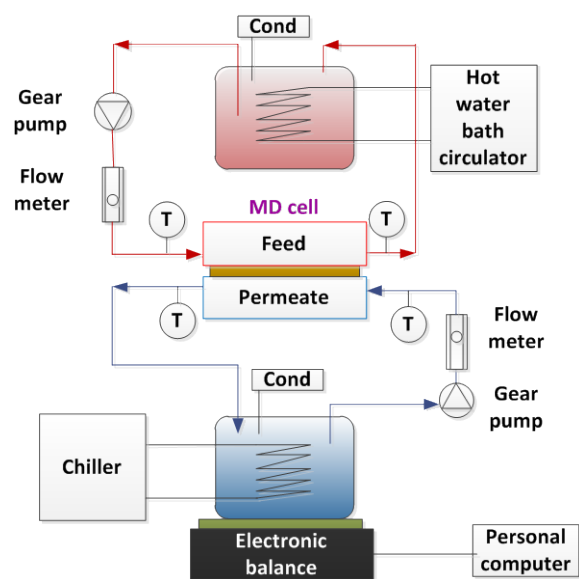
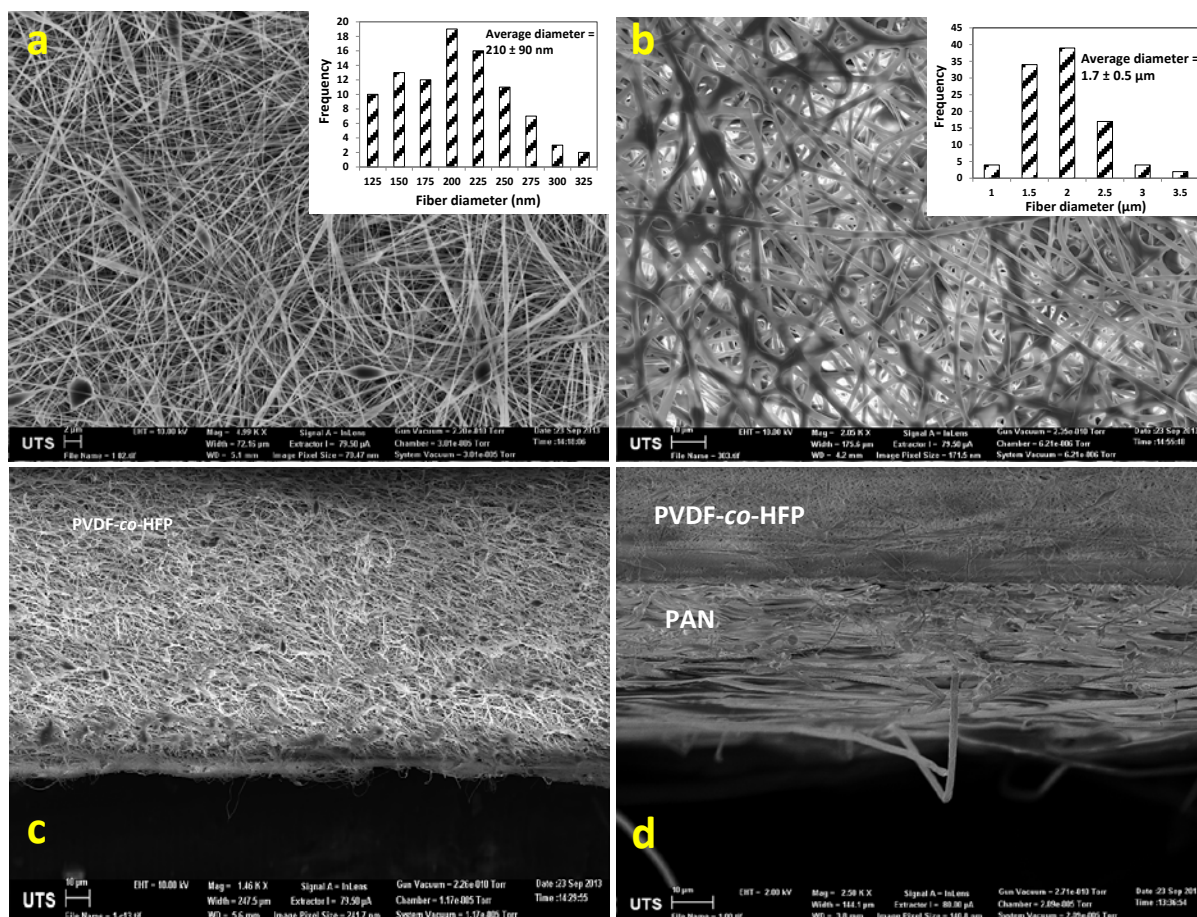**Figure 1.** Schematic illustration of the DCMD set-up.

