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Graphical Abstract

Research Highlights

- Multi-wall carbon nanotubes (MWCNTs) membrane was tested for seawater pretreatment
- MWCNTs membrane showed a high permeate flux with organic reduction in seawater filtration
- MWCNTs membrane can contribute to lessening the sludge volume in pretreatment.
- Ionic strength significantly affected organic removal efficiency in seawater filtration.

Performance evaluation of carbon nanotube enhanced membranes for SWRO pretreatment application

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Abstract

Multi-wall carbon nanotube (MWCNT) membrane was tested for SWRO pretreatment. The MWCNT membrane itself showed a superior permeate flux (321.3 LMH/bar), which was 4-times as polyethersulfone ultrafiltration (PES-UF) membrane. Reduction of dissolved organic matter improved to 66% with fewer amounts of powder activated carbon (PAC) (0.5 g/L) in MWCNT membrane filtration maintaining a high permeate flux of 600 LMH/bar. It was due to the increased porosity (84.5%) and hydrophilicity (52.9°) by incorporating MWCNT/Polyaniline into PES membrane. Ionic strength affected organic removal in seawater filtration by altering electrostatic interaction between organic matter and surface charge of the positively charged MWCNT membrane.

Keywords: Adsorption; Carbon nanotube membrane; Seawater organic matter; Seawater pretreatment; Ultrafiltration

Abbreviations

BSA: Bovine serum albumin; DOC: Dissolved organic carbon; DOM: Dissolved organic matter; EPS: Extracellular polymeric substances; HA: Humic acid; HS: Humic substances; LC-OCD: Liquid chromatography–organic carbon detection; LMW-DOMs: Low molecular weight dissolved organic matters; MF: Microfiltration; MWCNTs: Multi-wall carbon nanotubes; NOM: Natural organic matter; PAC: Powder activated carbon; PANI: Polyaniline; PES: Polyethersulfone; SEC: Size exclusion chromatography; SWOM: Seawater organic matter; SWRO: Seawater reverse osmosis; UF: Ultrafiltration; UPW: Ultrapure water; UVD: Ultraviolet detector

1. Introduction

Seawater reverse osmosis (SWRO) desalination technology requires an effective pretreatment to inhibit the decline in performance with irreversible fouling on the membrane and degradation by frequent cleaning [1, 2]. Such a drawback is caused by the poor qualities of seawater (feed water) in RO desalination plants. Seawater organic matters include extracellular polymeric substances (EPS) or biopolymers, humics, fulvic acids, carboxylic acid and other low molecular weight dissolved organic matters (LMW-DOMs). Of these substances, colloidal matters in the 3 – 20 nm range such as humic substances and biopolymers are the main membrane foulant adsorbed on the membrane surface or in the membrane pores. In most cases, LMW-DOMs forming in seawater organic matter (SWOM) account for 50% of such matter. Organic foulants are the precursor to biological growth which then accelerates biofouling on the membrane. Low-pressure membranes such as microfiltration (MF) and ultrafiltration (UF) can serve as an option for seawater pretreatment because they can remove particulate, bacteria and large molecular weight organic matter. However, direct MF/UF filtration can overpass the technical

limits of the process, resulting in RO membrane fouling [3]. In particular, a low-pressure membrane with a cut-off higher than 100 kDa could not remove LMW-DOMs (less than 350 Da) which can accelerate biofouling on RO membranes [4].

A solution to improve the MF/UF membrane system's organic removal performance is to integrate physico-chemical processes such as adsorption or coagulation/flocculation [5, 6]. It has been documented in previous studies that ferric chloride (FeCl_3) as a coagulant forms flocs with organic matter by co-precipitation [7, 8]. Such a coagulation/precipitation system in seawater pretreatment has shown to be effective in total DOM removal. Basically, however, it cannot remove LMW-DOMs in seawater. Recently, to overcome the limitations of the physico-chemical process with a low-pressure membrane, one particular membrane hybrid system coupled with adsorption (with the addition of powder activated carbon, PAC) has demonstrated enhanced performance in removing LMW-DOMs containing around half the amount of SWOM [9]. PAC (as an adsorbent) adsorbed organic matter by covalence bonding [10], and removed LMW-DOMs with its affinity to them and by biological activity of microbial community developed [11].

