



Scaling Reduction in Carbon Nanotube-Immobilized Membrane during Membrane Distillation

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Abstract: Membrane distillation (MD) is fast evolving as a desalination technology for high-salinity waters where scaling remains a major challenge. This paper reports the scaling reduction in carbon nanotube-immobilized membranes (CNIMs) and by the use of the antiscalant polyacrylic acid. High concentrations of CaSO₄, CaCO₃, and BaSO₄ were deliberately used to initiate scaling on the membranes. It was observed that after ten hours of operation in a highly scaling CaSO₄ environment, the CNIM showed 127% higher flux than what was observed on a membrane without the CNTs. The trends were similar with CaCO₃ and BaSO₄, where the CNIM showed significantly improved antiscaling behavior. The normalized flux declination for CNIM was found to be 45%, 30%, and 53% lower compared to the pristine membrane with CaSO₄, CaCO₃, and BaSO₄, and the water vapor flux was 100% and 18% higher for the pristine polypropylene and CNIM, respectively. Results also showed that the presence of CNTs facilitated the removal of deposited salts by washing, and the CNIM regained 97% of its initial water flux, whereas the polypropylene only regained 85% of the original value.

Keywords: scaling; antiscalant; carbon nanotube; membrane distillation; desalination

1. Introduction

Reverse osmosis (RO), multistage flash, and multieffect distillation are the most common desalination techniques and have shown much promise. However, they have limitations such as fouling of RO membranes in the presence of scaling ions, and high energy and capital cost in thermal methods [1–3]. As a result, alternative desalination technologies, including solar evaporation and membrane distillation (MD), are being explored [4–7]. The MD process paired with solar energy or low-grade heat source can be an attractive alternate to the conventional membrane-based desalination [8,9]. MD is also evolving to be an effective desalination technique for treating the high-salinity water that RO is unable to handle due to high osmotic pressure and extensive pretreatment requirements [10–12].

A major obstacle in membrane-based desalination techniques is fouling [13–16] from the deposition of suspended or dissolved substances on the active membrane surface and/or within its pores [17–19]. Several types of fouling are common, including inorganic fouling or scaling, particulate and colloidal fouling, organic fouling, and biofouling [20–22]. Fouling has also been an important issue in RO, nanofiltration, and ultrafiltration [23–25]. Due to the use of porous hydrophobic membranes, the fouling in MD tends to be significantly less than in RO, but is still an important consideration for high-salinity water desalting. Several approaches for fouling reduction, such as the introduction of nanobubble, ultrasound, and microwave irradiation have been reported [26–30]. Of particular interest has been the deposition of inorganic salts such as calcium carbonate (CaCO₃), calcium sulfate (CaSO₄), and barium sulfate (BaSO₄), which are found in hard waters as well as industrial waste from power plants, hydraulic



fracturing, and wastewaters from industries such as textiles and pulp and paper [31]. The formation of a scaling layer comprising of salt crystals formed on/within the pores of MD membranes are known to cause progressive wettability of the membrane [32]. The reduction of scaling [33] by adding several antiscalants has been reported for RO and thermal distillation processes. The use of antiscalants could potentially help to lower the scaling in thermally driven MD process without any adverse effect [34–36].

We have described the development of a carbon nanotube-immobilized membrane (CNIM), where the carbon nanotubes (CNTs) increased the partitioning of water vapor while rejecting the liquid phase, leading to a dramatic increase in MD flux [37–40]. Besides this, it is expected that the presence of CNTs may reduce scale formation on membrane surfaces where the CNTs serve as a screen. This may resist membrane pore blocking by salt deposition, and it is conceivable that the salt crystals deposited on the screen-like CNTs can be removed or washed off rather easily (as shown in Figure 1). In this way, the CNT screen maintains pore opening for the permeation of water vapor while repelling liquid water and salt clusters for longer periods of time. The objective of this project was to study the scaling behavior of the CNIM for various highly concentrated feed mixtures and to evaluate the performance of CNIM with addition of antiscalant.



Figure 1. Screening effect of carbon nanotubes (CNTs) in preventing the salt deposition on the membrane surface.

2. Experimental

2.1. Materials and Chemicals

Flat polypropylene (PP) membrane (0.45 micron pore size, from STERLITECH Inc., Kent, WA, USA) was used in this study. Calcium sulfate (CaSO₄), calcium carbonate (CaCO₃), and barium sulfate (BaSO₄) salts and the antiscalant (AS) polyacrylic acid (PAA) (63 wt% solution in water, MW ~2000) were purchased from Thermo Fisher Scientific Chemicals Inc. (Fair Lawn, NJ, USA). Deionized water (Barnstead 5023, Dubuque, IA, USA) was used to prepare the feed solutions and as cold distillate.

