



Short communication

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

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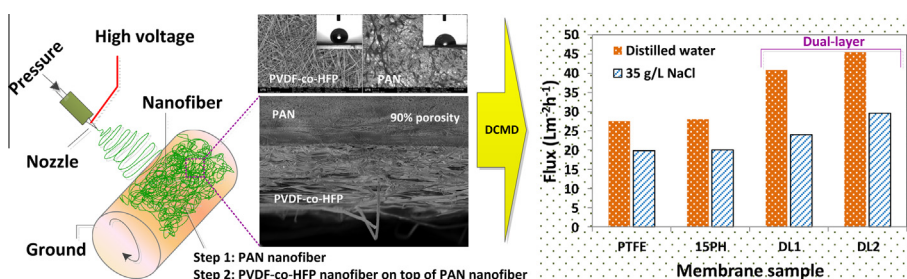
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## HIGHLIGHTS

- A nanofibrous membrane composed of two layers was fabricated for DCMD.
- The membrane was composed of PVDF-co-HFP nanofibers and PAN micro/nanofibers.
- The PVDF-co-HFP nanofibers showed a superhydrophobic property and high porosity.
- A high flux performance was obtained for the dual-layer nanofibrous membrane.
- The present dual-layer nanofibrous membrane showed good potential for DCMD.

## GRAPHICAL ABSTRACT



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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(vinylidene fluoride-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 L m<sup>-2</sup> h<sup>-1</sup> was obtained for distilled water and 35 g L<sup>-1</sup> 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.

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## 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 vapor is allowed to pass through the membrane driven by vapor pressure difference [1]. The ideal MD membrane design should be hydrophobic, has high porosity and good pore size distribution, and thin thickness. The currently-used MD membranes are usually made of microfiltration membranes, which are not specifically designed for MD

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[2]. Thus, there is a need to improve the MD membrane design and structure for a better MD performance. 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 [3]; (b) surface modification by the use of coatings and post-treatments [4]; (c) 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 ultra-fine fibers in nonwoven form with high porosity, high strength-to-weight ratio, and high specific surface area [5]. Electrospinning involves the use of high electric fields applied on a polymer solution forming elongated and stretched nanofibers and collected on a grounded collector. Recently, a few research groups have reported on the performance of engineered nanofibers for MD application [6]. Most of these studies involved the use of single-layer nanofibers with or without nanoparticle incorporation or surface modification [7,8]. Majority of the studies used polyvinylidene fluoride (PVDF) for electrospinning because of its excellent properties and it can also be easily dissolved in a solvent, however, other polymers such as polyazole [9], polytetrafluoroethylene (PTFE) [10] and polystyrene [11] were also investigated for MD. For instance, Essalhi and Khayet [7] 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. [8] prepared PVDF nanofiber membranes with and without heat press treatment. The heat-pressed PVDF nanofiber membrane showed stable permeate flux of about  $21 \text{ kg m}^{-2} \text{ h}^{-1}$ , which was higher compared to the performance of commercial membranes. In a recent study [12], a triple-layer MD membrane composed of a PVDF nanofiber layer, a PVDF solution-casted microporous layer, and a polyethylene terephthalate (PET) support layer was investigated on its performance in air-gap membrane distillation (AGMD). The triple-layer membrane showed increased hydrophobicity and wetting resistance (i.e., high liquid entry pressure (LEP)), which resulted to increased flux, salt rejection and long term performance of the membrane.

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. However, it must be noted that having a dual-layer hydrophobic/hydrophilic structure alone will not directly result to increased flux, but other important parameters such as thickness and porosities of each layer should be considered. Some reports have indicated that support layers that are thick, less hydrophobic, and with big pore sizes could lead to pore wetting [13]. Dual-layer membranes have been investigated for MD performance [14] but not in the nanofiber structure. For example, the group of Khayet and Matsuura [15,16] conducted a series of experiments using dual-layer flat-sheet membranes fabricated by phase inversion. The base polymer used was either polyetherimide (PEI) [15] or polysulfone [16], which were both hydrophilic, and the surface was modified based on the migration of hydrophobic surface modifying macromolecules (SMM). Bonyadi and Chung [17] 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  $55 \text{ kg m}^{-2} \text{ h}^{-1}$  DCMD flux at  $90^\circ\text{C}$  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. We used PVDF-co-HFP because it was reported to have superior hydrophobicity and high free volume compared to PVDF [18]; while PAN has good mechanical and thermal stability, and excellent solvent resistance, and is commonly used for microfiltration and ultrafiltration applications. 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 ( $M_w = 455,000 \text{ g mol}^{-1}$ , 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 ( $M_w = 150,000 \text{ g mol}^{-1}$ , Sigma) dissolved in DMF at  $55^\circ\text{C}$  and was stirred overnight.