Even though such an enhanced DOM removal outcome was achieved by the membrane hybrid system in seawater pretreatment, a large amount of chemical sludge was generated due to employing a relatively high amount of adsorbent. In this sense, an approach to reducing chemical dosage must be investigated, and it is desirable to develop membrane with higher water flux and the anti-biofouling effect for sustainable pretreatment in SWRO.

Recently, there have been many attempts to enhance UF membrane performance by incorporating nanomaterials. Of these nanomaterials, carbon nanotubes (CNTs) constitutes a favored approach due to their unique characteristic of excellent adsorption capacity for organic matter [12]. In particular, the introduction of functionalized CNTs to the polymeric UF membrane has contributed in delivering

increased permeate flux by changing the membrane's surface hydrophilicity [13-16], improved rejection of bovine serum albumin (BSA) and alleviated membrane fouling [17-21]. Although developing the CNTs membrane has generated certain benefits for water treatment, only a few research papers have been published on its application to seawater pretreatment for removing DOM. Therefore, a feasibility study of CNT membrane in seawater pretreatment for effective removal of LMW-DOMs would greatly assist in solving the current limitation of the membrane system for seawater pretreatment. Based on the recent progress made in nanocomposite membrane in water treatment, development of the membrane having an enhanced adsorption capacity will contribute to lowering chemical dose, resulting in the less sludge volume.

Seawater contains high concentrations of ions, and this ionic strength has been recognized as seriously compromising DOM removal and fouling potential in membrane operation [22, 23]. For this reason, an in-depth study on the effect of ionic strength on membrane performance would contribute to the successful application of CNTs membrane to SWRO pretreatment.

In this study, the multi-wall carbon nanotube (MWCNT) membrane was fabricated by incorporating MWCNT/PANI complex by *in-situ* polymerization, since it was previously reported that the membrane exhibited high water flux and effective natural organic matter (NOM) removal [24]. The aims of this study were as follows. Firstly, to test the MWCNT membrane in the seawater pretreatment with reducing adsorbent dose by employing the MWCNT membrane with enhanced adsorption capacity of SWOM. In particular, the objective was to improve rejection efficiency of LMW-DOMs with high permeate flux in MWCNT membrane filtration compared to the conventional UF membrane. Secondly, the effect of ion strength on organic removal and performance in the MWCNT membrane filtration was examined. Thirdly, the effects of salinity and ion strength on the organic rejection efficiency and permeate flux were investigated in MWCNT membrane system.

2. Experimental

2.1 Materials

Seawater was taken from Chowder Bay, Sydney in Australia. It was pumped from 1 m below the sea surface level and filtered through a centrifuge filtration system (140 μm) to remove large particles.

Turbidity and pH of seawater used in this study were 0.5-0.7 NTU and 7.8-8.0, respectively. Hydroxylated MWCNT was supplied by BuckyUSA. The CNTs have the following properties: 5-15 nm of diameter, 1-5 μm of length and 98-wt% of purity.

MWCNT membrane was prepared by two steps - firstly, synthesis of 1.5 wt% MWCNT/ 50 wt% Polyaniline (PANI) complex by *in-situ* polymerization; and secondly, fabrication of MWCNT/PANI/PES membrane (MWCNT/PANI to PES). The first step was making the MWCNTs/PANI complex by chemical oxidation. A solution of 3 mM aniline monomer and 0.8 mM APS was prepared in 1 M HCl and 99.5% NMP. MWCNTs were dispersed in 99.5% NMP solution by sonication (500 W) for one hour. Three substances (i.e., aniline, APS and MWCNTs) were mixed in a 100 mL glass vessel and stirred for 48 hour at 4 °C. The second step was the production of the MWCNT/PANI/PES membrane by the phase inversion method. Here, MWCNTs/PANI/PES membrane is referred as to the MWCNT membrane. The fabrication procedure of MWCNT membrane is explained in detail in our previous paper [24]. PES membrane was used as a control in this study. 15 % of PES was dissolved in N-methyl pyrrolidone (NMP) for 7 hour. It was then kept at room temperature for 1 d to remove air bubbles from the casting solution. Once casting solution was prepared, it was cast onto a glass plate with 300 μm gap height. The glass plate was immersed in deionized (DI) water at room temperature. All membranes were stored in DI water prior to use.

Characteristics of membranes used in this study are given in **Table 1**[24] .

Coal-based PAC (MDW3545CB, James Cumming & Sons Pty Ltd) was used as an adsorbent in this study. The mean diameter and the nominal size (80 % min. finer than) of PAC were 19.7 μm and 75.0 μm , respectively. More details of PAC can be found in elsewhere [6] .