Multiwalled CNTs were purchased from Cheap Tubes, Inc. (Brattleboro, VT, USA). The MWCNTs were functionalized with carboxylic acid groups in a Microwave Accelerated Reaction System (Model: CEM Mars, CEM Corporation, Matthews, NC, USA) in our laboratory. The PP membrane was used as the base membrane to fabricate the carbon nanotube-immobilized membrane (CNIM). The CNTs are immobilized on the membrane surface using small amount of polyvinylidene fluoride (PVDF) as binder. Excess PVDF was removed from the surface by washing with acetone after fabrication. The functionalization process and CNIM fabrication methods have been previously reported [41–43]. Our previous studies have already proven the ability to retain the CNT coating on the surface for longer periods of time [44,45].

2.2. Experimental Procedure

Figure 2 demonstrates the DCMD experiment setup in the laboratory. The details have been previously described [29]. The hot aqueous feed solutions were circulated on one side of the membrane in the DCMD cell. The initial salt concentrations in the feed were 2.95 g/L for CaSO₄ solution, 3.5 g/L for CaCO₃, and 2.5 g/L for BaSO₄ salt solution. Antiscalant (50 mg) was added in 1 L of feed solution for the experiment. The data were reported after repeating each experiment at least three times to confirm reproducibility.



Figure 2. Schematic representation of the experimental setup.

Scanning electron microscopy (SEM) (JEOL, Model JSM-7900F, JEOL USA Inc.; Peabody, MA, USA) was used to characterize the surface morphology of the PP membrane and the CNIM before and after the experiment. Thermogravimetric analysis (TGA, PerkinElmer Pyris 7 TGA system at a heating rate of 10 °C/min in air) was used to investigate the thermal stability of the membranes.

2.3. DCMD Performance

The MD performances of CNIM membrane with and without the antiscalant were studied as a function of time, temperature, and feed flow rate. The water vapor flux, Jw, is measured as

$$Jw = Wp/t \cdot A \tag{1}$$

where Wp is the mass of permeated water in time t through surface area A. The flux can also be denoted as

$$Jw = k \left(P_f - P_p \right). \tag{2}$$

The overall mass transfer coefficient (k) was computed as

$$k = Jw / (P_f - P_p) \tag{3}$$

where P_f and P_p are the feed and permeate side water vapor pressure, respectively.

To compare scaling between the PP membrane and CNIM, the flux was measured over time and the normalized flux decline, *FDn*, was determined as

$$FDn(\%) = \left(1 - \frac{J_f}{J_0}\right) \times 100\tag{4}$$

where J_0 and J_f are the respective initial and final permeate flux over a period of time, t.

3. Results and Discussion

3.1. Characterization of the Membranes

Figure 3a,b shows the surface SEM images of the original PP membrane and CNIM. Figure 3a illustrates the pores present on PP membrane surface, and the incorporation of the carboxylated CNTs led to a modification in morphology as can be seen from Figure 3b. AFM images from our previous studies have shown that the incorporation of CNTs on membrane surface also increases the surface roughness [45]. The gas permeation test of the membranes demonstrated no significant change in the effective surface porosity over the effective pore length of the membranes as only a small quantity of CNTs were immobilized on the membrane surface [42,46].





Figure 3. Surface SEM image of (**a**) polypropylene (PP) membrane and (**b**) carbon nanotube-immobilized membrane (CNIM). (**c**) The TGA curves of plain and modified membranes.

The thermal stability of the PP membrane and CNIM was studied using TGA. The TGA curves of the two membranes are shown in Figure 3c. It can be seen from the TGA curves that both membranes are quite stable within the operating temperature ranges. The initial weight loss of the membrane was started at ~270 °C and it completely decomposed at ~380 °C. The TGA curve for CNIM shifted slightly upward, which exhibited the enhanced thermal stability of the CNIM due to the presence of CNTs [47].

The contact angles of the unmodified PP and CNIM for pure water and salt solution are shown as above in Figure 4. A droplet size of 4 mm was used to measure contact angles. The presence of CNTs dramatically altered the contact angle. With 100% water in the feed, the contact angle for CNIM was higher (125°) than the unmodified PP membrane (115°). In presence of salt, the contact angle was slightly reduced. The liquid entry pressure (LEP) was measured using a previously described method [42]. The LEP of the pure water solution was found to be 207 and 186 kPa, which changed to 179 and 165 kPa with CaSO₄ salt solution (2.95 g/L) for unmodified PP and CNIM, respectively.



Figure 4. Photographs of pure water on (**a**) unmodified PP and (**b**) CNIM and aqueous CaSO₄ salt solution (2.95 g/L) on (**c**) unmodified PP and (**d**) CNIM.

