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Forward osmosis membrane with lightweight functionalised multiwall carbon nanotube nanofillers

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ABSTRACT

Thin-film nanocomposite (TFN) membranes with a polyamide (PA) active layer modified with carbon nanotubes (CNTs) hold promise for water desalination and wastewater reuse via forward osmosis (FO). We hypothesise that modifying the PA active layer with hydroxyl-functionalised multi-wall carbon nanotubes (f-MWCNTs) will enhance the water flux of the FO membrane while maximising salt rejection. TFN membranes were modified using in situ interfacial polymerisation, with varying f-MWCNT mass content to minimise agglomeration. These modified FO membranes are designated as CTFN-x, where x represents the mass content of f-MWCNTs, ranging from 0.001%, CTFN-1 to 0.008%, CTFN-8 (w/v). The surface properties of CTFN-x were characterised using electron microscopy, atomic force microscopy, and molecular spectroscopy. IR spectroscopic data confirm the successful adherence of f-MWCNTs as a bridging agent between the 1,3-phenylenediamine (MPD) and trimesoyl chloride (TMC) polymers, preserving FO membrane integrity. The CTFN-4 FO membrane shows the highest water flux (29 LMH) and the lowest reverse salt flux (2.90 gHM), attributed to preferential water flow channels in the f-MWCNTs. The integration of f-MWCNTs into the active layer improved water flux, reduced reverse salt flux, and enhanced the antifouling properties of FO membranes.



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Multi-walled carbon nanotubes; forward osmosis membranes; membrane fouling; hydroxyl functional groups

1. Introduction

Forward osmosis (FO) membrane treatment is an emerging and attractive supplement to widely used pressuredriven membrane technologies for water desalination, addressing the needs of over 9 billion people facing water scarcity globally [1]. However, FO technology's efficiency faces challenges including internal concentration polarisation (ICP), reverse salt flux, membrane fouling [2], and draw solution selection [3]. Thus, modifying the FO membrane layers with functionalised multiwalled carbon nanotubes (f-MWCNTs) is crucial because of their unique adjustable properties[4,5]. These properties include selective solute sieving [6], decreased roughness [7], enhanced hydrophilicity [7], improved charge characteristics, better water flux[7], reduced biofouling propensity[8], and greater durability

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[9]. Most modifications using f-MWCNTs have focused on enhancing the performance of the polyamide (PA) active layer. Incorporating f-MWCNTs into the PA layer creates controlled water flow routes in the membranes and can increase flux through both internal and external water transport mechanisms[10]. Water moves along a frictionless path through the f-MWCNTs, whose functional groups can be tuned to facilitate selective solute rejection.

Amini et al. [11] functionalised the PA active layer of the FO membrane with amino-functionalised -MWCNTs (NH₂-MWCNTs) to enhance its performance [11]. These modifications increased the water flux of the FO membrane while reducing solute flux, attributed to the narrowing of water transport channels and the covering of PA layer pores by f-MWCNTs [12]. Carboxylate functionalised MWCNTs demonstrated enhanced water flux due to aligned carbon nanotubes, increased hydrophilicity, and larger specific surface area [13]. However, only a few discussions have focused on applying hydroxyl-functionalised MWCNTs in the active layer of the forward osmosis membrane. Further previously, always f-MWCNT mass concentrations over 0.01% (w/v) were used to functionalise the PA active layer, which may agglomerate the substrate thus reducing the performance of the FO membranes.

However, the bonding efficiency of amino (-NH₂) or carboxyl (-COOH) functional groups in MWCNTs through to the active layer polymers such as 1,3-phenylenediamine (MPD) and trimesoyl chloride (TMC) is somewhat limited due to the reduced accessibility of the functional groups to the reactive sites on TMC and MPD [7]. This indicates the need for re-assessing the threshold mass of f-MWCNTs and evaluating the relative chemical strengths of the organic groups used in MWCNT functionalization for the PA layer activation.