2.2 Membrane filtration test

The performances of PES (a laboratory-prepared UF membrane) and MWCNT membrane were evaluated in the membrane system with adsorption (i.e. PAC addition). For the membrane system with PAC adsorption, PAC (0.5 – 1.5 g/L based on feedwater volume) was added to seawater in the adsorption system. Then, pretreated seawater was underwent membrane filtration. Membrane filtration without adsorption pretreatment (PAC=0g/L) was also conducted to evaluate the performance of membrane filtration system itself. Membrane filtration was done in dead-end mode under 200 kPa with 0.00146 m^2 of effective membrane area. 1L of seawater was filtered, and permeability was monitored during this time.

2.3 Dissolved organic matter measurement

Dissolved organic concentration (DOC) and the detailed organic fractions in feed/permeate were measured by liquid chromatography–organic carbon detection (LC-OCD) [25]. Hydrophilic organic fractions were separated into each fragment depending on their molecular size by the retention time in the size exclusion chromatography (SEC) column. Dual columns were applied in this study with 180 min retention time. Two different detectors (an ultraviolet detector (UVD) (absorption at 254 nm) and an organic carbon detector (OCD) (after inorganic carbon purging)) were utilized to measure the concentration of separated hydrophilic organic compounds. The eluted order of each fragment was biopolymers – humic substances/building blocks – LMW organics (acids and neutrals). The amount of each organic fraction was calculated using a software program (ChromCALC DOC-LABOR, Karlsruhe,

Germany) based on the chromatogram obtained from LC-OCD analysis. A previous study has detailed the relevant procedure [26].

Removal efficiency (%) of organic matter was calculated by the following equation:

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100$$

Where, C_f is the concentration ($\mu\text{g/L}$) of feed water and, C_p is the concentration ($\mu\text{g/L}$) of permeate (or membrane filtrate) from the membrane filtration system with PAC adsorption or membrane filtration itself.

2.4 Surface charge of membrane

The surface charge (in terms of zeta potential, mV) of the membrane surface was measured using the streaming potential technique (Anton Paar Electrokinetic Analyzer, USA). The measurement was conducted at different ionic strengths ranging between 0.001 and 0.010 M of KCl and pH 7.8.

2.5 Fouled membrane characterization

After filtering 1L of feed water (684.9 L/m^2 of seawater with or without PAC adsorption), membrane samples were taken and dried for 24h prior to analysis.

The morphology and chemical compositions of fouled membranes were observed using scanning electron microscopy with an energy dispersive X-ray spectrometry (SEM-EDX, Zeiss Ultra, Germany). For SEM-EDX analysis, membranes then were then coated with a thin layer of gold. The contact angle was established to measure the membrane hydrophilicity using 4 – 8 μL sessile droplets of Milli-Q water with a Krüss Easy Drop goniometer (Germany).

3. Results and discussion

3.1 Seawater filtration performance (without PAC addition)

3.1.1 Permeate flux

Fig. 1 shows the permeability (permeate flux) pattern of MWCNT and PES-UF membrane in UPW and seawater filtration. The MWCNT membrane shows significantly increased UPW permeability (initial permeate flux was 1298.4 L/m²-h-bar (LMH/bar)) while initial permeate flux of the PES-UF membrane was 66.2 LMH/bar. In seawater filtration, a substantial decline in permeate flux was observed with the MWCNT membrane. The initial permeate flux was 321.3 LMH/bar, which was almost 4 times lower compared to UPW permeability. However, there was no significant change in permeate flux in seawater filtration by PES-UF membrane. Interestingly, UPW permeate flux in the PES-UF membrane was lower than that of seawater. Such lower UPW flux could be due to the enlarged pore size by salinity. Thus, slightly higher initial permeate flux was observed in this case.

Superior performance of the MWCNT membrane is mainly due to the change of physico-chemical properties of the membranes by MWCNT/PANI complex [24]. As reported in our previous study [24], the insertion of MWCNT/PANI complex to the PES polymer matrix completely overcame CNT aggregation. On the other hand, the simply blended CNTs did not enhance the membrane performance due to the CNT aggregation. In the previous study [24], the dispersity of MWCNT was evaluated through the measurement of UV absorbance at a wave length of 295 nm probably. This is due to the π - π transition on the benzoid and quinoid excitation bands in MWCNT/PANI complex [27-29]. Dispersed MWCNT/PANI in NMP was compared with dispersed MWCNTs in NMP in order to see the effect of MWCNT/PANI complex on the dispersion of MWCNT. The UV absorbance of MWCNT dispersed in NMP significantly decreased in 1 h. On the other hand, the absorbance of the MWCNT/PANI dispersed in NMP was constant over 10 h.