3.2. Effect of Temperature and Feed Flowrate on the Water Vapor Flux

The influence of feed solution temperature on water permeation rate for PP membrane and CNIM with pure water and aqueous CaSO₄ solution (2.95 g/L) at feed and distillate flow rate 200 mL min⁻¹ is shown in Figure 5a. The legend key PP-AS or CNIM-AS in the graph denotes the membrane performance using AS in the feed solution. In all cases, the initial permeate flux followed a direct relationship with temperature as the vapor pressure gradient increased with temperature. Among the two membranes, CNIM exhibited higher flux at any particular temperature, which was in line with our previously reported results [42]. It is important to note that the addition of PAA (antiscalant) did not show any negative effect on water permeation. Similar water vapor flux was observed for both membranes with antiscalant when pure water was used as feed. The mass transfer coefficient (k) was observed to be enhanced for CNIM (5.67×10^{-4} and 5.01×10^{-4} kg/m²·s·kPa, for CNIM and PP membrane, respectively) compared to the PP membrane. However, the addition of antiscalant in pure water feed did not show any significant change in the mass transfer coefficient for both membranes. At such high concentrations, the CaSO₄ was expected to quickly foul the membrane and the temperature dependence graph did not show an exponential increment pattern as observed using pure water as feed, as the scaling rate increased at higher temperatures [1,48]. A slight increase in initial flux was due to the antiscaling effect of antiscalant for short time periods (1 h). At a temperature of

60 °C, the water vapor flux with antiscalant increased from 25.1 to 31.8 kg/m²·h and 32.7 to 37.7 kg/m²·h for PP and CNIM, respectively.



Figure 5. (a) Effect of temperature on permeate flux of pure water and CaSO₄ solution at 200 mL/min feed and distillate flow rate (run time 1 h). (b) Effect of flow rate on permeate flux of CaSO₄ solution at 70 °C and 200 mL/min distillate flow rate (run time 1 h).

Figure 5b illustrates the performance of the PP and CNIM as a function of feed flow rate at 100, 150, and 200 mL/min, while the permeate side flow rate was maintained constant at 200 mL/min at a feed temperature of 70 °C. Results indicate that the water vapor flux was enhanced by feed flow rate for all membranes. With increase in feed flow rate from 100 to 200 mL/min, the Reynolds number increased from 662 to 1324, which improved the heat transfer efficiency from the bulk to the membrane surface [49]. The increase in feed flow rate reduced the boundary layer resistance at the feed solution–membrane interface, and generated more water vapor per unit time [50]. The use of antiscalants in feed solution with CNIM did not show any significant effect with respect to flow rate. The conductivity of the permeated water was found 2–10 μ S/cm and salt rejection was determined to be high (>99%) for both membranes.

3.3. Membrane Scaling

The scaling of PP membrane and CNIM was studied with highly saline feed solutions, namely CaSO₄ (2.95 g/L), CaCO₃ (3.5 g/L), and BaSO₄ (2.5 g/L). The high concentrations were deliberately selected so that the membranes would foul quickly. The membrane scaling was evaluated by the reduction of permeated water flux with time during the operation. Figure 6a–d, show the deviation of water vapor flux as a function of time for all salts at 70 °C feed temperature, feed, and permeate flow rate of 200 mL/min.





Figure 6. Water vapor flux in PP membrane and CNIM at 70 °C and 200 mL/min feed flow rate for (**a**) pure water (run time 1 h), (**b**) CaSO₄ solution (2.95 g/L) (**c**) CaCO₃ solution (3.5 g/L), and (**d**) BaSO₄ solution (2.5 g/L) (**b**–d run time 10 h). AS: antiscalant.

Figure 6 depicts the decline in water vapor fluxes with time for both the membranes as an outcome of scaling. It is clear from the figures that the CNIM exhibited higher antiscaling properties in comparison with PP membrane. This may be due to additional screening effect of CNTs which

reduced pore blocking from salt deposition (as shown in Figure 1). Figure 6a shows the short-term scaling behavior of $CaSO_4$ salt solutions with PP membrane and CNIM with and without antiscalant. The water vapor flux declined with time as expected. However, the use of antiscalant lowered the scaling tendency, hence generating higher water vapor flux.

It can be seen from Figure 6b that for $CaSO_4$ solution, the flux declined to 13.4 from 39.4 kg/m²·h for PP, and to 30.5 from 47.6 kg/m²·h for the CNIM after 10 h of operation. The results show that by using CNIM, the water vapor flux after 10 h was still 126.7% higher than the PP membrane. The lower scaling tendency of CNIM can be explained via its 'screening effect', where the net-like presence of CNTs prevent salt clusters from depositing on the membrane surface or pores. Furthermore, the experiments were carried out using antiscalant (PAA) to study its effect on CNIM. It was observed that the use of AS in the feed solution improved the antiscaling behavior of the membranes and the water vapor flux after 10 h of operation was 26.8 and 36 kg/m²·h for PP membrane and CNIM, respectively, which is 100% and 18% higher compared to the system without AS. This may be due to the fact that the antiscalant delays the clustering process and prevents the precipitation of salt on the membrane surface [51–54]. The presence of AS was found to be more effective with the PP membrane than the CNIM.