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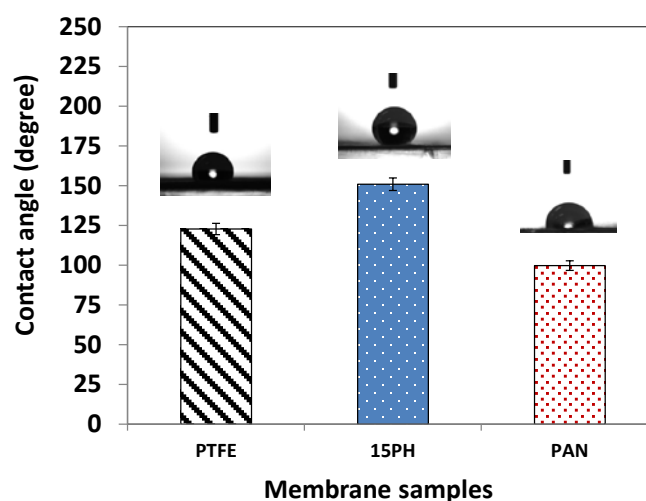

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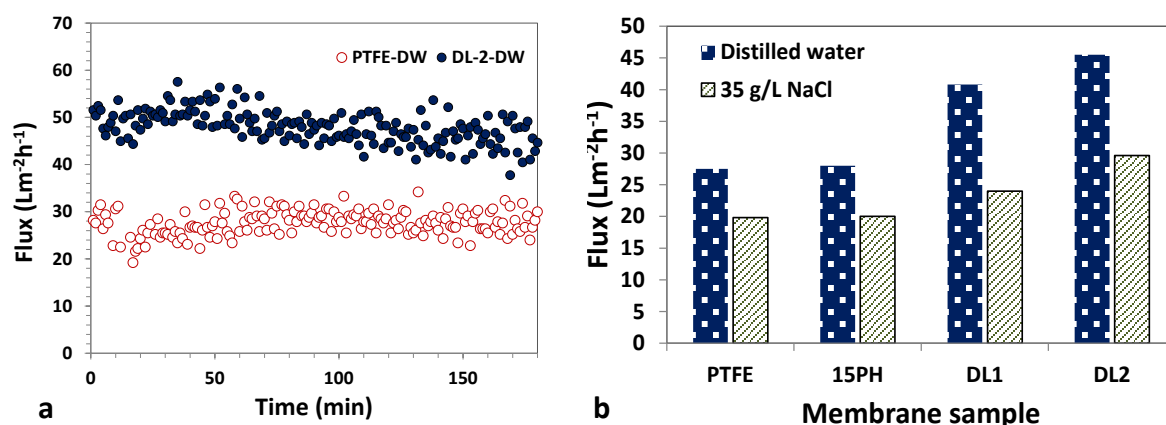
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Table 1. Characteristics of the electrospun nanofibrous membranes and the commercial flat-sheet membrane.

Membrane/ composition	Thickness (µm)	Porosity (%)	Surface pore size range (µm)	Mean surface pore size (µm)	LEP (kPa)	Contact angle (deg)	Average fiber diameter, (µm)
Neat 15PH	80	90	0.6-2.5	1	77	150	0.210/1.7[a]
DL1 (50/50 PH/PAN)	80	90	0.6-2.5/6-16 [a]	1/11 [a]	85	150/100 [a]	0.210/1.7 [a]
DL2 (25/75 PH/PAN)	82	90	0.6-2.5/6-16 [a]	1/11[a]	94	150/100 [a]	0.210/1.7 [a]
PTFE with PP support layer	179 total (20 µm PTFE layer)	70	-	0.22 (provided by manufacturer)	273	124	-

[a] signifies dual-layer PH/PAN values