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Theoretical modeling and experimental validation of transport and separation properties of carbon nanotube electrospun membrane distillation

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Abstract

Developing a high flux and selective membrane is required to make membrane distillation (MD) a more attractive desalination process. Amongst other characteristics membrane hydrophobicity is significantly important to get high vapor transport and low wettability. In this study, a laboratory fabricated carbon nanotubes (CNTs) composite electrospun (E-CNT) membrane was tested and has showed a higher permeate flux compared to poly(vinylidene fluoride-co-hexafluoropropylene) (PH) electrospun membrane (E-PH membrane) in a direct contact MD (DCMD) configuration. Only 1% and 2% of CNTs incorporation resulted in an enhanced permeate flux with lower sensitivity to feed salinity while treating a 35 and 70 g/L NaCl solutions. Experimental results and the mechanisms of E-CNT membrane were validated by a proposed new step-modeling approach. The increased vapor transport in E-CNT membranes could not be elucidated by an enhancement of mass transfer only at a given physico-chemical properties. However, the theoretical modeling approach considering the heat and mass transfers simultaneously enabled to explain successfully the enhanced flux in the DCMD process using E-CNT membranes. This indicates that both mass and heat transfers improved by CNTs are attributed to the enhanced vapor transport in the E-CNT membrane.

Keywords: Carbon nanotubes; Desalination; Direct contact membrane distillation; Electrospun membrane; Heat and mass transfers.

Nomenclature

B	Membrane distillation coefficient [$\text{kg/m}^2 \cdot \text{s} \cdot \text{Pa}$]
c_p	Specific heat capacity [$\text{kJ/kmol} \cdot \text{K}$]
D	Diffusion coefficient [$\text{m}^2 \cdot \text{s}$]
d_h	Hydraulic diameter [m]
h	Convective heat transfer coefficient [$\text{W/m}^2 \cdot \text{K}$]
h_c	Channel height [m]
ΔH	Enthalpy of water evaporation [J/kg]
J	Permeate flux [$\text{kg/m}^2 \cdot \text{h}$]
k	Conductive heat transfer coefficient [$\text{W/m}^2 \cdot \text{K}$]
L	Membrane length [m]
M_w	Molecular weight [g/mol]
P	Pressure [Pa]
Q	Heat flux [W]
r	Mean pore size [μm]
R_K	Correlation form of Knudsen diffusion
R_M	Correlation form of molecular diffusion
R_p	Correlation form of Poiseuille or viscous flow
T	Temperature [$^{\circ}\text{C}$]
v	Velocity [m/s]
x	Molar fraction in liquid phase [-]
z	Axial coordinate [m]

Dimensionless numbers

Nu	Nusselt number [-]
Pr	Prandtl number [-]
Re	Reynolds number [-]

Greek letters

δ	Membrane thickness [m]
ε	Porosity [-]
θ	Contact angle [degree]
μ	Dynamic viscosity [Kg/m.s]
ρ	Density [kg/m ³]
τ	Tortuosity [-]

Subscripts

f	Feed side
p	Permeate side
m	Mean, membrane or modification
w	Water

1. Introduction

Compared to conventional thermal distillation desalination processes, membrane distillation (MD) is a membrane based thermal driven separation process with the principle of vapor–liquid equilibrium. The temperature gradient as driving force generates the water vapor pressure difference between the liquid–vapor interfaces. The evaporated water vapor transport through the hydrophobic membrane pores from feed side to permeate side due to the water vapor pressure difference. Typically, MD is operated at moderate feed temperature (60 to 90°C), which is significantly lower than thermal-based processes, such as multi-stage flash (MSF). Thus, recently, the MD process has been focused for desalination and many applications due to the attractive features and especially the relatively low operating feed temperature, which is suitable to apply the solar energy or utilizing low-grade heat source. [1-4].

The advantages of MD compared to the conventional desalination processes are as follows: (i) lower operating conditions, such as temperature and pressure compared to MSF and multi effect distillation (MED), and reverse osmosis (RO), respectively, (ii) theoretically high rejection efficiency (100%) of non-volatile solute, and (iii) low effect of high osmotic pressure or concentration to vapor flux [5-7]. However, there is a need to develop membranes offering high flux and better selectivity (solute passage) in order to make the MD process competitive in seawater desalination applications [8]. High flux and selective membrane in MD process depends on membrane hydrophobicity, which enhances vapor transport and reduces possibility of wetting. Wetting is the main problem to increase solute passage through the membrane pores [9].

The developing of novel MD membrane architecture is of great value to enhance the MD performance. Several hydrophobic polymeric membrane materials including polypropylene (PP), polyvinylidene fluoride (PVDF) and polytetrafluoroethylene (PTFE) have been tested [10]. Various surface modification methods of MD membrane, such as by radiation graft polymerization, plasma polymerization, grafting ceramic membranes, hydrophobic or hydrophilic surface coating, casting hydrophobic polymer over flat sheet or porous fibers as supports, co-extrusion spinning and use of surface modifying macromolecules have been conducted [11-13].

Another attempt to improve the MD performance with developing membrane material is incorporating nanomaterials into polymeric membrane materials. Of nanomaterials, carbon

nanotubes (CNTs) is one of the suitable candidates to the membrane for MD process [14]. This is mainly due to slippage effect to increase the vapor flux by the molecular smoothness of nanotube wall providing hydrophobicity. In addition to that CNTs are easy to functionalize [15]. CNTs have tunable physical, chemical and electrical properties. Moreover, if CNTs are incorporated, it enables to change the physical/chemical properties, which are the dominant parameters influencing MD performance, such as porosity, pore size, surface roughness, hydrophobicity and surface charge of the membrane [14, 16]. For the MD membrane, hydrophobicity is essential to prevent the membrane from the pore wetting problem and have a shorter transport path of water vapor [17].

The relatively straightforward composite method led to the progress on MD system with CNTs embedded polymeric membranes [18, 19]. CNTs enhanced MD has been started to apply for water desalination and showed that the immobilization of the CNTs in the pores of a hydrophobic membrane promoted vapor permeability while preventing liquid penetration into the membrane pores with 1.85 and 15 times increase in flux and salt rejection, respectively by altering the water-membrane interactions [20]. A recent publication introduced a carboxyl-functionalized CNTs composite membrane having a high water vapor flux, thermal stability, and mass transfer coefficient, which was contributed to the hydrophilic-hydrophobic interaction between water molecules and the membrane surface to provide additional water vapor path [21].

Electrospinning is a versatile process to produce fibers in the non-woven mat form with diameters ranging from few micrometers to nanometers by applying high electric fields [22, 23]. The electrospun non-woven mats provide very large specific surface area, high strength-to-weight ratio, and high porosity (~80%) and degree of interconnection, which make them attractive for water treatment applications. Moreover, the properties of nanofibers such as layer thickness, fiber diameter, and porosity can be altered and enhanced functionalities by selecting materials and incorporating them into dope solution [24, 25].

It is interesting to note that most of the studies using electrospun nanofibers for MD application only utilized PVDF as main polymer for electrospinning [26, 27]. One main reason is its ease of dissolution with common solvents, and easy electrospinnability. Nanofibrous membrane can be fabricated at an optimal (or thinner) thickness and higher porosity, without sacrificing much of its mechanical integrity [24, 25]. One important aspect of nanofibrous membranes is the increased hydrophobicity primarily due to their engineered scaffold surface

structure compared to conventional membranes [28]. The nanofiber membranes are fabricated by intersecting fibers and formed bumps on the surface, which has lotus leaf-like hierarchical structure. Air pocket formation between the bumps on the membrane surface minimizes the contact area between water molecule and membrane surface thus increasing the hydrophobicity of the surface and preventing the wetting. Further manufacturing of membrane was made by coating the physical/chemical properties changed CNTs onto unmodified polyvinylidene fluoride-co-hexafluoropropylene (PcH) nanofiber membrane [29].

