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Article

Novel Polysulfone/Carbon Nanotube-Polyamide Thin Film Nanocomposite Membranes with Improved Water Flux for Forward Osmosis Desalination

Ahmed O. Rashed, Amal M. K. Esawi,* and Adham R. Ramadan

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ABSTRACT: Forward osmosis (FO) is a promising alternative to reverse osmosis (RO) in membrane-based water desalination. In the current study, carboxylated multiwalled carbon nanotubes (MWCNTs) were incorporated in a polyamide (PA) layer formed on tap of a polyaulfong poroug support resulting in a thin film	Polysulfone support Definition of the support of t
nanocomposite (TFN) membrane. The amount of MWCNTs was varied (0.01, 0.05, 0.1, and 0.2 wt/vol %). The FO performance	FS Feed solution

was investigated using deionized water as the feed solution and 2 M NaCl as the draw solution. It was found that the carboxylated MWCNTs enhanced the membrane hydrophilicity, surface roughness, and porosity. Such combined effects are believed to have led to enhanced FO water flux. TFN 0.2 showed the highest FO water flux to the blank thin-film composite (TFC) membrane and significantly better

have led to enhanced FO water flux. TFN 0.2 showed the highest FO water flux of 73.15 L/m^2 h, an improvement of 67% compared to the blank thin-film composite (TFC) membrane and significantly better than the values reported in the literature. Direct observation by transmission electron microscopy revealed the presence of some open-ended CNTs favorably oriented across the PA layer. Those are believed to have facilitated the transport of water through their inner cores and contributed to the increase in water flux. However, this was at the expense of salt rejection and reverse solute flux performance. The best performing membrane was found to be TFN 0.01. It exhibited a salt rejection of 90.1% with a FO water flux of 50.23 L/m^2 h, which is 13% higher than the TFC membrane, and a reverse solute flux of 2.76 g/m² h, which is 21% lower than the TFC membrane. This TFN 0.01 membrane also outperformed the TFN membranes reported in the literature.

1. INTRODUCTION

Desalination has become a vital solution for the global water scarcity problem. Membrane-based desalination is being widely used because it is simple, continuous, and energy-efficient.^{1,2} Reverse osmosis (RO) membranes are commonly used in water desalination. In the RO membrane technology, a semipermeable membrane positioned between a saline feed solution and a fresh water permeate solution allows the water to flow from the feed to the permeate solution while rejecting the salts. However, this requires the application of an external pressure exceeding the osmotic pressure. Unlike RO, forward osmosis (FO) is a spontaneous process that allows the movement of water across a specially designed semipermeable membrane from a low osmotic pressure side to a high osmotic pressure.^{3,4}

Draw solutions of various salinities are used for this purpose. The difference in osmotic pressure between the feed and draw solutions drives the flow across the membrane,^{5,6} thus making the process energy-efficient.^{7,8} Membranes used in FO desalination are typically thin-film composite (TFC) membranes.⁹ Ideally, TFC FO membranes consist of a highly porous support on which a thin-film rejection layer is

synthesized.¹⁰ The highly porous, less tortuous support membrane with hydrophilic properties is essential to minimize the internal concentration polarization (ICP) and to increase the FO water flux, while the rejection layer is required to increase the salt rejection with a minimum reverse solute flux. Most TFC membranes have been synthesized with a polyamide (PA) rejection layer and a support of polysulfone (PSF) or polyethersulfone (PES).^{11,12}

In general, the support membrane is prepared by immersion precipitation phase inversion (PI). Pore-forming agents such as polyvinylpyrrolidone (PVP) are typically doped with the support membrane casting solution to increase the membrane porosity and hydrophilicity.^{13,14} On the other hand, the thin-film PA rejection layer is typically prepared by the conventional interfacial polymerization (IP) reaction between multi-functionalized monomers. One of the monomers usually has a

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nucleophile reactant (amine) in aqueous solution and the other monomer has an electrophile reactant (acid chloride) in organic solution.^{15–17} TFC PA membranes are vulnerable to fouling as a result of their surface physicochemical characteristics, such as the surface charge and surface roughness that can attract organic foulants, leading to a reduction in the FO water flux.^{18,19}