Electrospinning was carried out using the set-up shown in Fig. S1 (Supporting Information, SI). To fabricate dual-layer membranes, PAN microfibers 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 fibers 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 =  $1 \text{ ml h}^{-1}$ ; chamber humidity = 30–36%; chamber temperature =  $23\text{--}28^\circ\text{C}$ , and; drum speed = 700 rpm. The nozzle (21G, inner diameter =  $510 \mu\text{m}$ ) 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  $80 \mu\text{m}$  were fabricated. The thickness of the different membrane layers were controlled by manipulating the electrospinning time duration between 1.5 and 6 h. Neat single-layer PH nanofibers were also fabricated. After electrospinning, the fabricated nanofibers were dried in an oven at  $60^\circ\text{C}$  for 48 h to remove the residual solvents.

### 2.2. Characterization and measurements

Details of characterization and measurements can be found 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  $60 \pm 0.5$  and  $20 \pm 0.5^\circ\text{C}$ , respectively. First, distilled water (DW) was used as feed and then followed by  $35 \text{ g L}^{-1}$  NaCl solution. The initial electrical conductivities of DW and NaCl solution were maintained at  $<5 \mu\text{S/cm}$  and  $62,000 \mu\text{S/cm}$ , respectively. The feed and permeate circulation rates were maintained at  $400 \text{ ml min}^{-1}$  and  $200 \text{ ml min}^{-1}$ , respectively. The MD cell had a dimension of  $77 \times 26 \times 3 \text{ mm}$  (L  $\times$  W  $\times$  H) with an effective membrane area of  $20 \text{ cm}^2$ . The electrical conductivity of the solutions

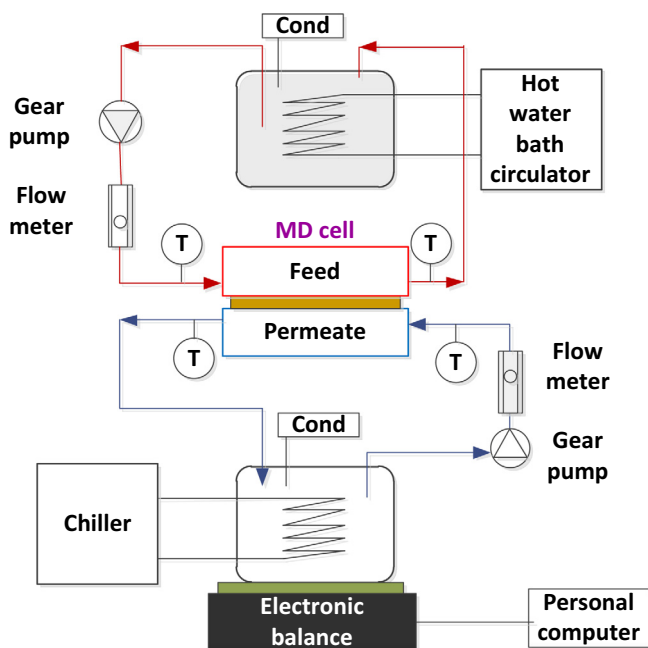


Fig. 1. Schematic illustration of the DCMD set-up.

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 mem-

brane (GE, with polypropylene support layer) was used for comparison.

### 3. Results and discussion

#### 3.1. Morphology

Fig. 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 to 3.5  $\mu\text{m}$  (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 [19]. The PAN nanofibers showed bigger fiber sizes and had more interconnecting nodes. The PTFE flat-sheet membrane (Fig. S3, SI) was an expanded type showing submicron fiber sizes with many flat dense areas. One can see the differences in structure between PTFE surface (Fig. S3a, SI) and the PH surface (Fig. 2a), wherein the PH showed highly porous structure with interconnecting pore structures. The support layer of PTFE membrane was