However, to our knowledge there has been no effort on finding the mechanism of CNTs composite electrospun membrane in enhancing MD performance with modeling study. Modeling study will be helpful to find the role of CNTs in the enhancement of MD performance based on theoretical phenomena [30]. Therefore, our work attempted to elucidate the mechanism behind the quick vapor transport ability of the CNTs incorporated electrospun membrane with simulation approaches. A new step modeling approach was used to match the theoretical simulation result with experiment data. In addition, assumptions for the model study were proved systematically and possible mechanisms were discussed in terms of both mass and heat transfers.

2. Materials and methods

2.1 Preparation of electrospun membranes

In this study, two kinds of electrospun nanofibrous membranes of i) poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP or PH) (E-PH membrane) and ii) CNTs composite PVDF-HFP (E-CNT membrane) were prepared by electrospinning process.

2.1.1 CNTs functionalization

Multiwalled CNTs (referred herein as CNTs) was purchased from Carbon Nano-material Technology Co., Ltd. (Republic of Korea) for E-CNT membrane fabrication and 1H,1H,2H,2H-perfluorooctyl triethoxysilane (FTES) used in the fluorination (functionalizing) was purchased from Sigma-Aldrich. To successfully composite CNTs in polymeric matrix, proper dispersion and appropriate interfacial adhesion between the CNTs and polymer are required [31].

Hence, in this study, the CNTs was functionalized by the following procedure. The raw CNTs (2g) was underwent the oxidation process by mixing with 400 mL of concentrated nitric acid under a reflux for 18 h. The oxidized CNTs was then centrifuged, rinsed with deionized (DI)

water and air-dried overnight. The CNTs was added into a beaker containing 50 mL toluene and the CNTs mixed solution (*Solution A*) was sonicated for 1 h. Meanwhile, another solution (*Solution B*) was prepared by mixing 0.5 g of FTES with 0.75 mL of DI water and 50 mL of toluene for 1 h. The *Solution B* was added dropwise via syringe to the *Solution A* and stirred in a glove box filled with nitrogen gas for 18 h to allow the FTES to bond with the CNTs as shown in **Fig. 1**. The resulting mixture solution (A+B) was centrifuged to collect the functionalized CNTs. It was then dried at 120°C for 3 h and heated up to 180°C for 30 min in order to completely remove the unreacted FTES.

Figure 1. CNT functionalization process used in this study.

2.1.2 Electrospinning

In order to fabricate the E-PH membrane, the polymer dope was prepared by dissolving 20 wt% of PH ($M_w = 455,000$ g/mol) into a mixture of N,N- Dimethylformamide (DMF) and acetone (4:1 by weight) (**Table 1**). Lithium chloride (LiCl , 0.005 wt%) was used as an additive to enhance the dope electrospinning stability. All the chemicals for dope solution were purchased from Sigma-Aldrich. The polymer solution was electrospun at a rate of 0.7 mL/h and was ejected onto a non-woven textile pre-attached on a rotating collector 15 cm away from the tip of the nozzle. A positive voltage of 18 kV was applied across the tip-to-collector. The solvents in the nascent nanofibers evaporated and nanofibers curled up concurrently at a rotational speed of 500 rpm. In order to eliminate the residual solvent remained in the resultant membrane, the E-PH

membrane was subsequently placed in a fume cupboard under a vacuum condition at 60°C overnight.

For fabrication of E-CNT membranes, the polymer dope solutions containing different CNTs wt% were prepared (**Table 1**). In this study, 1 and 2 wt% CNTs composite membranes were fabricated and they were referred as E-CNT1 and E-CNT2 membranes, respectively. The electrospinning process and the post-treatment for E-CNT membranes were the same as those for E-PH membrane while the applied voltage across the tip-to-collector was 19 kV for E-CNT membranes.

Table 1. Compositions of dope solutions for electrospun membranes fabricated in this study.

Electrospun membranes	PH (wt%)	DMF (wt%)	Acetone (wt%)	CNTs (wt% to PH) ⁽¹⁾
E-PH	20	64	16	0
E-CNT1	20	64	16	1
E-CNT2	20	64	16	2

(1) Weight percentage (wt%) to polymer (PH).

2.2 Electrospun membrane characterization

The surface morphology of the electrospun membranes was observed by Scanning Electron Microscopy (SEM) (EVO MA10, ZEISS, Germany). The thickness of membranes was measured using Digital Calipers (Mitutoya, USA). A capillary flow porometer (Porometer, POROLUX™ 1000, Germany) was used for the measurement of pore size (mean), and liquid entry pressure (LEP) of membranes. The gas-liquid displacement porometry method was employed. The porosity as void volume of the membrane was measured using a gravimetric method. It was acquired by calculating the volume of ethanol filled in the membrane (based on weight difference between dry and wet membrane samples, and the material densities of ethanol and the PH polymer). Here, membrane samples were fully wetted with ethanol for 30 min. The water contact angle (or hydrophobicity) was measured by the EASYDROP Contact Angle Measuring System (Kruss, Germany). This measurement was conducted by dropping a 5-mL droplet of DI water on a membrane specimen placed on a sample board via a syringe equipped with a thin needle. A video-digitizer board was used to capture images of the water drops on the membrane. DSA1 software was used to the contact angle by a geometrical method (sessile drop). The

thermal conductivity was measured by Thermal Conductivity Analyzer (C-Therm TCI, Canada). All measurements were made at least in triplicate and average values were reported in this paper.

Table 2. Characteristics of the electrospun membranes fabricated in this study.

Membrane properties	Electrospun membranes		
	E-PH	E-CNT1	E-CNT2
Mean pore size, r (μm)	0.702	0.818	0.855
Thickness, δ (μm)	96	96	95
Porosity, ε (%)	89.3	89.8	90.2
Contact angle, θ ($^\circ$)	142.9 $\pm$ 2.1	148.0 $\pm$ 1.1	150.5 $\pm$ 1.7
LEP ⁽¹⁾ (kPa)	79.7 $\pm$ 0.8	69.0 $\pm$ 2.1	55.1 $\pm$ 2.2
Thermal conductivity, k (W/m K)	0.051	0.06	0.064

(1) LEP: liquid entry pressure.

2.3 Direct contact membrane distillation (DCMD) operation

DCMD tests were done using electrospun membranes laboratory-fabricated in this study (**Fig. 2**). The configuration of the membrane flow channel was 6.2 cm $\times$ 1.5 cm $\times$ 0.5 cm with an effective membrane area of 9.3 cm². Three different feed solutions containing 0 (DI water), 35 and 70 g/L of NaCl were heated up to either 40 or 60°C. The permeate solution was DI water and was maintained to at 20 $\pm$ 1°C. Both solutions were circulated in opposite directions across the flat sheet membrane at same flow rate (0.5L/min). The tests were completed when water flux was constant for at least 30 min.