Researchers have focused on addressing the drawbacks of the existing FO membranes, namely, the low water permeability and membrane fouling, by adopting various approaches. Some researchers added nanofillers to the support layer, whereas others conducted surface modifications to enhance membrane performance. For example, Ma et al.²⁰ added NaY zeolite to the support layer of PSF with the aim of controlling the ICP. Emadzadeh et al.²¹ incorporated titanium dioxide (TiO_2) nanoparticles in different amounts (from 0 to 1 wt %) into a PSF support membrane and reported that the addition of TiO₂ nanoparticles increased the porosity and hydrophilicity of the resulting nanocomposite membranes. Other investigations entailed adding different nanofillers such as graphene oxide,²² inorganic nanoparticles,^{23,24} inorganic nanotubes, such as aluminosilicate,²⁵ imogolite,²⁶ and titanate²⁷ to both the support and rejection layers of thinfilm nanocomposite (TFN) membranes and investigating their effect on membrane performance. Chemical modification of FO membrane surfaces was also reported to improve the water flux.²⁸ Although most studies added nanofillers in the support layer, adding them in the active layer to form a nanocomposite active layer,^{19,23} adding them as a separate coating on the active layer, and introducing them as an additional interlayer between the active layer and the porous substrate were also reported.29

Recently, carbon nanotubes (CNTs) have been used in the synthesis of novel TFN membranes for water desalination.³⁰ However, such studies have largely focused on RO applications. On the other hand, the potential of CNT use in FO membranes has not been extensively explored. A recent review paper concluded that carbon-based nanomaterials in FO membranes are still at the early stage of laboratory investigation with no currently available commercial products.²⁹ Multiwalled CNTs (MWCNTs) exhibit low hydrophilicity that makes their dispersion in the polymer matrix challenging. This can be overcome by functionalization.^{31,32} Researchers incorporated MWCNTs in the membrane support layer to enhance the mechanical strength and improve membrane performance. For example, Wang et al.³³ synthesized TFN FO membranes by introducing functionalized MWCNTs in the support membrane and reported improved tensile strength, salt rejection, and FO water flux. Similarly, Tian et al.³⁴ synthesized TFN FO membranes with a CNTreinforced nanofibrous substrate and reported enhanced water flux and membrane mechanical strength. Choi et al.³⁵ fabricated TFN FO membranes with a functionalized CNTblended PES support layer for integrated seawater desalination and wastewater reclamation and reported a 72% increase in the water flux and enhanced fouling resistance.

Investigating the effect of adding amine-functionalized MWCNTs to the rejection layer was conducted by Amini et al.³² who introduced 0.01–0.1 wt % MWCNTs in the PA rejection layer and reported improvements in the water flux and salt rejection. Another group focused on improving the membrane hydrophilicity by investigating the use of sulfonated MWCNTs. They reported enhanced water flux and a lower

reverse solute flux.³⁶ Song et al. investigated the effect of the CNT location on the membrane performance for both nanofiltration and FO applications. The CNTs were introduced in the substrate, in the active layer, and in both. The membrane structures, properties, and performances were compared and related to their location.³⁷ Despite the previously reported efforts, this area of study has yet to reach a thorough understanding of the role of CNTs in the FO performance, particularly with regard to different CNT functionalization treatments and to different and higher CNT concentrations.

The current study aims to investigate the effect of incorporating carboxylated MWCNTs—in amounts up to 0.2 wt % in the rejection layer—on the FO performance and to study their impact on FO membrane hydrophilicity, porosity, and morphology.