Similar trends were observed with the other two salts and are shown in Figure 6c,d. As can be seen from Figure 6c, the water vapor flux of CaCO₃ solution (3.5 g/L) declined to 22.6 from 47.2 kg/m²·h and 32.4 from 51.1 kg/m²·h for PP membrane and CNIM, respectively. These represent 52.1% and 36.6% reductions in flux, respectively. The use of AS further subsides the flux reduction for both membranes. For BaSO₄ salt solution (2.5 g/L concentration, shown in Figure 6d), the flux declined to 23.7 from 47.7 kg/m²·h for PP membrane, and to 37.7 from 49.4 kg/m²·h with CNIM. The results exhibited higher membrane antiscaling performance using CNIM and the water vapor flux was found to be 59% higher for CNIM compared to PP membrane after 10 h of operation. However, by using the antiscalant materials with CNIM, the membrane scaling was reduced further and the flux increased by ~18%. Among all thee salts, CaSO₄ fouled the membrane most drastically and the use of AS in the feed solution also was found to be more effective for CaSO₄. In general, by using CNIM, the scaling on the membrane surface was reduced and the MD performance enhanced. The addition of AS further increased the antiscaling properties of the system.

The normalized flux declination (*FDn*) for different membrane systems with various salt solutions are shown in Table 1. It is clear from the table that the CNIM exhibited lower flux decline for all salts compared to PP, indicating a clear lowering of the scaling tendency. The use of AS further improved the antiscaling property of both membranes. For CaSO₄, the flux decline for CNIM-AS and CNIM were found to be 30.8% and 36%, respectively, which were 23% and 45% lower than that of the PP membrane.

Salt		FDn (%) of Vario	us Salt Solutior	15
Suit -	РР	CNIM	PP-AS	CNIM-AS
CaSO ₄	66	36	40	30.8
CaCO ₃	53	37	25	27
$BaSO_4$	51	24	17	22

Table 1. Normalized flux decline (FDn) for various salt solutions.

3.4. Deposition of Salts on the Membranes

The deposition of the salt crystals on the membrane surface was measured by weighing the amount of salt on the membrane before and after the 6 h run, and then drying the membrane overnight in an oven at 70 °C. The weight measurements were done very carefully to avoid any loss of deposited salt from the surface. The results are shown in Table 2.

Salt	Amount of Salt Deposited o	% Weight Decrease	
Suit	РР	PP-AS	
CaSO ₄	12.4	8.9	28.2
CaCO ₃	22.6	16.8	25.7
$BaSO_4$	6.8	5.3	22.1
	CNIM	CNIM-AS	
CaSO ₄	8.6	6.4	25.6
CaCO ₃	10.5	7.9	24.8
BaSO ₄	5.2	4.1	21.2

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From Table 2, it is clear that the amount of salts deposited on the membrane surface was lesser for CNIM than the PP membrane for all cases. The lower salt deposition on CNIM may be attributable to the screening effect of CNTs [55]. The table also demonstrates the advantage of using antiscalant in reducing the salt deposition on the membrane surface [56,57]. The AS influenced the PP membrane-based desalination slightly more than the CNIM, where the salt deposition was reduced by 25.6% and 28.2%, respectively, for CNIM and PP for CaSO₄.

SEM images of the deposition of various salt crystals on different membrane surfaces with and without using antiscalant are shown in Figure 7. The SEM images clearly show the difference in crystal configuration of different salt clusters. It is also revealed from the images that the use of AS significantly reduced the scaling layer on the membrane surface [1,35,58]. The foulants interact with each other and with the membrane surface to form deposits [59–63], The antiscalant interact with the foulants and with the membrane surface to breakdown the salt crystals (foulants) and reduce the scaling as is shown in Figure 7a–c for all salts.



Figure 7. Cont.

(c)

Figure 7. (**a**) SEM image of CaSO₄ deposition on (**i**) PP, (**ii**) PP-AS, (**iii**) CNIM and (**iv**) CNIM-AS after running the experiment given in Figure 6b. (**b**) SEM image of CaCO₃ deposition on (**i**) PP, (**ii**) PP-AS, (**iii**) CNIM, and (**iv**) CNIM-AS after running the experiment given in Figure 6c. (**c**) SEM image of BaSO₄ deposition on (**i**) PP, (**ii**) PP-AS, (**iii**) CNIM, and (**iv**) CNIM-AS after running the experiment given in Figure 6c. (**c**) SEM image of BaSO₄ deposition on (**i**) PP, (**ii**) PP-AS, (**iii**) CNIM, and (**iv**) CNIM-AS after running the experiment given in Figure 6d.