The water flux (in unit of kg/m²h) was calculated by dividing the changes in weight (kg) of permeate tank (placed on a digital balance connected to data logger) over membrane area (0.000976 m²) and unit time (h). Salt rejection efficiency (%) was calculated by measuring the electrical conductivities in the initial feed and final permeate solutions.

Figure 2. Schematic diagram of the DCMD test unit (1: Permeate tank, 2: Digital balance connected to a computer, 3: Thermometers, 4: Cooling unit, 5: Pumps, 6: Flat sheet membrane module, 7: Flow meters, 8: Feed reservoir, 9: Hotplate).

3. Modeling approach

In order to theoretically investigate the performance of the DCMD process using electrospun membranes, one dimensional simulation model, which considered both heat and mass transfers, as well as transport model was employed [30, 32]. The driving force of MD process is attributed by the difference in water vapor pressures (by temperature gradient) between liquid-vapor interfaces of the feed and permeate sides. The transmembrane temperatures in both feed and permeate sides could not be measured directly, thus the theoretical approach had to be conducted to estimate those temperatures for the prediction of the MD performance.

3.1 Mass transfer through membrane

The partial vapor pressure of pure water ($p_{w,m}$) is calculated by Antoine's equation (Eq. 1):

$$p_{w,m} = \exp\left(23.1964 - \frac{3816.44}{T - 46.13}\right) \quad (1)$$

For calculation of partial vapor pressure of feed solution (i.e. saline water) ($p_{f,m}$), the Rault's law is considered [33]:

$$p_{f,m} = (1 - x_f) p_{w,m} \quad (2)$$

where x_f is the mole fraction of feed solution.

The permeate flux (J) through the membrane can be calculated using the following equation (Eq. 3):

$$J = B(p_{f,m} - p_{p,m}) \quad (3)$$

where B is the mass transfer coefficient.

The dusty gas model, which consist of the three models; Knudsen diffusion, molecular diffusion, and Poiseuille or viscous flow transition, has been applied to describe the permeate flux through the membrane as follows.

$$R_K^{-1} = \frac{r\varepsilon}{\tau\delta}(M_w / RT_m)^{0.5}, R_M^{-1} = \frac{\varepsilon}{\tau\delta}(DM_w / P_{aM} RT_m), R_P = \frac{r^2\varepsilon}{\tau\delta}(p_m M_w / \mu RT_m) \quad (4)$$

$$B = (R_K + R_M)^{-1} + R_P \quad (5)$$

where R_K , R_M and R_P represent the Knudsen diffusion, molecular diffusion and viscous flow, respectively; p_m is the mean water vapor pressure inside the membrane ($p_m = (p_{f,m} + p_{p,m}) / 2$), and P_{aM} is the log-mean air pressure at both sides of the membrane. The binary diffusion coefficient (D) is calculated by Fuller-Schettler-Giddings empirical equation, which can be expressed as below:

$$D = 1.19 \times 10^{-4} (T_m^{1.75} / P_m) \quad (6)$$

3.2 Heat transfer through the membrane

In the DCMD process, the heat transfer includes the heat transferred across the boundaries of the feed side (Q_f) and permeate side (Q_p), and through the membrane (Q_m).

(i) Within the boundary layer of the feed side

$$Q_f = h_f (T_f - T_{f,m}) \quad (7)$$

where T_f is the bulk feed temperature and $T_{f,m}$ is the liquid-vapor interface temperature on the feed side of the membrane.

(ii) Through the membrane

$$Q_m = \left[J\Delta H + \frac{k_m}{\delta} (T_{f,m} - T_{p,m}) \right] \quad (8)$$

where, ΔH is the enthalpy of evaporation at the mean temperature across the membrane (T_m), $T_m = (T_{f,m} + T_{p,m}) / 2$, and k_m is the thermal conductivity of the membrane.

(iii) Within the boundary layer of the permeate side

$$Q_p = h_p (T_{p,m} - T_p) \quad (9)$$

where, T_p is the bulk permeate temperature and $T_{p,m}$ is the temperature at the liquid–vapor interface on the permeate side of the membrane.

At the steady state, the overall local heat transfer through the DCMD is given by:

$$Q = Q_f = Q_m = Q_p \quad (10)$$

The heat transfer coefficients in feed and permeate, h_f and h_p , respectively can be expressed as follows [34, 35]:

$$Nu = \frac{h_i d_{h,i}}{k_i} = 3.66 + \frac{0.0668 Re_i Pr_i (d_{h,i} / L_i)}{1 + 0.04 [Re_i Pr_i (d_{h,i} / L_i)]^{2/3}} \quad i = \text{feed or permeate} \quad (11)$$

3.3 Transport model

The permeate flux is a function of the bulk flow variables such as pressure, velocity, and temperature of both feed and permeate sides. Thus, theoretical model should consider those variables to obtain the high accuracy prediction results. To investigate the transport behavior in the flat sheet module of DCMD, the momentum, mass and energy balances have been considered at both of feed and permeate sides.

The transport behaviors (the momentum, mass and energy balances) on the feed side can be expressed in terms of the pressure, velocity, composition and temperature as follows:

$$\frac{dP_f}{dz} = -\frac{3\mu_f}{h_c^2} v_f \quad (12)$$

$$\frac{d(\rho_f v_f)}{dz} = -\frac{J}{h_c} \quad (13)$$

$$\frac{d(\rho_f v_f x_f)}{dz} = 0 \quad (14)$$

$$\frac{d(\rho_f v_f c_{p,f} T_f)}{dz} = -\frac{Q_f}{h_c} \quad (15)$$

where P_f is the bulk feed pressure, μ_f is the bulk feed flow dynamic viscosity, v_f is the bulk feed flow velocity, x_f is the salinity of the bulk feed flow, $c_{p,f}$ is the specific heat of the bulk feed solution and ρ_f is the density of the bulk feed solution.

The boundary conditions of pressure, velocity, salinity and temperature for the feed side are as follows:

$$P_f(L) = P_a, \quad v_f(0) = v_{f,in}, \quad x_f(0) = x_{f,in}, \quad T_f(0) = T_{f,in} \quad (16)$$

where P_a is the ambient atmospheric pressure at both outlets of the fluids, $v_{f,in}$ is the inlet feed velocity, $x_{f,in}$ is the inlet feed salinity and $T_{f,in}$ is the inlet feed temperature.

On the permeate side, the momentum, mass and energy balances can be described as follows:

$$\frac{dP_p}{dz} = -\frac{3\mu_p}{h_c^2} v_f \quad (17)$$

$$\frac{d(\rho_p v_p)}{dz} = -\frac{J}{h_c} \quad (18)$$

$$\frac{d(\rho_p v_p c_{p,p} T_p)}{dz} = -\frac{Q_p}{h_c} \quad (19)$$

where P_p is the bulk pressure, μ_p is the bulk flow dynamic viscosity, v_p is the bulk flow velocity, x_p is the salinity of the bulk feed flow, $c_{p,p}$ is the specific heat of the bulk feed solution and ρ_p is the density of the bulk feed solution.

Figure 3. Solution procedure for a theoretical approach in this study.

Due to its characteristics of the counter current manner, the boundary conditions of pressure, velocity and temperature for the permeate side can be described as follows:

$$P_p(0) = P_a, v_p(L) = v_{p,in}, T_p(L) = T_{p,in} \quad (20)$$

where P_a is the ambient atmospheric pressure, $v_{p,in}$ is the inlet feed velocity and $T_{p,in}$ is the inlet feed temperature.