The intrinsic MWCNTs are dominated by -COOH and hydroxyl (-OH) groups. In TFC membrane formation, TMC reacts with MPD support to form polyamide structures. We hypothesise that the low content of carboxyl groups in hydroxyl functionalised MWCNTs enhances the interaction with the amide groups of MPD. Then TMC is added to this composite, and the acyl chloride groups on TMC condense with the -OH groups of MWCNTs, generating PA chains and ester bonds [7]. However, these excess –OH groups on MWCNTs disrupt the interaction between MPD and TMC and increase polymer crosslinking through mainly functional groups of f-MWCNTs. This process improves the dispersion of the modifier and enhances the mechanical and chemical properties of the membrane.

The formation of cross-linked polymers (such as TMC/ MPD) network through f-MWCNTs, resulting in a thin active layer on the PSU support layer. Thus, we hypothesised decreased surface roughness, porosity, and increased negative charge, thereby enhancing the membrane's structural integrity, permeability, and selectivity, ultimately improving separation and desalination efficiency. Compared to strongly acidic -SO₃H or -COOH organic groups, the -OH groups may induce a net negative charge on the PA layer which may block the pass of charged solutes through internal or external water transport routes resulting in a salinity cut-off. Therefore, we functionalised the active PA layer of FO membranes with hydroxyl-functionalised MWCNTs for water desalination. We also examined the optimal f-MWCNT mass below 0.01% (w/v) for enhanced water flux and reduced reverse salt flux. Employing an in situ interfacial polymerisation method, we fabricated TFN-FO membranes incorporating low masses (<0.01% (w/ v)) of f-MWCNTs, denoted as CTFN-x. Through permeate flux, reverse salt rejection ratios, and zeta potential measurements, we evaluated the hydraulic performance of CTFN-x membranes relative to f-MWCNT content. Additionally, we postulated a mechanism for in situ polymerisation of f-MWCNTs and TFC based on molecular spectroscopic data.

2. Materials and methods

2.1. Materials

Multi-walled carbon nanotubes functionalised with hydroxyl groups (outer diameter = 8 nm, typical length $= 10-30 \mu m$, -OH content = 5.58 wt%, 95% purity, hereafter f-MWCNTs) were purchased from Chengdu Organic Chemicals (China). Polysulfone (PSU) beads, dimethylacetamide (DMAc), n-hexane (97% purity, anhydrous), sodium chloride (NaCl, 99.5% purity), sodium alginate (SA, Mw: 98.11), potassium dihydrogen phosphate (KH₂PO₄, 99.5% purity), magnesium sulfate (MqSO₄, 99% purity), sodium bicarbonate (NaHCO₃, 99.5% purity), calcium chloride (CaCl₂, 96% purity) and ammonium chloride (NH₄Cl, 99.5% purity) were obtained from Kelong (China). Before use, the trimesoyl chloride (TMC, 98% purity, Sigma-Aldrich) and m-phenylenediamine (MPD, 99.5% purity, Sigma-Aldrich) were kept in a refrigerator.

2.2. Preparation of PSU membrane substrates

The mesh-embedded PSU substrate was fabricated using non-solvent-induced phase separation (NIPS). To prepare the substrate, 15% w/v PSU beads (15 g of PSU per 100 mL of solution) were dissolved in DMAc under continuous stirring for 24 h to form a

homogeneous and transparent solution. The solution was then kept overnight and degassed at ambient room temperature before casting. The polymer solution was cast onto a pre-cleaned glass plate using a 100 μ m casting knife for uniform dispersion. The plate was then rapidly immersed into a coagulation bath, where it was kept for 10 min at room temperature to facilitate the NIPS process. The resulting membrane was preserved in pure water at 5°C until further use.

2.3. Fabrication of polyamide active layer

The thin-film polyamide layer with f-MWCNT incorporation was fabricated on the membrane using in situ interfacial polymerisation [14]. Various mass proportions of f-MWCNT in a 2% (w/v) MPD solution were used, with f-MWCNT mass ranging from 0.001% to 0.008% (w/v). The membrane substrate was first rinsed with DI water for one minute, followed by a two-minute immersion to dissolve impurities. Excess MPD solution was removed using a rubber roller, and the substrate was dried in a fume hood for several minutes. To induce interfacial polymerisation (IP), a 0.15% (w/v) TMC/n-hexane solution was mixed with the saturated membrane substrates for one minute. After removing excess TMC, the membranes were air-dried and oven-dried at 60°C for two minutes. The membranes were labelled as TFC (0.0% f-MWCNT) and CTFN-x (where x varies from 1 to 8, corresponding to 0.001% to 0.008% f-MWCNT mass). Finally, the membranes were placed in distilled water at 4°C before commencing osmosis performance tests.