3.5. Membrane Regeneration and Stability

The regenerability of the fouled membranes using $CaSO_4$ as feed were studied with or without AS in the system. The MD experimentations were continued for 6 h followed by washing of the fouled membrane with circulating DI water at 70 °C for 30 min and then the MD experiments were continued again for another 6 h with the freshly prepared feed mixture. The water vapor flux after washing was compared with the initial flux.

Table 3 shows the regenerability of the membranes with $CaSO_4$ with and without AS. It is clear from the table that the CNIM was able to remove the deposited salts and attained around 97% of its initial water vapor flux. By contrast, the PP membrane only reached up to 85% of its original value, which clearly demonstrated the superiority of CNIM in terms of membrane regeneration.

Membrane	1st Day Flux (kg/m ² ·h)	2nd Day Flux (kg/m ² ·h)	Flux Regenerated (%)
PP	39.4	33.5	85.0
PP-AS	44.4	39.4	88.7
CNIM	47.6	45.2	95.0
CNIM-AS	52.0	50.2	96.5

Fable 3.	Membrane	regeneration	data.
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The outcomes were further confirmed by using SEM and measuring the weight of the salts that remained on the membrane surface after washing. Figure 8a–d show the surface SEM images of the CaSO₄ fouled PP membrane and CNIM with and without AS after washing. The salt precipitation was found to be less on the CNIM surface after washing, which further demonstrated the washability and regenerability of the CNIM.

Figure 8. SEM image of the fouled membrane after washing (a) PP, (b) PP-AS, (c) CNIM, and (d) CNIM-AS.

Table 4 shows the amount of salt remained on the membrane surface after washing the fouled membranes. The result showed the amount of salt remained on the membrane surface was significantly lower than that of the fouled membrane. Among PP and CNIM, the CNIM showed higher washability of the deposited salts.

Salt	Amount of Sa	lt Remained on the Me	embrane Surface afte	er Washing (mg)
CaSO4	PP	PP-AS	CNIM	CNIM-AS
	5.5	4.2	2.3	1.9
Removal (%)	55.6	52.8	73.3	70.3

Table 4. Amount of salt dep	position on the	membrane surfa	ce after washing.
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While running the experiment with CNIM, no CNTs were detected in the feed solutions that have been recycled. The CNIM was also run with aqueous solutions for 30 days (6 h per day) at 70 °C and then inspected to see is there was any loss of CNTs. However, any appreciable loss of CNTs was not observed, which demonstrates the ability of CNTs to be retained on the membrane surface [45].

4. Conclusions

This paper successfully demonstrates the enhanced antiscaling behavior of CNIM over pristine PP membrane. The addition of antiscalant to the feed solution resulted in a reduction in scaling on the surface of the membrane. The desalination performance of PP and CNIM were compared. The CNIM exhibited lower flux decline for all the salts. The washability and regenerability of the CNIM was observed to be superior to the pristine PP membrane. The addition of antiscalant materials and use of CNIM in MD was found to be highly effective in enhancing the membrane performance and membrane regenerability when treating with high concentration scaling salts.

Author Contributions: S.M. and S.R. conceived and defined the problem. M.S.H. and S.R. developed the methodology and case studies. All of the authors contributed to the discussion. S.M. and S.R. supervised the experiments and technical writing, and reviewed and finalized the paper structure.

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References

- 1. Warsinger, D.M.; Swaminathana, J.; Guillen-Burrieza, E.; Arafat, H.A.; Lienhard V, J.H. Scaling and fouling in membrane distillation for desalination applications: A review. *Desalination* **2015**, *356*, 294–313. [CrossRef]
- Humplik, T.; Lee, J.; O'Hern, S.C.; Fellman, B.A.; Baig, M.A.; Hassan, S.F.; Atieh, M.A.; Rahman, F.; Laoui, T.; Karnik, R.; et al. Nanostructured materials for water desalination. *Nanotechnology* 2011, 22, 292001. [CrossRef] [PubMed]
- 3. Roy, S.; Ragunath, S. Emerging membrane technologies for water and energy sustainability: Future prospects, constraints and challenges. *Energies* **2018**, *11*, 2997. [CrossRef]
- Guillén-Burrieza, E.; Blanco, J.; Zaragoza, J.; CésarAlarcón, D.; Palenzuela, P.; Ibarra, M.; Gernjak, W. Experimental analysis of an air gap membrane distillation solar desalination pilot system. *J. Membr. Sci.* 2011, 379, 386–396. [CrossRef]
- 5. Burn, S.; Hoang, M.; Zarzo, D.; Olewniak, F.; Campos, E.; Bolto, B.; Barron, O. Desalination techniques—A review of the opportunities for desalination in agriculture. *Desalination* **2015**, *364*, 2–16. [CrossRef]
- 6. He, T.-X.; Yan, L.-J. Application of alternative energy integration technology in seawater desalination. *Desalination* **2009**, *249*, 104–108. [CrossRef]