3.4 Solution procedure

The solution procedure of model used in this study is presented in **Fig. 3**. In order to calculate the set of coupled ordinary differential equations such as Eqs. (12)-(15) for the feed side and Eqs. (17)-(19) for the permeate side, have been discretized using the finite volume method and solved

using Eqs. (16) and (20) for feed and permeate side boundary conditions, respectively. Eqs. (7)-(11) for the heat transfers and Eqs. (1)-(6) for the mass transfers. The system of ordinary differential equations has been solved using Broyden's method and the convergence criterion is 10^{-6} .

3.5 Considerations for modeling

Figure 4. (a) Pictures of E-PH and E-CNT membranes and (b and c) SEM images (X30,000) of E-PH and E-CNT membranes, respectively.

The following considerations were made based on the DCMD performance using E-CNT membranes and properties of E-CNT membranes. Hence, the hypothesis was the mass and heat

transfers through the E-CNT membranes could be improved due to the enhancement of the hydrophobicity (**Table 2**) and the modification of the membrane structure by compositing of CNTs (**Fig. 4**), respectively. To verify our hypothesis, the impact of CNTs was taken into the consideration of modeling for mass transfer and heat transfer as follows.

Mass transfer. The enhanced hydrophobicity of E-CNT membranes can prevent the membrane pore from wetting and also may enhance the mass transfer. As shown in **Fig. 5**, in the inner pores of the membrane, the Knudsen and molecular diffusion can be enhanced due to the increment in the repulsion (which is a repelling phenomenon) to the inner wall by its hydrophobicity enhancement. In other words, the water vapor molecules may have the specular reflection or refraction behaviors in the pore walls of the membrane and the enhanced repelling characteristic by the superhydrophobicity can enhance the mass transfer by reducing the transport resistance of water vapor molecules. In addition, the viscosity flow can also be enhanced by the repulsion force due to the increment of the hydrophobicity at the inner pores interconnected by the electrospun nanofibers. It is believed that the viscous flow follows the principle of boundary layer of the channel. The non-slip condition has a negative effect to the permeate flux in the usual channel flow in a macro or micro sizes. However, the increased repelling on the pore walls could lead to the reduction of the non-slip condition zone [36]. Therefore, the viscous flow can be enhanced due to the fact that hydrophobic pore walls have a repulsive energy, which can repel the water molecules and make a slip condition on the pore walls. In other words, the mass transfer behavior within the E-CNT membrane can be described as having a shorter wall collision distance and less molecule collision to facilitate the flow of vapors through the membrane by decreasing the friction loss. Subsequently the tendency of the pores to become wet with liquid decreases, so higher transport of pure vapor could occur, moving through the pores like a magnetic levitation train.

Heat transfer. In addition, the heat transfer can be enhanced by the modified roughness of the membrane surface by incorporating the CNTs. **Fig. 4c** shows the E-CNT membranes fabricated with different CNTs concentrations and SEM images of E-CNT membrane surface structures. The crystalline structure was observed which increased the membrane surface roughness. Kandlikar et al. [37] showed the positive effect of the relative roughness on the Nusselt number as convection heat transfer under low Reynolds number (laminar flow). The diameters of electrospun nanofibers fabricated in this study were around 0.3×10^{-6} m and the order of

magnitude of the surface roughness measured was in the range of $2.04 - 2.53 \times 10^{-6}$ m, according to the CNTs concentration indicating that E-CNTs membranes are in the reasonable range to augment the convection heat transfer [37]. Similar to the effect with spacer on the membrane, these structures can enhance the convection heat transfer coefficient, however the effect of the increased roughness may not be enough to promote the flow like a spacer effect (i.e. from laminar to turbulence flow). **Fig. 4b** and **4c** envision the fiber structures of E-PH and E-CNT membranes.

In the following section, these assumptions will be verified and discussed by fitting with modified model.

Figure 5. Possible mechanism of the CNTs effect on mass transfer in the pore of E-CNT membranes (Dusty gas model: (a) viscous flow, (b) Knudsen diffusion and (c) molecular diffusion).

4. Results and discussion

4.1 Model validation

4.1.1 E-PH membrane

Firstly, the model prediction was conducted using the properties of the E-PH membrane (CNTs=0wt%) at inlet feed temperatures ranging from 40 to 60 °C, inlet permeate temperature of

20 °C, inlet feed and permeate volume flow rate of 0.5 L/min and the initial salinity of a feed solutions ranging from 0 to 70 g/L.

(a)

(b)

(c)

Figure 6. Effect of inlet feed temperatures on the mean permeate flux with E-PH membrane at different feed solutions: (a) 0 g/L, (b) 35 g/L and (c) 70 g/L of NaCl (permeate temperature = 20 °C).

Fig. 6 presents the mean water fluxes (experimented, Exp. and simulated, Sim.) using different feed solutions: DI water (0 g/L), 35 g/L and 70 g/L of NaCl with respect to bulk feed temperature from 40 to 60 °C at an inlet permeate temperature of 20 °C. The measured water flux with feed solution of 0 g/L increased from 14.88 to 34.15 kg/m²h with an increase in the inlet feed temperature from 40 to 60 °C, this is due to the increment in the water vapor pressure difference by increased feed temperature. Simulated permeate flux (from 13.58 to 32.28 kg/m²h) by model shows a good agreement with the measured data as shown in **Fig. 6a**. With the increase in salinity of feed solution (from 0 to 35 and 70 g/L), the water flux slightly decreased from 34.15 to 32.42 and 31.29 kg/m²h at 60 °C of feed temperature, respectively (**Fig. 6b and 6c**). This implies that the inlet feed salinity did not significantly affect the water flux in DCMD with E-PH membrane as the effect of concentration polarization (CP) on the permeate flux is less than that of temperature polarization (TP) [6, 38]. The model predictions on the permeate flux were validated with the measured results and maximum deviation was lower than 10%.

4.1.2 E-CNT membranes – CNTs effect

The experimental results showed that the water fluxes with E-CNT membranes increased with an increase in the concentration of the CNTs incorporated compared to those with E-PH membrane at different temperatures and feed concentrations (salinities) tested in this study (**Fig. 7**). Thus, in this section, the theoretical studies were conducted to analyze the enhancement of the water flux considering the effect of CNTs and to compare with the experimental results of DCMD using the E-CNT membranes.

Figure 7. Effect of inlet feed temperature on the mean permeate flux (experiment and simulated) with E-CNT1 membrane and inlet feed salinity of (a) 0 g/L, (b) 35 g/L and (c) 70 g/L, and E-CNT2 membrane with inlet feed salinity of (d) 0 g/L, (e) 35 g/L and (f) 70 g/L.

With E-CNT1 membrane, the measured water flux increased from 16.18 to 36.23 kg/m²h while the predicted water flux increased from 14.24 to 32.93 kg/m²h at inlet feed temperatures ranging from 40 to 60 °C using DI feed water, as shown in **Fig. 7a**. However with a feed concentration of 70 g/L the permeate flux increases from 14.73 to 34.23 kg/m²h, whereas the simulated permeate flux increases from 12.94 to 31.24 kg/m²h (**Fig. 7c**). The increased feed salinity resulted in lower permeate fluxes as observed in both E-PH and E-CNT membranes' simulated and measured data (**Fig. 7**). However, interestingly, their gaps in E-CNT membranes were lower than that of E-PH membrane indicating that the incorporation of the CNTs reduced the sensitivity of salinity. In other word, another effect of CNTs is the reduction of CP effect on the membrane surface. This phenomenon was also observed in DCMD operation with E-CNT2 membrane (**Figs. 7d-f**).