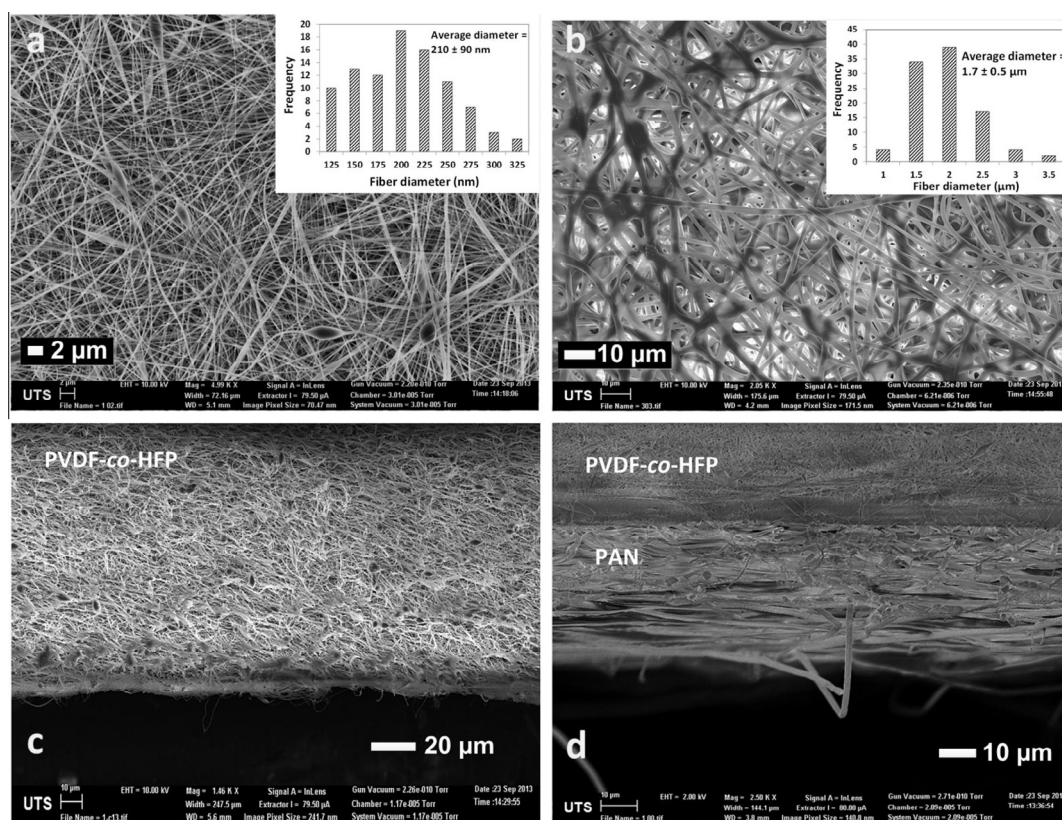


Fig. 2. SEM images of the dual-layer nanofibrous membranes: (a) PVDF-co-HFP nanofibers (top layer); (b) PAN microfibers (bottom layer), and cross-sectional view of (c) neat PH nanofibers and (d) dual-layer PH-PAN micro/nanofibers.

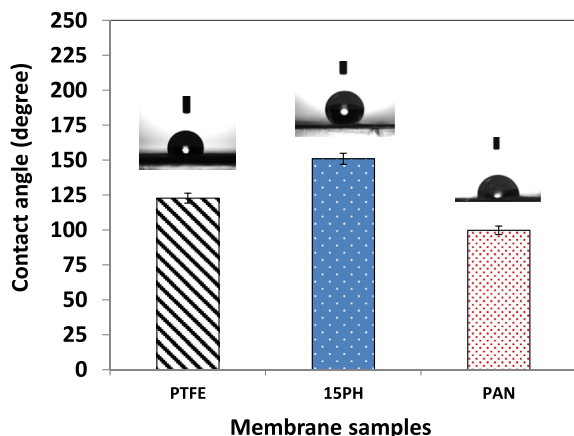
**Table 1**

Characteristics of the electrospun nanofibrous membranes and the commercial flat-sheet membrane. Otherwise stated, all values were measured in the present tests.

Membrane/composition	Thickness ( $\mu\text{m}$ )	Porosity (%)	Surface pore size range ( $\mu\text{m}$ )	Mean surface pore size ( $\mu\text{m}$ )	LEP (kPa)	Contact angle ( $^\circ$ )	Average fiber diameter, ( $\mu\text{m}$ )
Neat 15PH	80	90	0.6–2.5	1	77	150	0.210/1.7 <sup>a</sup>
DL1 (50/50 PH/PAN)	80	90	0.6–2.5/6–16 <sup>a</sup>	1/11 <sup>a</sup>	85	150/100 <sup>a</sup>	0.210/1.7 <sup>a</sup>
DL2 (25/75 PH/PAN)	82	90	0.6–2.5/6–16 <sup>a</sup>	1/11 <sup>a</sup>	94	150/100 <sup>a</sup>	0.210/1.7 <sup>a</sup>
PTFE with PP support layer	179 total (20 $\mu\text{m}$ PTFE layer)	70	–	0.22 (provided by manufacturer) <sup>b</sup>	273	124	–

<sup>a</sup> Signifies dual-layer PH/PAN values.