- 7. Roy, S.; Ragunath, S.; Mitra, S. Effect of module configuration on the overall mass recovery in membrane distillation. *Desalination Water Treat.* **2017**, *95*, 74–79. [CrossRef]
- 8. Charcosset, C. A review of membrane processes and renewable energies for desalination. *Desalination* **2009**, 245, 214–231. [CrossRef]
- 9. Qtaishat, M.R.; Banat, F. Desalination by solar powered membrane distillation systems. *Desalination* **2013**, 308, 186–197. [CrossRef]
- Ghaffour, N.; Missimer, T.M.; Amy, G.L. Technical review and evaluation of the economics of water desalination: current and future challenges for better water supply sustainability. *Desalination* 2013, 309, 197–207. [CrossRef]
- Gude, V.G.; Nirmalakhandan, N.; Deng, S. Renewable and sustainable approaches for desalination. *Renew. Sustain. Energy Rev.* 2010, 14, 2641–2654. [CrossRef]
- 12. Li, N.N.; Fane, A.G.; Winston Ho, W.S.; Matsuura, T. *Advanced Membrane Technology and Applications*; John Wiley & Sons: Hoboken, NJ, USA, 2011.
- 13. Ang, W.L.; Mohammad, A.W.; Hilal, N.; Leo, C.P. A review on the applicability of integrated/hybrid membrane processes in water treatment and desalination plants. *Desalination* **2015**, *363*, 2–18. [CrossRef]
- 14. Scott, K. Handbook of Industrial Membranes; Elsevier: Amsterdam, the Netherlands, 1995.
- 15. Soldenhoff, K.; McCulloch, J.; Manis, A.; Macintosh, P. *Nanofiltration in Metal. and Acid Recovery*; Elsevier Advanced Technology: Oxford, UK, 2005; pp. 459–477.
- 16. Al-Shammiri, M.; Safar, M.; Al-Dawas, M. Evaluation of two different antiscalants in real operation at the Doha research plant. *Desalination* **2000**, *128*, 1–16. [CrossRef]
- 17. Meng, F.; Chae, S.-R.; Drews, A.; Kraume, M.; Shin, H.-S.; Yang, F. Recent advances in membrane bioreactors (MBRs): membrane fouling and membrane material. *Water Res.* **2009**, *43*, 1489–1512. [CrossRef]
- 18. Gryta, M. Fouling in direct contact membrane distillation process. J. Membr. Sci. 2008, 325, 383–394. [CrossRef]
- 19. Bian, R.; Yamamoto, K.; Watanabe, Y. The effect of shear rate on controlling the concentration polarization and membrane fouling. *Desalination* **2000**, *131*, 225–236. [CrossRef]
- 20. Goosen, M.F.A.; SablanI, S.S.; Al-Hinai, H.; Al-Obeidani, S.; Al-belushi, R.; Jackson, D. Fouling of reverse osmosis and ultrafiltration membranes: a critical review. *Sep. Sci. Technol.* **2005**, *39*, 2261–2297. [CrossRef]
- 21. Guo, W.; Ngo, H.-H.; Li, J. A mini-review on membrane fouling. Bioresour. Technol. 2012, 122, 27–34. [CrossRef]
- 22. Curcio, E.; Curcio, E.; Ji, X.; Profio, G.D.; Sulaiman, A.O.; Fontananova, E.; Drioli, E. Membrane distillation operated at high seawater concentration factors: Role of the membrane on CaCO3 scaling in presence of humic acid. *J. Membr. Sci.* **2010**, *346*, 263–269. [CrossRef]
- 23. Peñate, B.; García-Rodríguez, L. Current trends and future prospects in the design of seawater reverse osmosis desalination technology. *Desalination* **2012**, *284*, 1–8. [CrossRef]
- 24. Yorgun, M.; Balcioglu, I.A.; Saygin, O. Performance comparison of ultrafiltration, nanofiltration and reverse osmosis on whey treatment. *Desalination* **2008**, *229*, 204–216. [CrossRef]
- 25. Van der Bruggen, B.; Vandecasteele, C. Distillation vs. membrane filtration: overview of process evolutions in seawater desalination. *Desalination* **2002**, *143*, 207–218. [CrossRef]
- 26. Ghadimkhani, A.; Zhang, W.; Marhaba, T. Ceramic membrane defouling (cleaning) by air Nano Bubbles. *Chemosphere* **2016**, *146*, 379–384. [CrossRef] [PubMed]
- 27. Hou, D.; Wang, Z.; Li, G.; Li, H.; Wang, J.; Huang, H. Ultrasonic assisted direct contact membrane distillation hybrid process for membrane scaling mitigation. *Desalination* **2015**, *375*, 33–39. [CrossRef]
- 28. Muthukumaran, S.; Kentish, S.E.; Stevens, G.W.; Ashokkumar, M. Application of ultrasound in membrane separation processes: a review. *Rev. Chem. Eng.* **2006**, *22*, 155–194. [CrossRef]
- 29. Humoud, M.S.; Intrchom, W.; Roy, S.; Mitra, S. Reduction of scaling in microwave induced membrane distillation on a carbon nanotube immobilized membrane. *Environ. Sci. Water Res. Technol.* **2019**, *5*, 1012–1021. [CrossRef]
- Roy, S.; Intrchom, W.; Humoud, M.; Mitra, S. Microwave-induced desalination via direct contact membrane distillation. ACS Sustain. Chem. Eng. 2017, 6, 626–632. [CrossRef]
- Coday, B.D.; Xu, P.; Beaudry, E.G.; Herron, J.; Lampi, K.; Hancock, N.T.; Cath, T.Y. The sweet spot of forward osmosis: Treatment of produced water, drilling wastewater, and other complex and difficult liquid streams. *Desalination* 2014, 333, 23–35. [CrossRef]
- 32. Rezaei, M.; Warsinger, D.M.; Lienhard, V.J.H.; Duke, M.C.; Matsuura, T.; Samhaber, W.M. Wetting phenomena in membrane distillation: mechanisms, reversal, and prevention. *Water Res.* **2018**, *139*, 329–352. [CrossRef]