Here, it must be highlighted that all the experimental results were greater than the predicted results by model indicating that the E-CNT membranes had another factor to provide a positive effect enhancing the permeate flux. This is probably associated with modified particular properties of E-CNT membrane. These membranes have high hydrophobicity not only on the membrane surface but also in the pores and inside the pore walls because the electrospun membranes have interconnected hydrophobic nanofibers and highly porous. CNTs are also distributed in/on nanofibers. As given in **Table 2**, contact angles of E-PH membrane and E-CNT2 membrane were 142.9±2.1 and 150.5±1.7°, respectively. This showed that 2wt% of CNT incorporation (E-CNT2 membrane) changed the membrane surface from hydrophobic to superhydrophobic (contact angle > 150°). Similarly, in order to increase the MD performance, recent researches have been attempted to develop/modify superhydrophobic membranes [39].

Porosity was also slightly enhanced by adding CNTs (i.e. E-PH membrane = 89.3% to E-CNT2 membrane =90.2%) as CNTs increased the membrane surface area. This could increase the mass transfer of vapor inside the pore as shown in **Fig. 5**. Moreover, CNTs incorporation could also modify the membrane roughness (**Fig. 4b and 4c**), which can enhance the heat transfer. Therefore, the effects of mass and heat transfer coefficients should be simultaneously considered to explain the positive effect of E-CNT membrane using prediction model. Following sections will explain the detailed procedure how to consider mass and heat transfers in E-CNT membranes as well as E-PH membrane.

4.2 Modification of mass transfer coefficient

In order to analyze the effect of mass transfer coefficient only on the mean permeate flux exclusively, the simulation study was conducted through modification of mass transfer coefficient ($C_{m,m}$) varying from 0.1 to 1.5 times at inlet feed temperature ranging from 40 to 60 °C, inlet feed salinity ranging from 0 g/L to 70 g/L and an inlet permeate temperature of 20 °C using the E-CNT membranes (CNTs from 1 to 2wt%), as shown in **Fig. 8**.

Figure 8. Effect of the modified mass transfer coefficient on the mean permeate flux with E-CNT1 membrane with inlet feed salinity of (a) 0 g/L, (b) 35 g/L and (c) 70 g/L, and E-CNT2 membrane with inlet feed salinity of (d) 0 g/L, (e) 35 g/L and (f) 70 g/L.

The modified mass transfer coefficient is calculated based on the dusty gas model as follows:

$$B_m = C_{m,m} B \quad (21)$$

where $C_{m,m}$ is the modification coefficient of the mass transfer, B_m is the modified mass transfer coefficient, and B is the mass transfer coefficient, which is calculated based on the dusty gas model (Knudsen and molecular diffusion and viscous flow).

When the properties of the E-CNT1 membrane are employed in the model calculation, the predicted water vapor flux increased from 19.62 to 33.80 kg/m²h with respect to the modification coefficient of mass transfer coefficient ranging from 0.1 to 1.5 times at inlet feed and permeate temperatures of 60 °C and 20 °C, respectively, and inlet feed salinity of 0 g/L as shown in **Fig. 8a**. With an increase in modified mass transfer coefficient from 0.1 to 1.5 times, the water flux increased asymptotically, under the same operating conditions. As typically the TP increases with an increase in the mass transfer coefficient, the mean permeate flux increased asymptotically with an increase in the mass transfer coefficient as observed in **Fig. 8**. However, even if the mass transfer coefficient is modified to 1.5 times as the initial (normal) value, the predicted water vapor flux shows always less than the experimental one, i.e., 33.80 (Sim.) < 36.23 kg/m²h (Exp.) and 33.91 (Sim.) < 39.84 kg/m²h (Exp.) using E-CNT1 (**Fig. 8a**) and E-CNT2 (**Fig. 8d**) membranes, respectively at 60 °C and 0g/L NaCl feed water. Thereby, it can

obviously suggest that the increment of mass transfer coefficient solely cannot explain the increase in the measured permeate flux of DCMD with E-CNT membranes.

4.3 Modification of heat transfer coefficient

In order to explain the enhancement of the permeate flux (which cannot be explained by mass transfer alone) in DCMD using E-CNT membranes, the heat transfer coefficient was also modified. The simulation was conducted to estimate the effect of the heat transfer coefficient modification ($C_{m,h}$) on the water flux from 1.0 to 1.5 times when E-CNT membranes were used at inlet feed temperatures ranging from 40 to 60 °C, inlet feed salinity ranging from 0 g/L to 70 g/L and inlet permeate temperature of 20 °C as shown in **Fig. 9**. The modified heat transfer coefficient is calculated by following equation:

$$h_m = C_{m,h} h_i \quad (22)$$

where the $C_{m,h}$ is the modification coefficient of the heat transfer, h_m is the modified heat transfer coefficient and the h_i is the heat transfer coefficient, which is calculated based on the Nusselt number (Eq. (11)).

(a)

(b)

Figure 9. Effect of the modified (or enhanced) heat transfer coefficient on the mean permeate flux with E-CNT1 membrane with inlet feed salinity of (a) 0 g/L, (b) 35 g/L and (c) 70 g/L, and E-CNT2 membrane with inlet feed salinity of (d) 0 g/L, (e) 35 g/L and (f) 70 g/L.

When the E-CNT1 membrane was employed, the predicted water flux increased from 33.93 to 48.13 kg/m²h according to the increment of the heat transfer coefficient from 1.0 to 1.5 times at an inlet feed temperature of 60 °C and an inlet feed salinity of 0 g/L as shown in **Fig. 9a**. As illustrated in **Fig. 9b**, the model-based permeate flux with 35 g/L of inlet salinity increases from 32.10 to 47.06 kg/m²h with an increase in feed temperature. In **Fig. 9c**, the predicted permeate flux increased from 31.24 to 45.95 kg/m²h when inlet salinity was 70 g/L. The mean water flux with DI feed water increased from 33.09 to 48.44 kg/m²h with respect to the increment of the heat transfer coefficient from 1.0 to 1.5 times with E-CNT2 membrane, as shown in **Fig. 9d**. As observed in **Fig. 9e**, the model-based permeate flux with 35 g/L of inlet feed salinity increased

from 32.23 to 47.35 kg/m²h. The predicted water flux with 70 g/L of inlet feed salinity increased from 31.34 to 46.21 kg/m²h (**Fig. 9f**).

As shown in **Figs. 9(a-f)**, the modification coefficient of heat transfer coefficient by CNTs effect can be positive effect to the mean permeate flux. In theory, the higher heat transfer coefficient can reduce the TP, which can be calculated by the temperature difference between the bulk and transmembrane temperature. It means that the driving force can be increased with an increase in the convection heat transfer coefficient. Typically, the conduction heat loss can be increased with the higher transmembrane temperature difference between feed and permeate side, however the increment of the conduction heat loss is significantly low compared to the increment of the latent heat for water vapor evaporation. Hence, the modification coefficient of the heat transfer coefficient can highly affect to the mean permeate flux compared to the modification coefficient of the mass transfer coefficient. In other words, the mass transfer coefficient from the geometrical properties of the membrane should be close to limitation permeate flux under a given operating condition. Despite the fact that the heat transfer coefficient calculated by Eq. (22), is considered, it didn't show a good agreement with experimental results. These simulation results suggest that theoretical study of CNTs effects should consider the intrinsic properties of CNTs embedded membrane such as surface roughness etc.