2.4. Characterisation of TFC and CTFN-x membranes

The morphology and micro-structures of PSU substrates and TFC-FO membranes were observed using a fieldemission scanning electron microscope. (FESEM, JSM-7800F, JEOL, Japan). Before SEM imaging, the samples were vacuum-dried at 30 °C for 12 h and coated with Au by sputtering. (SCD 050 BAL-TEC, Germany). The interactions between f-MWCNTs and PA were determined using Fourier transform infrared spectroscopy (Cary 630, Agilent Technologies, USA) and Raman spectroscopy against 785 nm excitation (inVia[™] Raman microscope, Renishaw_», UK). The surface hydrophilicity was determined at room temperature by contact angle measurements using an optical goniometer (DSA100, KRÜ SS) equipped with a video-capturing device; five measurements were averaged. For topological and roughness measurements, stripped membranes were placed on cover-slip glasses². Atomic force microscopic measurements were used to determine the roughness of the membranes (TT2AFM, AFM workshop, USA). The surface functionality and surface charge characteristics of the membranes were analyzed using an electro-kinetic analyzer using a clamping cell sampling accessory (SurPASSTM 3, Anton Paar GmbH, Austria). Membrane samples of minimum 35 mm × 15 mm dimensions were mounted with the asymmetric configuration on the clamping Cell used for zeta potential measurements on planar surfaces using 0.05M HCl or 0.05M NaOH in 0.001M KCl for pH adjustments.

2.5. Determination of osmosis performance

The cross-flow FO filtration system was used to measure the water flux (J_w) and reverse salt flux (J_s) , of TFC and CTFN-x membranes with an effective membrane area of 42 cm². On one side of the cell, the feed solution (FS) and on the other side draw solution (DS) were pumped through the membrane surface at a 6.40 cm³/ s flow rate. In the active layer facing FS orientation, 1 M NaCl, and DI water were employed as draw solution and feed solution, respectively. On the other side, the change in FS conductivity and DS weight were monitored through a conductivity metre (DDSJ-308A, INESA Scientific, USA) and a digital balance (BSA6202S-CW, Sartorius, Germany) connected to a computer. To confirm the stable average readings, data were acquired every two minutes, and the whole procedure was repeated three times. The J_w (Lm⁻²h⁻¹ referred to as LMH) was calculated by Equation 1:

$$J_w = \frac{\Delta V}{A_m \times \Delta t} \tag{1}$$

The draw solution changes volume ΔV (L) at intervals of time Δt (h), with an effective membrane surface area of A_m (m²). Water density is 1000 g/L. The Js (gm⁻²h⁻¹ or referred to as gMH) can be calculated from these values by Equation 2:

$$J_{s} = \frac{C_{t}V_{t}}{A_{m}\Delta t}$$
⁽²⁾

Where C_t (g/L) is salt concentration and V_t (L) is the volume of FO feed solution.

2.6. Antifouling test

The TFC membrane fouling test was conducted in FO mode at 25 °C using sodium alginate as the organic foulant. Two types of synthetic wastewater were employed as the feed. Feed solution -1 (FS-1) was prepared by dissolving 0.45 mM KH₂PO₄, 9.20 mM NaCl, 0.61 mM MgSO₄, 0.5 mM NaHCO₃, 0.5 mM CaCl₂, and 0.93 mM NH₄Cl in DI water with pH adjusted to 7.4;