2. EXPERIMENTAL METHODS

2.1. Materials. PSF (average molecular weight Mn \approx 22,000, MO, Sigma-Aldrich) was used for the membrane support layer. PVP powder (average molecular weight: 360,000, Sigma-Aldrich) was used as a pore former. Anhydrous dimethyl formamide (DMF) (density: 0.944 g/mL, 99.8% purity, Sigma-Aldrich) was used as a solvent. Deionized water (MilliPore) was used as a nonsolvent. For the PA rejection layer, *m*-phenylenediamine (MPD) flakes (molecular weight: 108.14 g/mol, 99% purity, Sigma-Aldrich) and 1,3,5benzenetricarbonyltrichloride (TMC) (molecular weight: 265.48 g/mol, 98% purity, Sigma-Aldrich) were used as reacting monomers. Deionized water (MilliPore) was used as a solvent for MPD. Hexane (density: 0.672, purity >98.5%, Sigma-Aldrich) was used as a solvent for TMC. Elicarb MWCNTs (diameter: 10–12 nm, length: tens of micrometers, and density: 1.7-1.9 g/cm³, manufactured by Thomas Swan, England) were used as nanofillers. H₂SO₄ (98% purity, Sigma-Aldrich) and HNO₃ (purity >69%, Sigma-Aldrich) were used in the oxidation functionalization of MWCNTs. Sodium chloride (purity \geq 99.5%, FLUKA) was used for evaluating salt rejection.

2.2. Preparation of Support Membranes. Twelve PSF support membranes were prepared using different concentrations of both PSF and PVP. The PSF concentration was varied from 15 to 20 wt %, while that of PVP was varied from 0 to 5 wt %. The prepared support membranes were characterized and tested in order to identify the PSF and PVP concentrations, leading to the highest water flux. This was found to be the support membrane prepared by stirring 18 wt % PSF and 2 wt % PVP in DMF at 200 rpm until PSF and PVP were completely dissolved reaching a clear homogenous solution. The solution was then sonicated for 30 min and left overnight to eliminate all air bubbles. This was followed by casting the solution on a glass substrate using an Elcometer 4040 automatic film applicator with a fixed speed rate of 90 mm/s and a moving casting knife with a height of 175 μ m. The glass substrate was subsequently immersed in a deionized water bath at room temperature to induce PI. Finally, the resulting support membrane was washed with deionized water to remove excess DMF.

2.3. Functionalization of MWCNTs. MWCNTs were functionalized by oxidation in an acidic solution using the method reported elsewhere.³⁸ This was done in order to improve their dispersion in aqueous solutions. Briefly, 2 g of MWCNTs was added to 50 mL of H_2SO_4 and 16.67 mL of



Figure 1. Schematic diagram of the FO test cell setup.

HNO₃ in a 100 mL round-bottom flask. The flask was then heated under reflux in an oil bath for 100 min with a gradual increase of the temperature from 90 to 133 °C. The flask was then allowed to cool to room temperature, and the resulting carboxylated MWCNTs were washed several times with deionized water and then filtered out using Whatman Teflon filter membranes of 0.2 μ m pore size. The filtered carboxylated MWCNTs were finally dried in a desiccator under vacuum for 24 h.

2.4. Preparation of TFC and TFN PA Rejection Layers. The rejection layer was prepared by IP on top of the support membrane in order to produce a TFC membrane. An aqueous 4 wt/vol % MPD solution was poured over the top surface of the support membrane and left for 5 min to ensure diffusion through the membrane support. Then, the excess solution was removed from the membrane by drying using an air drier. This was followed by pouring an organic 0.2 wt/vol % TMC/ hexane solution on the MPD-covered membrane top surface. The solution was left for 2.5 min for the IP reaction to take place. Then, the excess solution was removed from the membrane by air drying. The resulting TFC membrane was then cured at 80 °C for 10 min to promote more cross-linking of PA.^{39,40} A TFC membrane with 0% carboxylated MWCNTs was used as the blank membrane for comparison purposes. The carboxylated MWCNTs were incorporated in the rejection layer to produce TFN membranes. Different quantities of carboxylated MWCNTs (0.01, 0.05, 0.1, and 0.2 wt/vol %) were dispersed in aqueous solutions of 4 wt/vol % MPD. The dispersion was carried out by ultrasonication for 4 h. Then, the aqueous solution containing the carboxylated MWCNTs was reacted with the organic solution of TMC following the same method used for TFC preparation. This was followed by curing at 80 °C to produce TFN membranes denoted as TFN 0.01, TFN 0.05, TFN 0.1, and TFN 0.2, reflecting the different carboxylated MWCNT amounts.