4.4 Simultaneous modification of mass and heat transfer coefficients

Modification of heat and mass transfer coefficients were made simultaneously to estimate the correlation of the heat and mass transfer coefficients for the function of the CNTs concentration used in E-CNT membrane.

(a)

(b)

(c)

Figure 10. Comparison of experimental (Exp.) and simulated (Sim.) results using the modified heat and mass transfer coefficients when E-CNT1 and E-CNT2 membranes were used with inlet feed salinity of (a) 0 g/L, (b) 35 g/L, and (c) 70 g/L at different feed temperatures ranging from 40 to 60°C. The explanation of fitting process (determination of correlation equations) is presented in the supplementary information.

Fig. 10 presents the water fluxes using the simultaneously modified heat and mass transfer coefficients at inlet feed temperatures ranging from 40 to 60 °C, inlet permeate temperature of 20 °C, and inlet feed salinity ranging from 0 to 70 g/L, when E-CNT membranes were used in the DCMD process. The model-based permeate fluxes are in a good agreement with the measured permeate fluxes and as can be observed in **Fig. 10**, the maximum deviation is less than 3 %. In detail, as shown in **Fig. 10a**, when DI feed water is used as feed, the maximum deviations between the measured and predicted permeate fluxes are 1.97 % and 1.19 % with E-CNT1 and E-CNT2 membranes, respectively, at an inlet feed temperature of 40 °C. As illustrated in **Fig. 10b**, the maximum deviations are 1.66 % and 1.34 % with E-CNT1 and E-CNT2 membranes, respectively, with 35 g/L feed salinity at an inlet feed temperature of 60 °C. When the inlet feed salinity was increased to 70 g/L, the maximum deviations are 2.38 % and 1.55 % with E-CNT1 and E-CNT2 membranes, respectively at an inlet feed temperature of 50 °C.

Figure 11. The correlation of modified coefficients for both heat and mass transfer versus the CNTs concentration in the E-CNT membranes. The explanation of fitting process (determination of correlation equations) is presented in the supplementary information.

As discussed earlier, the model-based simulation studies were carried out to theoretically explain the CNTs effect on the heat and mass transfer. In addition, the separate effect of heat and mass transfers on the permeate flux was estimated. Finally, in order to develop a more accurate prediction model for CNTs effect on the mean permeate flux, the correlation of modified

coefficients of both heat and mass transfer according to the increment of the CNTs concentration were simultaneously considered in this study. As expected, the enhancement (of over 1.0 time) in both the modification coefficients of heat and mass transfer coefficients could affect the positive effect to permeate flux (**Fig. 11**). Both heat and mass transfer modified coefficients increased proportionally with the increase of the concentration of CNTs in the E-CNT membranes, but heat transfer was more sensitively increased with respect to the CNTs concentration compared to mass transfer under a given operation condition.

4.5. Possible mechanisms of E-CNT membrane (on mass transfer)

Previous papers mostly limit the CNTs effect on the MD processes experimentally, by presenting that the CNTs incorporated membrane could enhance the permeate flux due to the increment of the mass transfer (**Fig. 12**) [21, 29]. They have explained the reasons for increment of the mass transfer by the interaction with polar functional groups, activated diffusion via adsorption desorption on the surface of CNTs, direct permeation through membrane pores and highly porous structure, enhanced hydrophobicity generated by the polymer used for immobilization [21, 29]. However, they have explained the enhancement of the permeate flux mainly through the mass transfer effect.

Figure 12. (a) A schematic diagram of (a) the proposed mechanism for CNT-COOH-PP membrane [21] and (b) depiction of the working mechanism of CNT/PH nanofiber membrane for MD application [29].

4.6. CNTs effect on the mass and heat transfers in E-CNT membrane

In this study, the mass transfer effect on the permeate flux was investigated by the simulation to prove the assumptions made in previous papers [21, 29]. The mass transfer coefficient was considered with the Knudsen and molecular diffusion and the viscous flow, simultaneously. The electric circuit of the mass transfer considered the Knudsen and molecular diffusion and viscous flow can be shown in **Fig. 13** [40]. It was found that the effect of viscous flow on the membrane distillation coefficient was dominant from the calculation. Despite the fact that the Knudsen and molecular diffusion can slightly enhance the mass transfer coefficient, they were not ignored in this study. The CNTs effect on the permeate flux was hypothesized from the hydrophobicity enhancement on the membrane as well as inner pore walls, because the Knudsen and molecular diffusion considers the reflection phenomena on the pore walls and each other [40-42]. Therefore, it was expected that the CNTs membrane of inner pore wall, which has superhydrophobicity, could increase the repelling between pore walls and water vapor molecules as the Knudsen and molecular diffusion even though the interaction between the inner wall and water vapor is small.

Figure 13. Electrical analogy circuit presenting the different transport mechanisms in Dusty gas model [40].

As shown in **Fig. 8**, although the enhancement of the mass transfer can affect to the increment of the permeate flux, it was not enough to explain the increment of the mean permeate flux under given operating conditions. In fact, the mass transfer coefficient, which was calculated with the geometrical properties of the membrane such as the mean pore size, porosity, tortuosity and membrane thickness, is sufficiently high under a given operating condition. As given in **Table 1**, the porosity and mean pore size are relatively higher compared to the other typical membranes (i.e., 0.22 μm and 70%, respectively). Nevertheless, the permeate fluxes were relatively lower

than the experimental results according to the increment of the modification coefficient of mass transfer ranging from 1 to 1.5 times under a given operating condition.

Therefore, the effect of heat transfer modification through the increase in surface roughness due to CNTs effect was studied. Typically, the increment of the surface roughness can increase the heat transfer of internal flow [37, 43-45]. The enhanced heat transfer can reduce the TP, which can be easily determined by using the Eqs. (7)-(10). The temperature polarization coefficient (TPC) can be calculated, separately, by the following equation (Eq. (23)).

$$TPC = \frac{T_{f,m} - T_{p,m}}{T_f - T_p}, \quad i = \text{feed or permeate} \quad (23)$$

Figure 14. Temperature polarization coefficient (TPC) according to the modification coefficients for the heat transfer using the E-CNT1 membrane at 35 g/L of inlet feed salinity and inlet feed temperatures ranging from 40 to 60 °C with counter current flow mode.

Fig. 14 presents the effect of the modification coefficient for heat transfer on the TPC using the E-CNT1 membrane at 35 g/L of inlet feed salinity and inlet feed temperature ranging from 40 to 60 °C with counter current flow mode. The TPC increased with an increase in the modification coefficient for the heat transfer. This is because the higher heat transfer coefficient can reduce the local TP meaning that the local driving force can be increased. The TPC can decrease with a decrease in the temperature difference between feed and permeate inlets as easily expected by Eq. (23).

Under a given operating condition and properties of the membrane (E-CNT membranes), the effect of heat transfer is found to be a significant factor influencing the permeate flux.

Heat transfer in DCMD was made following three regions: i) heat transport through the feed boundary layer, ii) the membrane and iii) the permeate boundary layer. In the case of E-CNT membrane, the modified surface roughness of E-CNT membrane enhanced the convection heat transfer through both feed and permeate boundary layers and it can also achieve the enhancement of the latent heat of water vapor evaporation. Finally, the correlation of modified coefficients both for heat and mass transfer according to the CNTs concentrations in the E-CNT membranes have been developed considering two assumptions of the CNTs effect on DCMD process simultaneously, as shown in **Fig. 11**. Therefore, the role of CNTs in E-CNT membrane is enhancing both the heat and mass transfers and subsequently improving the permeate flux in DCMD.