- 33. Istirokhatun, T.; Dewi, M.N.; Ilma, H.I.; Susanto, H. Separation of antiscalants from reverse osmosis concentrates using nanofiltration. *Desalination* **2018**, *429*, 105–110. [CrossRef]
- 34. Adham, S.; Hussain, A.; Matar, J.M.; Dores, R.; Janson, A. Application of membrane distillation for desalting brines from thermal desalination plants. *Desalination* **2013**, *314*, 101–108. [CrossRef]
- 35. He, F.; Sirkar, K.K.; Gilron, J. Effects of antiscalants to mitigate membrane scaling by direct contact membrane distillation. *J. Membr. Sci.* 2009, 345, 53–58. [CrossRef]
- 36. Gryta, M. Polyphosphates used for membrane scaling inhibition during water desalination by membrane distillation. *Desalination* **2012**, *285*, 170–176. [CrossRef]
- 37. Bhadra, M.; Roy, S.; Mitra, S. Enhanced desalination using carboxylated carbon nanotube immobilized membranes. *Sep. Purif. Technol.* **2013**, 120, 373–377. [CrossRef]
- 38. Mitra, S.; Roy, S.; Bhadra, M. Nanocarbon Immobilized Membranes. United States Patent US20170333848A1, 2017.
- 39. Gethard, K.O.; Khow, S.; Mitra, S. Water desalination using carbon-nanotube-enhanced membrane distillation. *ACS Appl. Mater. Interfaces* **2010**, *3*, 110–114. [CrossRef]
- 40. Ragunath, S.; Roy, S.; Mitra, S. Carbon nanotube immobilized membrane with controlled nanotube incorporation via phase inversion polymerization for membrane distillation based desalination. *Sep. Purif. Technol.* **2018**, *194*, 249–255. [CrossRef]
- 41. Roy, S.; Bhadra, M.; Mitra, S. Enhanced desalination via functionalized carbon nanotube immobilized membrane in direct contact membrane distillation. *Sep. Purif. Technol.* **2014**, *136*, 58–65. [CrossRef]
- 42. Gupta, O.; Roy, S.; Mitra, S. Enhanced membrane distillation of organic solvents from their aqueous mixtures using a carbon nanotube immobilized membrane. *J. Membr. Sci.* **2018**, *568*, 134–140. [CrossRef]
- Roy, S.; Petrova, R.S.; Mitra, S. Effect of carbon nanotube (CNT) functionalization in epoxy-CNT composites. Nanotechnology reviews. 2018, 6, 475–485. [CrossRef]
- 44. Bhadra, M.; Roy, S.; Mitra, S. A bilayered structure comprised of functionalized carbon nanotubes for desalination by membrane distillation. *ACS Appl. Mater. Interfaces* **2016**, *8*, 19507–19513. [CrossRef]
- 45. Bhadra, M.; Roy, S.; Mitra, S. Flux enhancement in direct contact membrane distillation by implementing carbon nanotube immobilized PTFE membrane. *Sep. Purif. Technol.* **2016**, *161*, 136–143. [CrossRef]
- 46. Intrchom, W.; Roy, S.; Mitra, S. Functionalized Carbon Nanotube Immobilized Membrane for Low Temperature Ammonia Removal via Membrane Distillation. *Sep. Purif. Technol.* **2020**, 235, 116188. [CrossRef]
- Han, C.; Sahle-Demessie, E.; Varughese, E.; Shi, H. Polypropylene–MWCNT composite degradation, and release, detection and toxicity of MWCNTs during accelerated environmental aging. *Environ. Sci. Nano* 2019, *6*, 1876–1894. [CrossRef]
- 48. Tijing, L.D.; Woo, Y.C.; Choi, J.-S.; Lee, S.; Kim, S.-H.; Shon, H.K. Fouling and its control in membrane distillation—A review. *J. Membr. Sci.* **2015**, 475, 215–244. [CrossRef]
- Ali, A.; Macedonio, F.; Drioli, E.; Aljlil, S.; Alharbi, O.A. Experimental and theoretical evaluation of temperature polarization phenomenon in direct contact membrane distillation. *Chem. Eng. Res. Des.* 2013, *91*, 1966–1977. [CrossRef]
- 50. Camacho, L.M.; Ludovic, D.; Zhang, J.; Li, J.; Duke, M.C.; Gomez, J.; Gray, S. Advances in membrane distillation for water desalination and purification applications. *Water* **2013**, *5*, 94–196. [CrossRef]
- 51. Antony, A.; Low, J.H.; Gray, S.; Childress, A.E.; Le-Clech, P.; Leslie, G. Scale formation and control in high pressure membrane water treatment systems: a review. *J. Membr. Sci.* **2011**, *383*, 1–16. [CrossRef]
- 52. Tzotzi, C.; Pahiadaki, T.; Yiantsios, S.G.; Karabelas, A.J.; Andritsos, N. A study of CaCO3 scale formation and inhibition in RO and NF membrane processes. *J. Membr. Sci.* **2007**, *296*, 171–184. [CrossRef]
- 53. Drak, A.; Glucina, K.; Busch, M.; Hasson, D.; Laîne, J.-M.; Semiat, R. Laboratory technique for predicting the scaling propensity of RO feed waters. *Desalination* **2000**, *132*, 233–242. [CrossRef]
- Eriksson, R.; Merta, J.; Rosenholm, J.B. The calcite/water interface: I. Surface charge in indifferent electrolyte media and the influence of low-molecular-weight polyelectrolyte. *J. Colloid Interface Sci.* 2007, 313, 184–193. [CrossRef]
- Takizawa, Y.; Glucina, K.; Busch, M.; Hasson, D.; Laîne, J.-M.; Semiat, R. Effective Antiscaling Performance of Reverse-Osmosis Membranes Made of Carbon Nanotubes and Polyamide Nanocomposites. *ACS Omega* 2018, 3, 6047–6055. [CrossRef] [PubMed]
- 56. Gloede, M.; Melin, T. Physical aspects of Membr. scaling. Desalination 2008, 224, 71–75. [CrossRef]
- 57. Ghani, S.; Al-Deffeeri, N.S. Impacts of different antiscalant dosing rates and their thermal performance in Multi Stage Flash (MSF) distiller in Kuwait. *Desalination* **2010**, 250, 463–472. [CrossRef]