2.5. Testing of the Membrane FO Performance. The FO water flux and reverse solute flux were measured using a Sterlitech CF042-FO test cell in the FO mode with the rejection layer facing the feed solution with an active membrane surface area of 42 cm². A feed solution of deionized water and a draw solution of 2 M NaCl were circulated at a rate of 220 mL/min in a closed loop using diaphragm pumps controlled by DC voltage controllers. As shown in the schematic diagram of the FO cell setup in Figure 1, both concentrations of the feed and draw solutions were kept

constant during the experiment by circulating them in separate closed loops, and the FO experiment was conducted at room temperature in intervals of 30 min.

Water permeability and salt rejection of simulated seawater, a 20 mM NaCl solution, were measured using a Sterlitech HP4750 stirred dead-end cell with an applied pressure of 2.5 bar and an active membrane area of 14.6 cm². The FO water flux, reverse solute flux, and salt rejection were measured in triplicates for each membrane sample using eqs 1-3, respectively, and the average values were reported.

$$J = \frac{\Delta V}{A\Delta t} \tag{1}$$

where J (L/m² h) is the FO water flux, ΔV (L) is the draw solution volume change, A (m²) is the active membrane area, and Δt (h) is the time interval of the experiment.

$$J_{\rm s} = \frac{\Delta CV}{A\Delta t} \tag{2}$$

where J_s (g/m² h) is the reverse solute flux, ΔC (g/L) is the feed solution concentration change, V (L) is the feed solution volume at the end of the experiment, A (m²) is the active membrane area, and Δt (h) is the time interval of the experiment.

$$R \% = 1 - \frac{C_{\rm p}}{C_{\rm f}} \times 100 \tag{3}$$

where R % is the salt rejection percent, C_p is the permeate concentration, and C_f is the feed concentration.

2.6. Characterization of the Fabricated Membranes. Cross sections and top and bottom surfaces of the prepared membranes were examined using a Leo Supra 55 (ZEISS) field emission scanning electron microscope. Membranes were coated with gold using a sputter coater of current (15 mA) for 2 min. A drop shape analyzer (DSA 25) from Kruss, Germany, was used to evaluate the hydrophilicity of the membranes. Water contact angles were measured using the sessile drop method. The surface roughness of the prepared membranes was measured using a Dimension 3100 atomic force microscope from Digital Instruments (Veeco Metrology Group). Top surfaces were imaged in the tapping mode with a scan size of 10 μ m × 10 μ m. Membrane pore size distributions were determined by nitrogen gas adsorption at 77 K using a Micrometrics ASAP 2020 instrument. Finally, transmission

electron microscopy (TEM) was carried out on a 200 kV analytical JEOL 2100 instrument. TEM samples were prepared by embedding them in 4-part epoxy resin, cured for 48 h at 60 $^{\circ}$ C, and then microtomed using a Reichert Ultratome to a thickness of approximately 80–100 nm to provide electron transparent TEM samples on copper grids.

3. RESULTS AND DISCUSSION

3.1. PSF Support Membrane. The PSF membrane selected as a support for our TFC and TFN membranes was the one prepared using 18 wt % PSF and 2 wt % PVP. The differential pore surface area and pore volume distribution versus pore width of the support membrane is presented in Figures S1 and S2 in the Supporting Information. As can be observed in the differential pore surface area and pore volume distribution versus pore width (Figures S1 and S2), the support membrane shows a wide range of pore sizes. Figure S1 shows that the largest differential surface area of pores was exhibited between (30-50 nm) and (100-150 nm). However, the highest differential pore volume was exhibited by the pores between 100 and 150 nm, as presented in Figure S2, indicating the large number of these pores in the membrane structure. The support membrane exhibited a high FO water flux of $90.15 \pm 0.49 \text{ L/m}^2$ h. This can be attributed to the addition of PVP as a pore-forming agent, which contributed to the acceleration of the demixing rate between the solvent and the nonsolvent during the PI process, leading to the production of a highly porous support membrane with the presence of fingerlike pores, as shown in Figure 4. The impact of PVP on enhancing the PSF membrane porosity is reported by other researchers.^{41,42} The selected support membrane is also characterized by a very low surface roughness of 7.47 nm, as presented in Table 1. Such a smooth surface is suitable for the subsequent formation of the rejection layer by IP.