4.7. Why E-CNT membrane is suitable for desalination?

A previous study [46] examined ion exclusion and selectivity of carboxyl-functionalized CNTs at two solutions having different pH levels, one above the pK_a of COOH group on the surface ($pK_a=5.5$) and another below it. Here, COO^- group is protonated and neutral from high pH to low pH. In particular, more than 90 % of ion rejection was achieved at over $pH=7.2$, indicating that the major driving force for ion rejection is electrostatic interaction. Therefore, salt rejection of CNTs was superior in desalination where solution pH is around 8.0.

This CNTs effect can help in MD operation. As shown in **Fig. 1**, CNTs used in E-CNT membrane was also functionalized with COOH group. This might generate the barrier to salt on the surface of E-CNT membrane. In fact, salt rejection in MD is superior as it is almost 99%, if no wetting occurred [14]. However, in DCMD there is another limiting factor affecting the water flux: it is CP. In general, CP effects tend to reduce the driving force. CP decreases the driving force for mass transport in pressure-driven membrane processes. Similarly, in DCMD, the driving force for evaporation slightly is decreased with the increment of the CP at the feed–membrane interface. However, in DCMD process, the flow of solute in the feed channel and the relatively low hydraulic pressure can reduce the CP effect on the desalination performance. Nevertheless, if salinity is increased as investigated in this study (~ 70 g/L), CP effect is increased in DCMD and one can expect larger effect at higher salinities [6]. The CP effect of feed boundary layer is reduced with the increased repulsion force by CNTs on the surface of the E-CNT membrane, but surface charge is reduced at high salinity. E-CNT membranes are

negatively charged even in the presence of salinity. Therefore, E-CNT membranes are more effective in desalination than E-PH membrane as CNTs have low sensitivity to salinity (See the section 4.1.2).

5. Conclusions

In this study, theoretical approaches were conducted to prove the previously assumed mechanism of CNTs composite electrospun membrane that enhances the DCMD performance. New step modeling approaches were employed to match the theoretical simulation results with experimental data. First, in order to prove the previous assumptions related with the mass transfer enhancement only, the theoretical studies were conducted. Results showed that although the enhancement of the mass transfer can improve the permeate flux; it obviously indicated that only the increment of mass transfer coefficient could not explain the increase in the measured permeate flux of DCMD with E-CNT membranes. Secondly the possibility of the other assumption was considered that the effect of the heat transfer modification from enhanced surface roughness on the E-CNT membranes. The enhancement of the measured permeate flux can be explained using the heat transfer modification. Finally, the correlation of modified coefficients for both heat and mass transfer according to the increment of the CNTs concentration was suggested. In addition, assumptions for the model study were proved systematically and possible mechanisms were discussed. This is the first modeling approach dealing with heat transfer for explaining the enhanced flux in DCMD using E-CNT membranes.

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References

- [1] C. Koroneos, G. Roumbas, Geothermal waters heat integration for the desalination of sea water, *Desalination and Water Treatment*, 37 (2012) 69-76.
- [2] Y.-D. Kim, K. Thu, N. Ghaffour, K.C. Ng, Performance investigation of a solar-assisted direct contact membrane distillation system, *Journal of Membrane Science*, 427 (2013) 345-364.

- [3] P.A. Hogan, Sudjito, A.G. Fane, G.L. Morrison, Proceedings of the Twelfth International Symposium on Desalination and Water Re-use Desalination by solar heated membrane distillation, *Desalination*, 81 (1991) 81-90.
- [4] N. Ghaffour, J. Bundschuh, H. Mahmoudi, M.F. Goosen, Renewable energy-driven desalination technologies: A comprehensive review on challenges and potential applications of integrated systems, *Desalination*, 356 (2015) 94-114.
- [5] K.S.A. Basha, Membrane distillation test for concentration of RO brine at WESSCO, Jeddah, in: IDA World Congress, Perth Convention and Exhibition Centre (PCEC), Perth, Western Australia September, 2011, pp. 4-9.
- [6] J. Xu, Y.B. Singh, G.L. Amy, N. Ghaffour, Effect of operating parameters and membrane characteristics on air gap membrane distillation performance for the treatment of highly saline water, *Journal of Membrane Science*, 512 (2016) 73-82.
- [7] S. Adham, A. Hussain, J.M. Matar, R. Dores, A. Janson, Application of membrane distillation for desalting brines from thermal desalination plants, *Desalination*, 314 (2013) 101-108.
- [8] A.S. Alsaadi, L. Francis, H. Maab, G.L. Amy, N. Ghaffour, Evaluation of air gap membrane distillation process running under sub-atmospheric conditions: Experimental and simulation studies, *Journal of Membrane Science*, 489 (2015) 73-80.
- [9] G. Naidu, S. Jeong, S. Vigneswaran, T.-M. Hwang, Y.-J. Choi, S.-H. Kim, A review on fouling of membrane distillation, *Desalination and Water Treatment*, 57 (2016) 10052-10076.
- [10] B. Ashoor, S. Mansour, A. Giwa, V. Dufour, S. Hasan, Principles and applications of direct contact membrane distillation (DCMD): A comprehensive review, *Desalination*, 398 (2016) 222-246.
- [11] M. Essalhi, M. Khayet, Surface segregation of fluorinated modifying macromolecule for hydrophobic/hydrophilic membrane preparation and application in air gap and direct contact membrane distillation, *Journal of membrane science*, 417 (2012) 163-173.
- [12] A.K. An, J. Guo, S. Jeong, E.-J. Lee, S.A.A. Tabatabai, T. Leiknes, High flux and antifouling properties of negatively charged membrane for dyeing wastewater treatment by membrane distillation, *Water Research*, 103 (2016) 362-371.
- [13] E.-J. Lee, A.K. An, T. He, Y.C. Woo, H.K. Shon, Electrospun nanofiber membranes incorporating fluorosilane-coated TiO₂ nanocomposite for direct contact membrane distillation, *Journal of Membrane Science*, 520 (2016) 145-154.