<sup>b</sup> General Electric (GE), USA.



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

made of polypropylene (Fig. S3b, SI) with micron-sized diameters and very large pore sizes. By gravimetric method [20], 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.

### 3.2. Contact angle

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

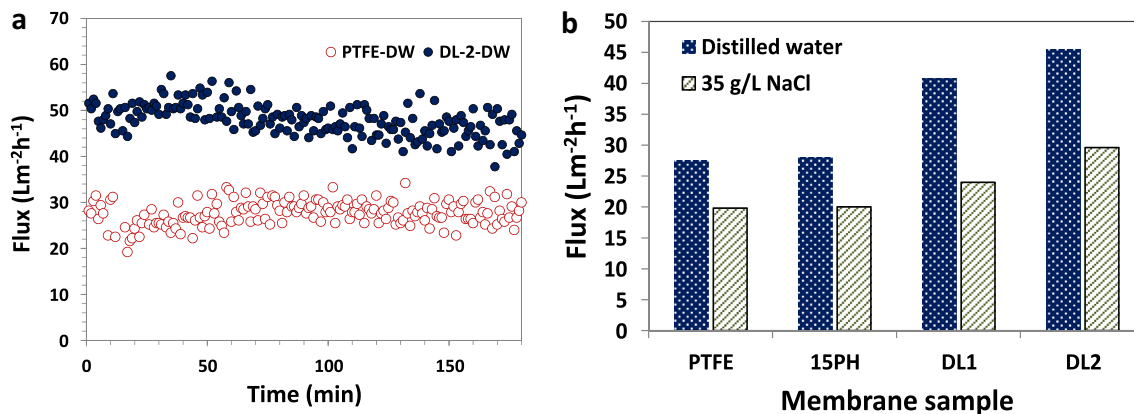
can be clearly identified in Fig. 2d. The top PH nanofibers showed a superhydrophobic property ( $\text{CA} = 150^\circ$ ), which was higher compared to the commercial PTFE flat-sheet membrane ( $\sim 124^\circ$ ) (Fig. 3). The higher hydrophobicity of PH nanofibers is attributed to the increased surface roughness due to overlapping nanofiber layers, which results in less contact area for the solid fiber and water leading to higher CA [21]. Moreover, the presence of some beads-on-string has added to the roughness of the membrane [22], thus enhancing its hydrophobicity. PAN nanofibers showed less hydrophobic behavior at  $100^\circ$ . The nanofibrous mats had a thickness of 80–82  $\mu\text{m}$ .

### 3.3. Liquid entry pressure (LEP)

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  $\mu\text{m}$ , while based from the manufacturer's data, the PTFE membrane had an average pore size of 0.22  $\mu\text{m}$ . The high LEP of PTFE membrane is mainly attributed to its small average pore size and smaller surface area for penetration (many dense areas) as observed on its morphological structure in Fig. S3a (SI).

### 3.4. Direct contact membrane distillation (DCMD)

Fig. 4a and b 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 g L<sup>-1</sup> NaCl solutions were



**Fig. 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 g L<sup>-1</sup> NaCl solution as feed (feed: inlet temperature = 60  $^\circ\text{C}$ , flow rate = 400 ml min<sup>-1</sup>; permeate: inlet temperature = 20  $^\circ\text{C}$ , flow rate = 200 ml min<sup>-1</sup>).

**Table 2**

Comparison of results using different membranes in DCMD mode in literature (Conditions: Feed inlet temp. = 60–63 °C, Permeate inlet temp. = 17–20 °C).

Ref	Membrane	Feed type (g L <sup>-1</sup> NaCl)	Salt rejection (%)	Permeate flux (L m <sup>-2</sup> h <sup>-1</sup> )
[8]	PVDF nanofiber	35	–	21
[14]	PVDF/PTFE dual-layer hollow fiber	35	100	20
[17]	PVDF/PAN dual-layer hollow fiber	35	–	21.6
Present study	PTFE flat-sheet	35	99.9	20
Present study	DL2	35	>98.5	30

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. 4b). These results are much higher compared to the reported results in the literature (see Table 2). 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 [23]. 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. Conclusions

In this study, dual-layer nanofibrous membranes made of PVDF-co-HFP and PAN layers have been fabricated by electrospinning. The following can be deduced from this study:

- (1) The PVDF-co-HFP nanofibers showed highly porous structure (~90% porosity) with interconnecting pores.
- (2) 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°.

- (3) 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 g L<sup>-1</sup> NaCl feed solution.
- (4) Based from the result, it suggests that a thinner more hydrophobic and high porosity layer would lead to better DCMD flux.
- (5) 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.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cej.2014.06.076>.

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