 Table 1. Surface Roughness Values and Measured Contact

 Angles for the Support and TFC and TFN Membranes

membrane	contact angle (deg)	surface roughness (R_a) (nm)
support	73.06	7.47
TFC	62.15	32.67
TFN 0.01	55.75	41.87
TFN 0.05	53.66	43.94
TFN 0.1	50.15	50.91
TFN 0.2	41.85	67.30

3.2. FO Membrane Performance. Figure 2 presents the effect of increase in the carboxylated MWCNT content on both the FO water flux and salt rejection of TFC and TFN membranes, while Figure 3 shows their effect on both the water permeability and reverse solute flux. It was found that increasing the amount of MWCNTs in the aqueous solution of MPD resulted in a noticeable increase in both the FO water flux and water permeability. The FO water flux of the TFC membrane was found to be $43.7 \pm 0.51 \text{ L/m}^2$ h, which is believed to be influenced by the intrinsic properties of the support PSF membrane to a large extent. The FO water flux was found to reach 73.15 \pm 2.66 L/m² h for TFN 0.2, an increase of about 67% compared to the TFC membrane. In FO, an increase in water flux is typically accompanied by an increase in the reverse solute flux as a result of the difference in osmotic pressure between the feed and draw solutions. This is



Figure 2. FO water flux and salt rejection of TFC and TFN membranes.



Figure 3. Water permeability and reverse solute flux of TFC and TFN membranes.

seen in Figure 3 where the reverse solute flux increased with the MWCNT concentration. 43,44

The trend of change in salt rejection, as observed in Figure 2, indicates that lower concentrations of carboxylated MWCNTs (<0.05 wt/vol %) have a positive effect on salt rejection, while for higher concentrations, the opposite is observed. This is believed to be due to the presence of MWCNT agglomerates in membranes with a higher MWCNT content, as observed by TEM analysis, as will be reported in the next sections. The presence of CNT agglomerates might have led to reduced MPD amounts on the PSF substrate surface, thus affecting the polymerization reaction, leading to the formation of a less effective PA rejection layer and a lower salt rejection.²⁴ Ineffective salt rejection due to the effect of nanofiller agglomerates on the IP process and accordingly the integrity of the PA rejection layer were also reported by Amini et al. (2013) using amine-functionalized MWCNTs in the rejection layer,³² Ma et al. (2013) using zeolite in the support layer,²⁰ and Emadzadeh et al. (2014) who used TiO₂ in the support layer.²¹ However, the FO water flux achieved in the current study is higher.^{20,21,32,33,46,47}

3.3. Morphologies of the Support and TFC and TFN Membranes. Figure 4 presents the SEM cross-sectional morphology of the TFC membrane and shows a finger-like



Figure 4. Cross-sectional morphology of the TFC membrane at low (1.50 kx) and high magnifications (40.00 kx).

structure of the PSF support, as well as a porous structure in the upper part of the support in contact with the PA layer. Figure 5 shows the top surface morphologies of the support



Figure 5. Top surface morphologies of the support and TFC and TFN membranes with different CNT loading amounts at 20.00 k×.

and TFC and TFN membranes. The images show the typical ridge-valley structure of PA formed on top of the porous support membrane as a result of the IP reaction between MPD and TMC.⁴⁸ Detailed observations show the effect of adding the carboxylated MWCNTs on the membrane morphology. For example, the TFC membrane exhibited a more uniform and finer structure than the TFN membranes, while TFN 0.01 had more ribbon-like crystal particles. In addition, the change in the TFN morphologies with an increase in the carboxylated MWCNT amounts could be attributed to the hydrogen bonding between the hydroxyl group attached to the MWCNTs and the PA chains that slowed down the IP reaction between MPD and TMC.^{32,48}