and feed solution-2 is of the same composition but with 250 mg/L sodium alginate added. Due to the large amount of draw solution used (1.5 L), its dilution effects are negligible. The FO cell was allowed to stabilise water flux for 1 h using distilled water (feed water) and draw solutions (2M NaCl) under cross-flow mode. Then the feed solution was transferred to FS-1 while 2M NaCl was used as the draw solution. After 1 h stabilisation time, the initial flux was recorded (J_{wo}) . Afterward, the feed solution was switched to FS-2 under the same draw solution conditions to initiate the rapid fouling process for 1080 min. The permeate flux, J_t was also recorded. The flow rates of all feed and draw solutions were maintained at 0.3 L/min (150 rpm) for all the above stages. Following the fouling test, the system was promptly and effectively cleaned by circulating a 15 mM NaCl solution through both the feed and draw sides for 30 min at a cross-flow velocity of 0.6 L/min (300 rpm). The water flux of the cleaned membrane was measured using the FO test, with DI water and 2 M NaCl as feed and draw solutions, respectively. The reduction ratio of the flux (FR%) and flux recovery ratio (FRR%) were calculated by Equations (3) and (4).

$$FR\% = \frac{J_{wo} - J_t}{J_{w0}} \times 100\%$$
(3)

$$FRR\% = \frac{J_c}{J_{wo}} *100\%$$
(4)

 J_{wo} : the initial flux; J_t : the flux after the accelerated fouling test, J_c : the final water flux after the physical cleaning stage.

$$FR\% - FRR\% = \left[\frac{J_c}{J_{wo}} - \left(\frac{J_{wo} - J_t}{J_{w0}}\right)\right] \times 100\%$$

FR% - FRR%; the improved water flux ratio after cleaning fouled membrane than the reduced ratio of the flux. FR% and FRR% were interpreted as normalised

water flux $\left[\frac{J_w}{J_{wo}}\right]$. Here J_w may be $|J_c|$ or $|J_{wo} - J_t|$.

3. Results and discussion

3.1. Characterisation of TFC and CTFN-*x membrane*

The IR and Raman spectroscopic analyses were conducted to elucidate the mechanistic interactions between TMC, MPD, and f-MWCNTs (Figure 1(A and B)). While the IR signatures of chemically modified membranes (CTFN-x) remained consistent across varying f-MWCNT content (Figure 1(A)), distinct bands suggested interactive mechanisms (Figure 2). During interfacial polymerisation (IP), -COOH on f-MWCNTs reacted with -CONH₂ on MPD, forming new amides and H-bonds [15] (Figure 2). This reaction was confirmed by new IR bands at 1240 and 691 cm⁻¹, representing amide II (C–N stretching and N-H in-plane vibrations). Upon TMC addition, interactions between -OH and -CONH₂ groups of f-MWCNTs and -COCI groups of TMC were evident from the IR band at 1100 cm⁻¹ [16] (Figure 1). Raman spectroscopy supported these findings, showing dominant bands at ~1150 cm⁻¹ (symmetric C–O-C stretching) and \sim 1590–1620 cm⁻¹ (phenyl ring vibrations[17]). Furthermore, characteristic IR bands at 1543 and 1660 cm⁻¹ corresponded to amide II and amide I, respectively, while the band at 557 cm⁻¹ indicated free C-Cl sites [18]. Notably, bands at 1478 and 1579 cm⁻¹ indicated enhanced aromaticity due to f-MWCNT incorporation [18].

The infrared (IR) bands around 870 cm⁻¹ signify aromatic C = C and C–H stretching[16]. Bands detected at



Figure 1. (A) FTIR spectra and (B) Raman of TFC and CTFN-x membranes.



Figure 2. The postulated mechanism for interfacial polymerisation of MPD, f-MWCNTs, and TMC. (Refer to Figure 1 for the details of IR spectrums and the Raman spectrum).

1010 and 1150 cm⁻¹ relate to C–O stretching in epoxy [19] and -O-H groups of f-MWCNTs[20], respectively. Raman analysis of f-MWCNT-modified thin film nanocomposite (TFN) membranes consistently reveals distinct bands at 1310 cm^{-1} (D band) and 1585 cm^{-1} (G band), confirming graphitic structures. However, the broadband at 1585 cm^{-1} suggests contributions from polysulfone phenyl rings and f- MWCNTs interactions.

Table 1. Raman intensity of 1150 and 1585 cm⁻¹ bands $\left(\frac{l_{1150}}{l_{150c}}\right)$.