Further, it increased membrane porosity (from 78.0 to 84.5 %) via pore former role of PANI during the phase inversion process. More hydrophilic and higher viscous MWCNT/PANI complex to the PES casting solution delayed the solvent (NMP) diffusion from non-solvent (water) bath during the mixing-demixing process [30, 31]. Thus, it led to form narrow pore size on the top layer and relatively large micro pores in the sub-layer, showing well-developed finger-like structure.

In addition, the membrane hydrophilicity also increased (in terms of contact angle, from 67.4° to 52.9°) as the MWCNT concentration increased up to 2-wt %. The improved membrane structure and synergetic effect of hydrophilicity and porosity contributed to the higher permeate flux of the MWCNT membrane than that of the PES-UF membrane.

3.1.2 Organic reduction

5 mg/L of humic acid (HA) was dissolved in UPW, and it was firstly tested with two membranes. Especially, as shown in **Table 2**, HA removal by MWCNT membrane was high (82±4%) in synthetic HA filtration. However, in seawater filtration, the removal of HS was only 2.62 - 4.62% by both membranes, even though HS concentration in seawater was only 0.496±0.012 mg/L (**Table 2**). The organic removal mechanism in the MWCNT membrane is explained in terms of the electrostatic interaction between the positively charged membrane surface and the negatively charged organic matter [24]. MWCNT/PANI complex altered the surface charge of the membrane to \positive. Doping process during MWCNT/PANI complex synthesis transformed a polymer to its conductive form via chemical oxidation [32-34]. Consequently, a positively charged MWCNT/PANI complex changed a negatively charged PES polymer to a positively charged one.

3.2 Effect of PAC addition

Fig. 2 shows the permeability patterns in seawater filtration (before and after PAC adsorption) of MWCNT and PES-UF membranes. When raw seawater was filtered, the initial permeability of the

MWCNT membrane was 300 LMH/bar. Interestingly, when PAC adsorption coupled, its permeability increased up to 600 LMH/bar. However, more rapid flux decline occurred in MWCNT membrane filtration. This was probably due to more organic adsorption on the membrane surface by electrostatic interaction at the initial stage of filtration with higher organic loading by high permeate flux. When the lower dosage of PAC decreased to 0.5 g/L, the permeability of MWCNT membrane was still maintained at a high value, and there was no significant decline. However, no change in the flux pattern was observed on the PES membrane no matter how PAC was incorporated.

The removal efficiencies of the organic fraction by the MWCNT membrane coupled with or without PAC adsorption summarized given in **Table 3**. PES-UF membrane itself removed only 13% of DOC from raw seawater with 60% of the biopolymers' removal efficiency. DOC reduction by the MWCNT membrane (26%) was slightly higher than PES-UF membrane.

PAC demonstrated a high removal efficiency of hydrophilic organics, especially biopolymers and humic substances (high molecular weight organics). However, the removal of LMW neutrals was marginal. For example, around 50% of DOC was removed by 1.5 g/L of PAC. This is mainly due to the significant reduction of biopolymers and humic substances, which were 87% and 48%, respectively. Reduced PAC dose (0.5g/L) lowered DOC removal efficiency to 37%.

PES-UF membrane filtration with PAC adsorption increased DOC removal efficiency to 53% compared to PAC adsorption only (49%). In addition, DOC removal efficiency of MWCNT membrane filtration significantly increased to more than 60%, when it was corporated with PAC adsorption (1.5g/L). In particular, the removal of LMW neutrals in MWCNT membrane filtration increased by PAC adsorption from 8% to 34% (without PAC adsorption). It should be noted, however, that there was a small reduction of LMW neutrals by either the MWCNT membrane itself or PAC adsorption itself. Moreover, DOC removal of MWCNT membrane, even though low PAC dose was used (0.5g/L), was comparable

to that of PES-UF membrane filtration with 1.5g/L of PAC. This indicates that the MWCNT membrane had effective hydrophilic DOC removal efficiency when PAC adsorption was coupled.