3.4. Membrane Hydrophilicity and Surface Roughness. Contact angle measurements were used to evaluate the hydrophilicity of the support layer and the TFC and TFN membranes, while atomic force microscopy (AFM) was used to investigate the effect of the presence of carboxylated MWCNTs on the surface roughness (R_a). Table 1 presents the surface roughness (R_a) values for the different membranes and the corresponding contact angle values. It was found that increasing the amount of carboxylated MWCNTs decreased the contact angle consistently from 62.15° for TFC to 41.85° for TFN 0.2, reflecting the increase in membrane hydrophilicity. This is believed to have contributed to the observed enhancement of the FO water flux with increasing concent

trations of MWCNTs because of a strong attraction between the water molecules and the hydrophilic surface of the membrane.⁴⁹ On the other hand, the surface roughness (R_a) increased gradually with an increase in the carboxylated MWCNT concentration in the rejection layer reaching 67.3 nm for TFN 0.2. The support membrane R_a was only 7.47 nm, while that of TFC was 32.67 nm reflecting the increase in the membrane surface roughness after introducing the rejection layer. Figure 6 shows the AFM 2D and 3D images of the support and the TFC and TFN membranes, respectively. These results confirm the coarsening of the ridge-valley structure of PA with the introduction of carboxylated MWCNTs. Because a higher surface roughness means a larger surface area, this is also expected to contribute to the observed improved FO water flux.^{32,45}

3.5. Porosity of TFC and TFN Membranes. The effect of the carboxylated MWCNTs on the porosity of the blank TFC and TFN membranes was investigated. Figures 7 and 8 present the differential pore volume distributions versus the pore width of the different membranes, while Figures 9 and 10 present the corresponding differential pore surface area distributions. When the differential pore volume distribution plots and the differential pore surface area distribution plots are considered together, they can give an indication of the number of pores, for example, large differential volumes and small differential surface areas would indicate a limited number of pores. In this regard, sample TFN 0.2 exhibited the largest differential pore volume with the corresponding largest differential surface area for pores between 10 and 130 nm, denoting a large number of these pores. This was also exhibited by sample TFN 0.1, though with values lower than those of TFN 0.2. The pore structures for these two samples might be responsible for the higher values of the FO water flux and reverse solute flux.

Comparing the three samples TFC, TFN 0.01, and TFN 0.05, which exhibited comparable salt rejection values but increasing FO water flux and reverse solute flux, it can be noted that their pore distribution patterns do not parallel this trend. Differential pore volumes and differential pore surface areas indicate that sample TFC has the highest number of pores and that sample TFN 0.05 has the lowest number of pores of these three samples. This would be expected to lead to a decrease in FO water flux and reverse solute flux between samples TFC, TFN 0.01, and TFN 0.05. However, the opposite is found, which seems to indicate that the incorporation of carboxylated MWCNTs facilitated water transport even when added in small amounts. Similar observations were reported in our earlier work on cellulose acetate membranes.⁵⁰ In such cases, the role of the CNTs has to be studied in more depth to confirm the flow mechanism.

A close examination of the pore volume versus pore width and pore area versus pore width results for pores less than 10 nm (Figures 8 and 10) confirms the presence of large amounts of small pores in the range of 1-2 nm in all samples. Such pores are believed to be present in the PA layer and to be responsible for salt rejection.

3.6. TEM Analysis. TEM analysis of the PA layer of the TFN 0.2 sample, shown in Figure 11, revealed the presence of individual CNTs as well as CNT clusters. The PA layer was found to be irregular and with a thickness of approximately 200 nm. Some CNTs were found to be favorably oriented across the PA layer in a perpendicular direction to the interface between the porous support and the PA layer, whereas others were not. What was also noticeable is that the CNTs appear to



Figure 6. Surface roughness captured by AFM imaging (3D and 2D) of (a) support, (b) TFC, (c) TFN 0.01, (d) TFN 0.05, (e) TFN 0.1, and (f) TFN 0.2, where 3D images are on the left and 2D images are on the right.