- 58. Yang, Q.; Liu, Y.; Li, Y. Control of protein (BSA) fouling in RO system by antiscalants. *J. Membr. Sci.* **2010**, 364, 372–379. [CrossRef]
- 59. Shirazi, S.; Lin, C.-J.; Chen, D. Inorganic fouling of pressure-driven membrane processes—A critical review. *Desalination* **2010**, 250, 236–248. [CrossRef]
- 60. Brant, J.A.; Childress, A.E. Assessing short-range membrane–colloid interactions using surface energetics. *J. Membr. Sci.* **2002**, 203, 257–273. [CrossRef]
- 61. Hausmann, A.; Sanciolo, P.; Vasiljevic, T.; Weeks, M.; Schroën, K.; Gray, S.; Duke, M. Fouling of dairy components on hydrophobic polytetrafluoroethylene (PTFE) membranes for membrane distillation. *J. Membr. Sci.* **2013**, *442*, 149–159. [CrossRef]
- 62. D'souza, N.; Mawson, A. Membrane cleaning in the dairy industry: a review. *Crit. Rev. Food Sci. Nutr.* 2005, 45, 125–134. [CrossRef]
- 63. Shakkthivel, P.; Vasudevan, T. Acrylic acid-diphenylamine sulphonic acid copolymer threshold inhibitor for sulphate and carbonate scales in cooling water systems. *Desalination* **2006**, *197*, 179–189. [CrossRef]

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