The poor HS removal efficiency in the MWCNT membrane filtration could be explained by its reduced adsorption capacity in feed water with high ionic strength. In previous research, the NOM removal mechanism by MWCNT membrane was found to be a greatly enhanced electrostatic interaction between a humic acid (HA) and positively charged MWCNT membrane. However, ionic strength in seawater may probably weaken the surface charge of both the membrane and humic substances. Negatively charged humic substances form metal ion-humic precipitation and aggregation in seawater with reducing surface charge of HA [35]. It may, therefore, reduce the affinity of the MWCNT membrane to the humic substances by reducing electrostatic interaction between HA (negatively-charged) and MWCNTs enhanced membrane (positively-charged). This is consistent with previous research done by Jermann et al. [36]. They reported that metal ions neutralize the negatively charged foulants and the charge on the membrane. Furthermore, salinity could weaken the surface charge of the membrane. It will be discussed in the section 3.4.1 *via* zeta potential measurement of the membrane under different ionic strengths as well as reduced electrostatic interaction between humic substances and MWCNT membrane, insufficient contact time may be considered as the main reason for low humic substances removal efficiency. Due to the rapid permeate flux, MWCNT membrane system had only a short time to adsorb humic substances. On the basis that the removal mechanism of the MWCNT membrane is the enhanced adsorption by electrostatic interaction, contact time may also be a critical factor in removing LMW organic matter with reduced surface charge by salty water. Consequently, organics easily pass through the MWCNT membrane due to the fast permeate flux.

Consequently, the MWCNT membrane-PAC adsorption system exhibited 60-66 % DOC removal, and led to a very high flux of 600 LMH/bar without permeate flux decline even when PAC dosage decreased

from 1.5 to 0.5 g/L. Compared to the previous study of UF-PAC system with 60–70 % DOC rejection and relatively low UPW permeability (220 – 230 LMH/bar) [9], the MWCNT membrane-PAC system exhibited superior permeate flux with the same removal efficiency. Recently published UF-GAC system for SWRO also exhibited nearly 70 % of DOC removal, while only 20 % of DOC could be removed by 50 kDa UF membrane (400 LMH/bar) [37]. In comparison, the MWCNT membrane-PAC system exhibited the comparable DOC removal (up to 66 %), and MWCNT membrane itself showed a superior organic removal efficiency (36 %) with delivering much higher water permeability (1400 LMH/bar).

3.3 Effect of salinity and divalent cation on HA rejection

In the previous section, poor efficiency in removing humic substances was observed in seawater filtration where high salinity water samples were treated. To examine the effect of salinity on humic acid (HA) rejection, membrane filtration was conducted with 5mg/L of HA under different NaCl concentrations. Further, the effect of ionic strength on membrane performance in HA rejection test was investigated in the presence of divalent cation (CaCl_2). **Fig. 3** and **4** depict the permeate flux and HA removal under different NaCl concentrations, respectively. Overall, salinity significantly contributed to the enhanced permeability and reduced HA removal efficiency in the MWCNT membrane. In contrast, PES-UF membrane performance was marginally affected by monovalent ion strength (NaCl).

As can be seen from **Fig. 3**, permeate flux increased by 40 % when 0.01 M of NaCl was present with 0.5mg/L of HA compared to 5mg/L of HA without NaCl. Permeate flux decline at the initial stage (30 min) was overcome when NaCl increased to 0.1 M, revealing virtually the same permeability as the one under 0.01 M NaCl. By contrast, HA removal efficiency was shown to reduce considerably under increasing concentration of ionic strength (**Fig. 4**). Especially at the final stage, it decreased sharply (80 % to 30 %) as ionic strength increased. Such a result demonstrates that adsorption capacity of the MWCNT membrane reduced under higher concentration, and increasing concentration accelerated to

reach HA adsorption capacity. It may appear due to the reduced electrostatic interaction between negatively charged humic substances and positively charged membrane surface. As ionic strength increases to 0.1 M, it may weaken the surface charge of humic substances by forming a double layer of humic substances. Such an outcome can be interpreted to contribute to the flux enhancement by hindering adsorption of HA from the membrane surface, compared to the HA 5 ppm filtration without NaCl.