Figure 7. Plot of differential pore volume vs pore width for TFC and TFN membranes, range 10–250 nm.

have been shortened by the functionalization treatment and subsequent ultrasonication for 4 h with most appearing to be having lengths in the range 50-200 nm, which is an order of magnitude shorter than their as-received length of tens of



Figure 8. Plot of differential pore volume vs pore width for TFC and TFN membranes, range 0-10 nm.

microns reported by the supplier. Both functionalization and ultrasonication have been widely reported by researchers to result in significant shortening of CNTs.^{51,52}



Figure 9. Plot of differential surface area vs pore width for TFC and TFN membranes, range 10–250 nm.



Figure 10. Plot of differential surface area vs pore width for TFC and TFN membranes, range 0-10 nm.

Additionally, several of the observed CNTs were found to have open ends, also indicating that the chemical functionalization treatment has removed their end caps. These observations confirm that the observed high water flux of this particular sample is strongly affected by those open-ended, favorably oriented CNTs, as shown in Figure 11c,d. CNTs in the transverse directions, on the other hand, can act as barriers and can thus contribute to slowing down the water transport through the PA layer. In addition to the individual CNTs, CNT clusters were also observed in the TFN 0.2 sample, as shown in Figure 11c,d. The voids between such clusters could also be contributing to improving the flux and lowering the salt rejection, as explained earlier.

The TFN 0.01 membrane, on the other hand, showed considerably fewer CNTs in the cross section. As with the TFN 0.2 membrane, some CNTs were observed to be opencapped, whereas others had their end caps intact, as seen in the high-resolution TEM (HRTEM) images in Figure 12. No CNT clusters were observed, which is attributed to the small amount of CNTs used. CNT inner (pore) diameters were observed to be in the range of 5-8 nm, which is consistent with theoretical predictions relating the CNT inner core to its outer diameter and the number of walls. Higher magnification



Figure 11. TEM image of the TFN 0.2 membrane showing the PA layer at different magnifications: (a) 25 kx, (b) 100 kx, (c) 250 kx, and (d) 400 kx. Individual CNTs as well as CNT clusters are shown.



Figure 12. HRTEM images of some CNTs in the PA layer of TFN 0.01 at different magnifications: (a) 800 kx and (b) 1200 kx.

images showed no interfacial gaps between the PA and CNTs as well as a well-defined CNT graphitic structure.

4. SUMMARY AND DISCUSSION

The present work focused on studying the effect of incorporating carboxylated MWCNTs in the rejection layer of TFC FO membranes on their performance and structure. It was found that the FO water flux sharply increased with an increase in the concentration of MWCNTs in the PA rejection layer. The highest FO water flux of $73.15 \pm 2.66 \text{ L/m}^2$ h was achieved by TFN 0.2. This represents a significant increase—67%—compared to the blank membrane.

The membrane salt rejection performance was not adversely impacted by the presence of small amounts of carboxylated MWCNTs. Higher concentrations of MWCNTs (>0.05 wt/ vol), however, led to a decrease in salt rejection, possibly attributed to a higher membrane porosity resulting from the negative effect of MWCNT agglomerates on the IP of the PA rejection layer.

Considering the reports in the literature on FO membrane performance with regard to salt rejection, water flux, and

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membrane type	nano-filler loading amount for best incorporation performance		FO water flux $(L/m^2 h)$	NaCl salt rejection (%)	reverse solute flux (g/m² h)	references	
TFN	carboxylated MWCNTs	0.01 wt/vol % in the rejection layer	50.23 ± 0.93	90.05 ± 0.25	2.76 ± 0.21	this work	
TFN	carboxylated MWCNTs	2 wt % in the support layer	12	90	2.2 ± 0.90	33	
TFN	amine MWCNTs	0.05 wt/vol % in the rejection layer	30	89.30	2.86 ± 0.40	32	
TFN	amine MWCNTs	0.01 wt/vol % in the rejection layer	40	88	3.62 ± 0.80	32	
TFN	TiO ₂	0.5 wt % in the support layer	29.70	92.70	7.30	21	
TFN	zeolite	0.4 wt/vol % in the rejection layer	15	90.50	9.17	46	
TFN	zeolite	0.5 wt % in the support layer	39	90	28	20	
TFC PSF/PA			12	93.40	4.90	47	
CTA flat sheet			9	81.90	5.30	47	