					(-1303)
Wavenumber, cm ⁻¹	TFC	CTFN-1	CTFN-2	CTFN-4	CTFN-8
1150 1585	663.1 388.9	2086.2 1744.0	1304.1 956.4	1744.5 1126.6	559.4 626.1
$\left(\frac{I_{1150}}{I_{1585}}\right)$	1.7	1.2	1.4	1.5	0.8

The intensity of the 790 cm⁻¹ band, indicative of out-ofplane benzene ring C–H deformations, increases with f-MWCNT content in the TFN membrane. Additionally, Raman bands at 1110 cm⁻¹ and 1612 cm⁻¹ correspond to the C = C stretching vibration of the polyamide [21] and the amide I carbonyl stretch, respectively. These findings suggest that f-MWCNTs serve as a bridging structure during IP, potentially enhancing membrane water flux and IP efficiency through the formation of hydrophilic functional groups such as carboxyl and hydroxyls.

The interactive effects of f-MWCNTs with MPD and TMC were confirmed by the changes in $\left(\frac{l_{1150}}{l_{1585}}\right)$ intensity ratio [22]. A significant decrease in the $\left(\frac{l_{1150}}{l_{1585}}\right)$ ratio confirmed the successful binding of f-MWCNTs (0.001% (w/v))to the TMC and MPD membrane [23]. Then, the intensity value increase due to the -C-O-C- band formed between the polyamide and MWCNTs would be increased with the f-MWCNTs amount increasing. At 0.008% (w/v), the presence of excess f-MWCNTs with uneven distribution and agglomeration of f-MWCNTs may lead to decreased MPD and TMC cross-linking on the membrane surface. As a result, the $\left(\frac{l_{1150}}{l_{1585}}\right)$ ratio of the CTFN-8 membrane is reduced (Table 1).

3.2. Morphology and zeta potential of TFC and CTFN-x membrane

Cross-sectional of TFC and CTFN-x membranes substrate with different MWCNTs loadings were analyzed by SEM analysis in Figure 3. In the cross-sectional images, a typical asymmetric structure was observed (Figure 1-S). For the synthesis of the polyamide active layer on PSU, MPD and TMC were used (viz., TFC). As the SEM image of the TFC on the PSU substrate, the pore structures toward the TFC side of the support appear blocked due to the leaching of MPD and TMC sequentially used in active layer formation, resulting in a reduction of water flux. However, when f-MWCNTs are incorporated into the fabrication process of the TFC, this leaching phenomenon is significantly reduced, thus preserving the pore structure of the PSU support. However, the cross-sectional images of CTFN-1 show differential corrugated structures within PA active layers, whereas the bare TFC membrane exhibits voids. (Figure 3, CTFN-1) This observation is consistent in all cases where f-MWCNTs are used in TFN fabrication. The postulated mechanism of f-MWCNT mediation in the TFN formation process is also supported by IR spectroscopy evidence.

However, in the presence of f-MWCNTs-derived FO membranes, the water flux value was enhanced with desalinated water. Reducing the thickness of the PA layer is well known to represent a shorter water pathway, which is favourable for improving water permeability. (Figure 3) Water salination occurs largely due to the presence of major solutes in water. Therefore, f-MWCNTs derived FO membrane play a critical role in water desalination.