Divalent ion (CaCl_2) mostly affected to significantly reduced permeability in the MWCNTs and PES-UF membranes. In contrast, the addition of CaCl_2 considerably enhanced HA removal efficiency in these two membranes. Permeate flux behavior and HA rejection efficiency under divalent cationic strength (CaCl_2) is presented in **Fig. 5**. Severe flux decline was observed in the MWCNT membrane after 660 min filtration, in comparison to the flux under monovalent ionic strength (NaCl). The PES membrane also exhibited much lower flux behavior (7.4 LMH/bar) at the initial stage. The removal rate of the MWCNT membrane at the initial stage increased by 12%, and no drop was observed during whole filtration period (filtered volume = 684.9 L/m²), compared that there was a sharp decrease in HA removal efficiency under increasing NaCl concentration by approximately 50 %. The enhanced HA removal efficiency is largely due to the increased HA aggregation under divalent cation such as Ca^{2+} . It may establish a compact network between HA by neutralizing negative charge on HA under around pH 6, resulting in larger size of HA. Even if the surface charge of MWCNTs enhanced membrane was weakened by salt ions, the synergetic effect of Ca^{2+} was able to contribute to the enhanced HA removal [38].

The synergetic effect of CaCl_2 mostly contributed to the PES-UF membrane, which was shown to have poor HA removal efficiency. PES-UF membrane exhibited higher removal efficiency (87 %) over the whole period. The notable thing is its removal rate increased by final stage. It appeared probably due to

the fact that divalent cation increases HA aggregation by cross-linking of HA, which accelerated adsorption of humic acid on the membrane. In addition to the enhanced adsorption by the larger size of HA, Ca ion has a bridge between HA adsorbed on the membrane surface and the one in feed water by reducing repulsion force among HA. Thus, a relatively lower removal rate was observed at the initial stage (100 mL filtration), and increased at the final stage. Furthermore, sufficient HA adsorption contact time due to the severe flux decline caused by CaCl_2 combining with HA led to increased HA rejection efficiency in the PES-UF membrane.

3.4 Factors affecting membrane performance

3.4.1 Surface charge of membrane under different ionic strength – organic removal

According to the previous study, the surface charge of the membrane was found to be the most critical factor of organic matter removal by membrane [24]. The surface charges of the membranes depending on ionic strength (under a different background electrolyte, KCl) were examined in order to verify the effects of ionic strength on membrane performance. **Fig. 6** shows that zeta potential of the MWCNT and PES-UF membrane under different KCl concentrations at pH 7.8. Zeta potentials of the MWCNT and PES-UF membrane at 0.001M of KCl were 9.8 and -21.0 mV, respectively. It indicates the MWCNT membrane charged positively while PES-UF membrane had negatively charged surface. Zeta potential of the MWCNT membrane significantly decreased when KCl concentration increased from 0.001 to 0.010 M. However, there was not a significant decline in zeta potential in the PES-UF membrane in spite of increasing KCl concentration. It indicates that the positively charged MWCNT membrane is more strongly influenced by ionic strength, in comparison to the negatively charged PES-UF membrane. Based on the results, it implies that organic matter removal efficiency of the MWCNT membrane could be lowered by increased ionic strength. This may be due to the weakened electrostatic interaction between membrane surfaces and mostly negatively charged SWOM such as humic substances.

Based on the zeta potential trend as a function of KCl (electrolyte) concentration as shown in **Fig. 6**, it is assumed that the MWCNT membrane would be neutrally charged at around 0.1 M ionic strength. Such trend in permeate flux at different ionic strength is presented in **Fig. 3 (a)**. Overall, an increase in NaCl concentration decreased permeate flux. The permeate flux decreased from 250 LMH/bar to around 150 LMH/bar as NaCl concentration increased from 0.01 M to 0.1 M.

3.4.2 Chemical precipitation on membrane – filtration behavior

SEM-EDS analysis on the fouled membranes surface was performed to observe the morphology of membrane surface and chemical precipitation (elements). **Fig. 7** presents SEM images and EDS results of each membrane surface (a: MWCNT membrane and b: PES-UF membrane) before and after seawater filtration tests. Both virgin membranes (before filtration) mainly consisted of carbon (C), oxygen (O) and sulfur (S) since they were fabricated based on PES. As expected, organic/inorganic foulants oriented from seawater (or PAC) were observed on the fouled membranes with/without PAC adsorption. As shown in **Fig. 7**, some crystals were found on the surface of fouled membranes. The main components of the crystals were carbon (C) and oxygen (O) as the components of foulants by organic matter [9]. Sodium (Na), chloride (Cl) and magnesium (Mg) were found to be other components of these crystals, which are the main constituents of seawater. More crystals binding with organic contaminants were observed on the surface of the MWCNT membrane than the PES-UF membrane. In particular, the proportion of inorganic foulants such as Na (7.85 %), Cl (15.53 %), S (6.14 %), Fe (5.79 %) and Mg (2.23 %) was shown to increase in crystal form when PAC adsorption was used, compared that only Na (3.40 %) and Cl (9.93 %) were detected on the surface MWCNT membrane filtered with raw seawater (without PAC adsorption). This result explains flux behaviors in the MWCNT membrane filtration coupled with PAC adsorption. Deposition of accelerating crystallization on the surface of the membrane may cause rapid flux decline in the MWCNT membrane filtration with higher organic removal