Table 2	. Performan	ce of	TFN	Membranes	Reported	l in	the	Literature	and	TFN	0.01	of	This	Stu	dy
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reverse solute flux, the commonly reported values for salt rejection are ca. 90%. The corresponding water flux values range between 9 and 40 L/m² h, and the reverse solute flux values range between 2.2 and 28 g/m² h. In this respect, the TFN 0.01 membrane of this work exhibiting a FO water flux of 50.23 ± 0.93 L/m² h for a salt rejection of $90.05 \pm 0.25\%$ and a reverse solute flux of 2.76 ± 0.21 g/m² h outperforms reports in the literature. This is summarized in Table 2.

Several researchers have discussed the role of nanoparticles such as MWCNTs in enhancing the performance of membranes in general. For example, Dlamini et al.53 argued that water molecules flow into the nanogaps around the nanoparticles rather than through the nanoparticles, as is often believed. Similarly, Amini et al.³² attributed the enhanced water flux in their TFN membranes to water predominantly flowing into the interfacial gaps between the CNTs and the polymer. On the other hand, Lee et al.⁵⁴ presented the experimental evidence that water molecules diffuse through both the PA layer (as in conventional TFC membranes) and the inner walls of open-ended CNTs. They reported that in spite of the random orientation of CNTs, improvements in flux were achieved, which was attributed to a fraction of CNTs that were favorably aligned. This agrees with observations in the current study. Relatedly, Ma et al.55 produced ultrathin PA rejection layers in which open-capped CNTs were uniformly dispersed using an electrospray-assisted IP method and reported enhanced water permeability. They attributed this enhancement to the combined effect of improved membrane hydrophilicity and the presence of nanochannels in the CNTs.

Owing to the difference in the explanations of the water diffusion pathways reported by various researchers, with the most common being through the CNT inner channels or the nanogaps at the interface between the CNT surface and the polymer matrix, further in-depth studies are still needed to better understand the role of CNTs and to confirm the flow mechanism.

Although the ideal CNT membrane would have opencapped vertically aligned closely packed CNTs, experimental evidence from our work as well as from Lee et al.⁵⁴ and Ma et al.⁵⁵ confirmed that introducing randomly oriented CNTs in the PA rejection layer—which does not need complicated fabrication procedures—can also lead to significant improvements in flux. However, because of the random orientation of the CNTs, their exact contribution to the enhancement in water permeability could not be confirmed. To this end, a closer control of the properties of the CNTs such as their inner core diameters, aspect ratios, functionalization treatment, degrees of cap opening, orientation, and volume fraction can impart better improvements in performance. This can eventually lead to commercial membranes with significantly improved water permeability and high salt rejection capacities.

5. CONCLUSIONS

TFN membranes were synthesized by the addition of carboxylated MWCNTs to a PA rejection layer on top of a PSF/PVP support layer in order to be used in FO water desalination. The incorporation of carboxylated MWCNTs in the PA rejection layer was found to be effective in improving the FO water flux. TEM direct observations confirmed that the high water flux is associated with some CNTs being favorably oriented across the PA layer. In addition, the improved FO water flux is also believed to be due to a combination of factors entailing increased hydrophilicity, higher surface areas due to increased roughness, and increased porosity. The observed drop in salt rejection with increased CNT content is believed to be due to CNT agglomerates and their possible negative impact on the IP process of the PA rejection layer.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c00973.

Plots of differential surface area versus pore width and differential pore volume versus pore width for the PSF support membrane, range 10-250 nm (PDF)

AUTHOR INFORMATION

Corresponding Author

Amal M. K. Esawi – Department of Mechanical Engineering, The American University in Cairo, New Cairo 11835, Egypt; orcid.org/0000-0001-9515-400X; Phone: +202 26153254; Email: a esawi@aucegypt.edu

Authors

- Ahmed O. Rashed Department of Chemistry, The American University in Cairo, New Cairo 11835, Egypt; Orcid.org/ 0000-0003-4661-0579
- Adham R. Ramadan Department of Chemistry, The American University in Cairo, New Cairo 11835, Egypt

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c00973

Author Contributions

All authors contributed equally. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

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