As shown in SEM and AFM images (Figure 4), the f-MWCNTs modified TFC membranes (e.g. CTFN-x) show enhanced surface homogeneity with low defect density with the increase of f-MWCNT loadings ratios ¹⁴. At a low f-MWCNT loading (0.001% (w/v)), the surface of the CTFN-1 membrane shows a leaf-like morphological structure by filling in the pores and gaps between the membrane matrix and the substrate (Figure 4). Thus, the surface roughness decreased due to the enhanced IP due to hydrogen bonding between the polyimide layer and the hydrophilic groups of the modified MWCNTs [5]. Further, the CTFN-4 membrane (0.004% (w/v)) shows an optimal value $(53 \pm 3 \text{ nm})$ corresponding to the smoothest surface. However, in some parts of the CTFN-4 membrane surface still, the nodular structures are shown thus inducing heterogeneity. When loading of f-MWCNT > 0.004% (w/v), superfluous f-MWCNT can exhibit readily agglomerates on the active layer of the membrane. In this context, the roughness value exhibits minimal variations. However, at high concentrations of f-MWCNTs increasing surface roughness due to enhanced ionic interactions and wrinkling from increased active hydroxyl groups. Often, the polyamide FO films (TMC and MPD composite) charged negatively due to -COO⁻ on the membrane surface [24]. When pH > 7.00, the epoxide and hydroxyl surface groups also dissociate yielding a negatively charged surface (Figure 4). Upon the addition of f-MWCNTs, the surface charge of the CTFN-x membranes increased towards a negative direction at a given pH due to the ubiquity of -OH groups [25] (Figure 4). The functionalised f-MWCNTs at the CTFN-4 membrane exhibit maximum interfacial polymerisation of MPD and TMC. As a result, the zeta potential shifts in the positive direction due to the lack of free negatively charged groups. Adding more f-MWCNTs increases the negative surface charge,



Figure 3. A schematic diagram of CTFN-x membrane. The fine structures of the SEM images are shown in dotted lines (however, unable to capture MWCNTs because of their low weight of $\leq 0.008\%$). The thickness of the PA layer is also shown.

confirming that excess f-MWCNTs are present at the CTFN-8 membrane.

3.3. FO performance of TFC and CTFN-x membranes

As shown in Figure 5(A), the contact angle values of the TFC and CTFN-x membranes have steadily decreased with the f-MWCNTs loading. The abundance of -OH on the membrane during the loading of f-MWCNTs increased its hydrophilic character, thereby improving the water flux [26]. As shown in AFM data, the degree of roughness of both CTFN-4 ($Ra = 53 \pm 3 \text{ nm}$) and CTFN-8 (Ra = 54 ± 4 nm) membrane surfaces are comparable. However, according to contact angle measurements, the water flux values of these two membranes are reversed which indicates that in the presence of f-MWCNT, preferential water passage routes are operational in addition to the pores on the membranes, e.g. CTFN-4 and CTFN-8 [27]. The bare TFC membrane had a permeate flux of 14 LMH, which nearly doubled with the use of CTFN-4 or CTFN-8 membranes in the experiments (29 LMH for CTFN-8 membrane). (Figure 5 (B))

The variation of salt flux (J_s) as a function of the f-MWCNT loading against 1M NaCl DS is also shown in Figure 5(B). As shown in the data the salt reject is increased by about 58%-fold with the MWCNT loading into the TFC membrane. The lowest salt flux (2.9 gMH) is observed for CTFN-8. The antifouling propensity of CTFN-x membranes was determined using feed solution-1 in a batch FO cell for 60 min text cycles. The normalised water flux, $\left(\frac{J_w}{J_{wo}}\right)$ values show a steady rise with the f-MWCNT content used in TFC. Compared to the TFC membrane, over fold increase in the $\left(\frac{J_w}{J_{wo}}\right)$ values was recorded in CTFN-8. (Figure 5(C)) This observation confirms that the antifouling properties of modified membranes are improved by the addition of f-MWCNTs compared to TFC. The CTFN-8 (98%) membrane exhibits the highest normalised flux after cleaning.

An additional experiment was arranged to determine the propensity of antifouling with FS-2 solution for 1080 min (18 hr). As shown in the data the flux values decline due to deposition of foulants onto the membrane as time proceeds. However, the highest normalised flux after membrane fouling is noticed for the



Figure 4. Images of SEM and AFM, and zeta potential/ ζ of TFC, i.e. CTFN-x, x = 1-8.

CTFN-8 (94%) membrane, which is much higher than for the bare TFC membrane (44%). The CTFN-4/8 membranes have higher restoration affinity compared to TFC membranes, which suggests that the bare TFC membranes are more affected by irreversible fouling. This observation indicates that the f-MWCNTs embedded membrane achieved a stable flux, which suggests that the adsorption and desorption of foulants to the membrane surface reached equilibrium over time, compared to the initial membrane.