efficiency (due to more bonding with organics) despite the improved permeate flux compared the MWCNT membrane alone. In contrast, there was no increase of crystal bonded with organic foulants on the PES-UF membrane after PAC adsorption was integrated. It may be due to the fact that crystallization occurs in the interactions between crystals containing humic substances and salts, and membrane surface [10]. Due to the bridging effect of hydrophilic organic contaminants on salt and positively charged membrane surface, more crystallization deposited on the more hydrophilic surface of the MWCNT membrane, compared to the less hydrophilic PES-UF membrane.

3.4.3 Membrane hydrophilicity (water contact angle)

Hydrophilicity of fouled membranes was measured in terms of water contact angle. **Table 4** shows contact angle of the fouled membrane before and after filtering of 684.9 L/m² of seawater samples (untreated and PAC treated). As can be seen from **Table 4**, the MWCNT membrane has more hydrophobic membrane surface. After filtration of 684.9 L/m² of raw seawater, contact angles of the PES-UF and MWCNT membranes decreased from 57.6±0.4° to 53.9±1.9° and from 45.4±0.1° to 42.7±2.6°, respectively. It indicates that the membrane surface became to be more hydrophilic than the virgin membranes. It may be due to the adsorption of hydrophilic contaminants in seawater onto the membrane surface. Such a result may occur due to the fact that organic matter in seawater forms ion-humic precipitation and agglomeration by the interaction between salt ions and negatively charged organic matters [35]. Such precipitates are adsorbed onto the membrane surface during the filtration test, resulting in contact angle increase of the fouled membrane. However, an interesting trend on contact angle was observed on the MWCNT membrane when it was filtered the PAC treated seawater. However, when pretreated seawater with PAC adsorption was used in the MWCNT membrane filtration, contact angle increased slightly to 45.9±2.1°, indicating that hydrophilic organic compounds were removed by PAC adsorption. It is the fact that SWOM contains mostly hydrophilic organic compounds,

which were effectively removed by PAC. However, regarding the PES-UF membrane, no significant change occurred in contact angle when PAC adsorption was incorporated into the process. SEM-EDX observation confirmed it, indicating there was no significant crystallization formation on the PES-UF membrane even though PAC adsorption was coupled.

4. Conclusion

This study evaluated the MWCNT enhanced UF membrane in the respect of improving conventional low pressure driven membrane process for SWRO pretreatment. The results show that MWCNT membrane can be an alternative SWRO pretreatment option. The MWCNT membrane exhibited greatly enhanced permeate flux when PAC adsorption was coupled, compared to the PES-UF membrane. This is mainly due to the increased porosity, hydrophilicity and finger-like structure having narrow pore size on top and relatively large micro-pores on the sub-layer. No declines in permeate flux and removal efficiency occurred even when PAC dosage decreased from 1.5 g/L to 0.5 g/L, which can substantially contribute to reducing sludge volume generated from SWRO pretreatment by reducing chemical usage. The salinity was found to affect mainly greatly enhanced permeate flux. It also contributed considerably to reducing organic matter removal efficiency. The effect on the organic matter removal efficiency in MWCNT membrane could most probably be due to the significantly reduced electrostatic interaction between positively charged membrane surface and negatively charged SWOM.

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List of Tables

Table 1 Characteristics of the membranes used in this study.

Table 2 Removal efficiencies of HS in seawater and 5 mg/L of HA in UPW by MWCNT and PES-UF membrane filtration (HS and HA concentrations were measured using LC-OCD and TOC analyzer, respectively).

Table 3 Concentration and removal efficiency (R) of organic fractions by MWCNT and PES-UF membranes with and without PAC adsorption.

Table 4 Changes in water contact angle of membrane before and after filtration (filtered volume = 684.9 L/m²).

Table 1 Characteristics of the membranes used in this study.