- [14] J. Lee, S. Jeong, Z. Liu, Progress and challenges of carbon nanotube membrane in water treatment, *Critical Reviews in Environmental Science and Technology*, (2016) 00-00.
- [15] B. Corry, Water and ion transport through functionalised carbon nanotubes: implications for desalination technology, *Energy & Environmental Science*, 4 (2011) 751-759.
- [16] R. Das, M.E. Ali, S.B.A. Hamid, S. Ramakrishna, Z.Z. Chowdhury, Carbon nanotube membranes for water purification: a bright future in water desalination, *Desalination*, 336 (2014) 97-109.
- [17] J. Zhang, N. Dow, M. Duke, E. Ostarcevic, S. Gray, Identification of material and physical features of membrane distillation membranes for high performance desalination, *Journal of Membrane Science*, 349 (2010) 295-303.
- [18] A.F. Ismail, P.S. Goh, S.M. Sanip, M. Aziz, Transport and separation properties of carbon nanotube-mixed matrix membrane, *Separation and Purification Technology*, 70 (2009) 12-26.
- [19] L. Dumée, V. Germain, K. Sears, J. Schütz, N. Finn, M. Duke, S. Cerneaux, D. Cornu, S. Gray, Enhanced durability and hydrophobicity of carbon nanotube bucky paper membranes in membrane distillation, *Journal of membrane science*, 376 (2011) 241-246.
- [20] K. Gethard, O. Sae-Khow, S. Mitra, Water desalination using carbon-nanotube-enhanced membrane distillation, *ACS applied materials & interfaces*, 3 (2010) 110-114.
- [21] S. Roy, M. Bhadra, S. Mitra, Enhanced desalination via functionalized carbon nanotube immobilized membrane in direct contact membrane distillation, *Separation and Purification Technology*, 136 (2014) 58-65.
- [22] M. Essalhi, M. Khayet, C. Cojocaru, M. García-Payo, P. Arribas, Response surface modeling and optimization of electrospun nanofiber membranes, *Open Nanosci J*, 7 (2013) 8-17.
- [23] E.-J. Lee, A.K. An, P. HADI, S. Lee, Y.C. Woo, H.K. Shon, Advanced multi-nozzle electrospun functionalized titanium dioxide/polyvinylidene fluoride-co-hexafluoropropylene (TiO₂/PVDF-HFP) composite membranes for direct contact membrane distillation, *Journal of Membrane Science*, doi:10.1016/j.memsci.2016.11.069 (2016).
- [24] L.D. Tijing, J.-S. Choi, S. Lee, S.-H. Kim, H.K. Shon, Recent progress of membrane distillation using electrospun nanofibrous membrane, *Journal of Membrane Science*, 453 (2014) 435-462.
- [25] A.K. An, J. Guo, E.-J. Lee, S. Jeong, Y. Zhao, Z. Wang, T. Leiknes, PDMS/PVDF hybrid electrospun membrane with superhydrophobic property and drop impact dynamics for dyeing wastewater treatment using membrane distillation, *Journal of Membrane Science*, (2016) doi:10.1016/j.memsci.2016.1010.1028.

- [26] Y. Liao, R. Wang, M. Tian, C. Qiu, A.G. Fane, Fabrication of polyvinylidene fluoride (PVDF) nanofiber membranes by electro-spinning for direct contact membrane distillation, *Journal of membrane science*, 425 (2013) 30-39.
- [27] Y.C. Woo, L.D. Tijting, M.J. Park, M. Yao, J.-S. Choi, S. Lee, S.-H. Kim, K.-J. An, H.K. Shon, Electrospun dual-layer nonwoven membrane for desalination by air gap membrane distillation, *Desalination*, 403 (2017) 187-198.
- [28] X.-M. Li, D. Reinhoudt, M. Crego-Calama, What do we need for a superhydrophobic surface? A review on the recent progress in the preparation of superhydrophobic surfaces, *Chemical Society Reviews*, 36 (2007) 1350-1368.
- [29] L.D. Tijting, Y.C. Woo, W.-G. Shim, T. He, J.-S. Choi, S.-H. Kim, H.K. Shon, Superhydrophobic nanofiber membrane containing carbon nanotubes for high-performance direct contact membrane distillation, *Journal of Membrane Science*, 502 (2016) 158-170.
- [30] J.-G. Lee, Y.-D. Kim, W.-S. Kim, L. Francis, G. Amy, N. Ghaffour, Performance modeling of direct contact membrane distillation (DCMD) seawater desalination process using a commercial composite membrane, *Journal of Membrane Science*, 478 (2015) 85-95.
- [31] P.-C. Ma, N.A. Siddiqui, G. Marom, J.-K. Kim, Dispersion and functionalization of carbon nanotubes for polymer-based nanocomposites: a review, *Composites Part A: Applied Science and Manufacturing*, 41 (2010) 1345-1367.
- [32] S. Shim, J. Lee, W. Kim, Performance simulation of a multi-VMD desalination process including the recycle flow, *Desalination*, 338 (2014) 39-48.
- [33] L.-H. Cheng, P.-C. Wu, J. Chen, Modeling and optimization of hollow fiber DCMD module for desalination, *Journal of Membrane Science*, 318 (2008) 154-166.
- [34] F.A. Banat, F.A. Abu Al-Rub, R. Jumah, M. Al-Shannag, Modeling of desalination using tubular direct contact membrane distillation modules, *Separation Science and Technology*, 34 (1999) 2191-2206.
- [35] L. Martínez-Díez, M.I. Vazquez-Gonzalez, Temperature and concentration polarization in membrane distillation of aqueous salt solutions, *Journal of membrane science*, 156 (1999) 265-273.
- [36] L. Zhu, D. Tretheway, L. Petzold, C. Meinhart, Simulation of fluid slip at 3D hydrophobic microchannel walls by the lattice Boltzmann method, *Journal of Computational Physics*, 202 (2005) 181-195.

- [37] S.G. Kandlikar, S. Joshi, S. Tian, Effect of Surface Roughness on Heat Transfer and Fluid Flow Characteristics at Low Reynolds Numbers in Small Diameter Tubes, *Heat Transfer Engineering*, 24 (2003) 4-16.
- [38] G. Naidu, S. Jeong, S. Vigneswaran, Influence of feed/permeate velocity on scaling development in a direct contact membrane distillation, *Separation and Purification Technology*, 125 (2014) 291-300.
- [39] C. Yang, X.-M. Li, J. Gilron, D.-f. Kong, Y. Yin, Y. Oren, C. Linder, T. He, CF 4 plasma-modified superhydrophobic PVDF membranes for direct contact membrane distillation, *Journal of Membrane Science*, 456 (2014) 155-161.
- [40] M. Khayet, T. Matsuura, *Membrane distillation: principles and applications*, Elsevier, 2011.
- [41] S. Santra, B. Sapoval, Interaction of ballistic particles with irregular pore walls, Knudsen diffusion, and catalytic efficiency, *Physical Review E*, 57 (1998) 6888.
- [42] J. Lee, R. Karnik, Desalination of water by vapor-phase transport through hydrophobic nanopores, *Journal of Applied Physics*, 108 (2010) 044315.
- [43] N. Abuaf, R. Bunker, C. Lee, Effects of surface roughness on heat transfer and aerodynamic performance of turbine airfoils, in: *ASME 1997 International Gas Turbine and Aeroengine Congress and Exhibition*, American Society of Mechanical Engineers, 1997, pp. V003T009A001-V003T009A001.
- [44] L.M. Camacho, L. Dumée, J. Zhang, J.-d. Li, M. Duke, J. Gomez, S. Gray, Advances in membrane distillation for water desalination and purification applications, *Water*, 5 (2013) 94-196.
- [45] E. Achenbach, The effect of surface roughness on the heat transfer from a circular cylinder to the cross flow of air, *International Journal of Heat and Mass Transfer*, 20 (1977) 359-369.
- [46] F. Fornasiero, H.G. Park, J.K. Holt, M. Stadermann, C.P. Grigoropoulos, A. Noy, O. Bakajin, Ion exclusion by sub-2-nm carbon nanotube pores, *Proceedings of the National Academy of Sciences*, 105 (2008) 17250-17255.

Highlights

- CNTs composite electrospun membrane (E-CNT) showed a high flux in DCMD.
- An increase in CNTs concentration enhances the flux.

- The mechanisms of E-CNT are validated with simulation approaches.
- A new step-modeling approach was used to match simulation results with experimental data.
- Simultaneous consideration of mass and heat transfers is proposed.