It's essential to achieve a balance between high water flux and low solute flux in FO membranes for optimal performance. Research on TFN-FO membranes indicates that increasing CNT content (>0.01% (w/v)) correlates with higher water flux and reverse salt flux (Figure 6) [11,13]. Our findings suggest that MWCNTs (>0.004% (w/v)) contribute to nanochannel formation, both internally and externally. External nanochannels, particularly the interfacial gap between functionalised

CNTs and the polymer at the active layer interface, facilitate solvent transfer efficiently[11]. The permeate water flux is favoured via MWCNT canals, kinetically somehow rejecting major solutes due to the Donnan effect, an electrostatic interaction between the solutes and membrane. Thus, the Donnan effectbased molecular sieving contributes to the overall separation efficiency of FO membranes, optimising the rejection of negative ions and improving water purification processes [28]. A controlled flow of the feed solution in forward osmosis membranes reduces fouling propensity by minimising concentration polarisation and preventing the build-up of positive ions and foulants through shear forces [29], [30]. They also enhance membrane surface hydrophilicity, leading to increased water and decreased reverse salt fluxes. Moreover, a higher load of functionalised CNTs (≥ 0.01% (w/v)) within the membrane contradicts established FO process theories, potentially hindering



Figure 5. (A) Water contact angle, (B) water flux and reverse salt flux (C) The variation of flux over time for a fouling episode of TFC and CTFN-x membranes and (D) fouling test of TFC, CTFN-4 and CTFN-8 membranes 2 M NaCl solution as DS with a 10 min intervals during test time (1080 min).



Figure 6. Performance of TFN membrane in the literature and current work.



Figure 7. Parameters contributing to antifouling properties of the membranes: CTFN-x, x = 1-8.

membrane efficacy in FO applications, depending on the functional groups present.

The membrane surface properties such as surface roughness, and zeta potential have a marked impact in controlling surface antifouling (Figure 7) [31]. It is less likely that fouling will occur on surfaces with low roughness. The smooth membrane surfaces can readily be cleaned and remove fouling materials since there are no intricate features on the surface where foulants may accumulate. Thus, reducing roughness minimises fouling, improving fluid flow and energy efficiency. Also, hydrophilic nanomaterials tend to repel hydrophobic impurities on impregnated surfaces, preventing their attachment and reducing fouling by creating a hydrated layer on the membrane surface. The liquid spreads and distributes evenly on a surface with a lower contact angle due to the low surface roughness and high concentration of hydroxyl groups. As a result, droplets are prevented from forming or localised dry areas, where fouling can occur. Reducing the contact angle and increasing wetting properties may promote the self-cleaning effect, where foulants are easily washed away with water or other cleaning agents due to constant flow of feed solution [32].

By maintaining smooth and negative charge hydrophilic membranes can be protected against fouling over long periods (Figure 5(D)). The f-MWCNTs embedded TFC membrane attains stable water flux which implies equilibrium of adsorption and desorption of the foulants to the membrane surface over a lengthy period compared to the initial membrane. These nanotubes have a direct effect on improving the surface morphology of the FO membrane and individually improve the antifouling properties and water permeability.

4. Conclusions

Our findings reveal that an optimal concentration of hydroxyl-functionalised multiwall carbon nanotubes (f-MWCNTs) in thin-film composite (TFN) membranes significantly enhances permeate flux and antifouling propensity in forward osmosis (FO) membranes. Adjustments in surface roughness improve hydrophilicity, and f-MWCNTs reduce active layer thickness via crosslinking. Molecular spectral analysis elucidates bonding mechanisms between f-MWCNTs, MPD, and TFC. These f-MWCNTs introduce additional permeate pathways and contribute to the charge-based separation of solutes through the Donnan effect-based molecular sieving. Our research highlights the potential of tuneable f-MWCNT mass loading in TFN membranes for improved FO desalination. Research into molecular dynamics simulations is also underway to elucidate water permeation in the presence of solutes through high-diameter (>1.1 nm) f-MWCNTs. These simulations focus on charge-based molecular filtering and hydrogen bond transfer mechanisms.

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Disclosure statement

No potential conflict of interest was reported by the author(s).

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Data availability

Additional data is available as support documentation. The other information not included in the support documentation can be provided upon requisition.

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