Membranes	UPW [*] permeability (LMH/bar)	Pore size by BET ^{**} (nm)	MWCO ^{***} (kDa)	Contact angle (°)	Zeta potential ^{****} (mV)
MWCNTs	1272 ± 103.8	5.0 ± 0.4	12	45.4 ± 0.1	9.8
PES	60 ± 4.3	4.6 ± 0.3		57.6 ± 0.4	-21

^{*}: UPW: Ultrapure water, ^{**}: Pore size was measured using N₂ adsorption/desorption at 77K (Micromeritics), and calculated by the Brunauer–Emmett–Teller (BET) method. ^{***}: MWCO: Molecular weight cut-off, ^{****}: Zeta potential was measured at pH 5.6 at a background electrolyte of 0.001M KCl.

Table 2 Removal efficiencies of HS in seawater and 5 mg/L of HA in UPW by MWCNT and PES-UF membrane filtration (HS and HA concentrations were measured using LC-OCD and TOC analyzer, respectively).

	HS in seawater (mg/L)	HS in permeate (mg/L)	R* (%)	HA in UPW (mg/L)	HA in permeate (mg/L)	R* (%)
MWCNTs	0.496±0.012	0.473±0.020	4.64±0.40	5.0±0.1	0.9±0.2	82±4
PES-UF		0.483±0.011	2.62±0.22		3.1±0.3	38±6
*R:	removal					efficiency

Table 3 Concentration and removal efficiency (R) of organic fractions by MWCNT and PES-UF membranes with and without PAC adsorption.

Membrane/treatment types		DOC	Hydrophilic DOC	Bio-polymers	Humic substances	Building blocks	LMW Neutrals	LMW acids
Raw seawater	(µg/L)	1,300	1,027	179	496	36	250	65
PAC1.5	(µg/L)	658	529	24	256	2	241	6
	R (%)	49	48	87	48	94	4	91
PAC0.5	(µg/L)	825	669	52	364	4	242	7
	R (%)	37	35	71	27	89	3	89
PES-UF	(µg/L)	1,135	894	71	483	35	246	59
	R (%)	13	13	60	3	3	2	9
PES-UF-	(µg/L)	607	474	16	204	19	233	2
PAC1.5	R (%)	53	54	91	59	47	7	97
MWCNTs	(µg/L)	968	767	21	473	29	229	15
	R (%)	26	25	88	5	19	8	77
MWCNTs	(µg/L)	439	386	14	193	8	165	6
-PAC1.5	R (%)	66	62	92	61	78	34	91
MWCNTs	(µg/L)	529	452	14	226	16	189	7
-PAC0.5	R (%)	59	56	92	54	56	24	89

Table 4 Changes in water contact angle of membrane before and after filtration (filtered volume = 684.9 L/m²).

	PES-UF membrane	MWCNTs enhanced membrane
	(°)	(°)
Virgin	57.6 ± 0.4	45.4 ± 0.1
Filtration of raw seawater	53.9 ± 1.9	42.7 ± 2.6
Filtration of 1.5 g/L PAC treated seawater	54.8 ± 3.2	45.9 ± 2.1

List of Figures

Fig. 1 Permeability pattern of MWCNTs and PES-UF membranes in UPW and seawater filtration.

Fig. 2 Permeability decline pattern in MWCNTs and PES membrane filtration of seawater with different PAC doses.

Fig. 3 Permeability of membranes with HA 5mg/L (ppm) under different NaCl concentrations.

Fig. 1 HA rejection (%) of membranes with HA 5mg/L (ppm) under different NaCl concentrations.

Fig. 5 Permeability and HA rejection (%) of membranes with HA 5 ppm under 0.01M of CaCl_2 .

Fig. 6 Zeta potential of membranes under different ionic strengths by streaming potential at pH 7.8 and different KCl (background electrolyte) concentrations (0.001, 0.005 and 0.010 M).

Fig. 7 SEM images and elements of the membrane surface using EDS analysis before and after seawater filtration (Filtered volume = 684.9 L/m^2): (a) MWCNT membrane, and (b) PES membrane.

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(a) Virgin

Raw seawater

PAC 1.5g/L
treated seawater

(b) Virgin

Raw seawater

PAC 1.5g/L
treated seawater

Fig. 7 SEM images and elements of the membrane surface by EDS analysis before and after seawater filtration (Filtered volume = 684.9 L/m²): (a) MWCNT membrane, and (b) PES membrane.