

## Research Article

# Synthesis, Characterization, and Evaluation of Evaporated Casting MWCNT/Chitosan Composite Membranes for Water Desalination

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Received 6 November 2019; Accepted 30 December 2019; Published 22 January 2020

Guest Editor: Hassan M. A. Hassan

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Fresh water scarcity and pollution turn out to be a most serious issue throughout the world due to the rapid population growth. The application of nanomaterials (NMs) for the removal of pollutants from water has attracted significant attention. The nanofiltration membrane was fabricated through the evaporative casting (EC) method using multiwalled carbon nanotubes (MWCNT) and chitosan (CHIT) as the surfactant to enable water purification. The developed EC membrane properties were characterized in mechanical, surface charging (zeta potential), surface morphology, and hydrophobicity properties. Results demonstrated that incorporation of MWCNT and the biopolymers (chitosan) resulted in suitable developments in mechanical properties of the membrane. For example, the membrane has shown values for tensile strength ( $28 \pm 1$  MPa), elongation ( $10.2 \pm 1.2\%$ ), Young's modulus ( $1.2 \pm 0.1$  GPa), and toughness of ( $1.9 \pm 0.2$  J/g). When more significant changes were investigated on the surface morphology of the EC membrane, it was observed that the pores on the surface morphology of the EC membrane decreased as the evaporative casting method was used. Moreover, the permeability of the membrane towards water, inorganic salts, and pH effect on salt rejections was studied using the NF/RO system. These established nanocomposite membranes signify the promising candidates for fresh water desalination and elimination of organic impurities.

## 1. Introduction

The progress in rapid population of growth united with untenable use of water resources and scarcity of water have turn out to be a major significant task in the world. It is vital to improve the capable approaches for water treatment. Efforts have been made over the past few decades to improve water desalination systems for providing fresh water from the saline water using several desalination techniques such as distillation, freezing, electrodialysis, and solar-powered membrane separation [1–5]. While these processes have evolved, there are still some obstacles. For instance, there are key issues for reverse osmosis (RO) membrane fouling and scaling and also other problems where high energy consumption is needed in thermal desalination [6]. Therefore, an effective, energy-efficient alternative to traditional

processes for desalination of seawater must be created. Consequently, nanofiltration (NF) is one of the membrane processes, which is pressure-driven, and have the properties of nanofiltration (NF) such as pore size, water permeability, and salt rejection between reverse osmosis (RO) and ultrafiltration (UF) membranes [7]. NF can be operated using low-pressure, comparing to reverse osmosis (RO), and it has several benefits, which are lower operating pressures, higher fluxes, high rejection of divalent ions, and lower energy consumption [7]. These advantages allow NF membranes to be employed in many applications such as biotechnology, pharmaceutical, and food industry. Moreover, the NF membranes also can be used particularly in desalination and wastewater treatment [7, 8]. Currently, advances in NF membranes were developed for removal of monovalent ions from the surface water, underground water, brackish water,

and seawater [7, 9]. The NF was used as a first stage before the RO process, and this leads to many benefits like higher monovalent ion rejection, accomplished higher RO design flux and recovery in water desalination plants, and increase in membrane lifetime [6]. However, NF membranes still need to discover new materials in order to improve a high selectivity for monovalent ions. In this context, carbon materials, for instance, activated carbons, graphene, and carbon nanotubes (CNTs), have been extensively castoff in water purification approaches [10].

During the last few decades, carbon nanotubes (CNTs) have become increasingly attracted by scientists for a wide range of applications [11–14]. CNTs are mainly useful for making membranes because they possess unique properties such as fast transport rates and small pore openings [15]. However, there are difficulties that limit the usage of carbon nanotubes in larger scale because carbon nanotube fabrication is quit expensive and limited to small-scale production. Another problem related to carbon nanotubes is hydrophobicity that can limit its application in the membranes field [14, 16]. Otherwise, carbon nanotubes can be dispersed in a polymer matrix, which may provide an appealing route for production of mixed matrix membranes with a high mass transport rate. In addition, dispersion in a polymer can also help to reduce the hydrophobicity of CNTs, making it easy to use as membranes.

The sonication method is considered one of the most successful ways of dispersing CNTs through a polymer due to easy filtering of the resulting dispersions in order to produce the membrane, which is also called as “buckypapers” [17]. A number of studies have shown that when ultrasonic energy is used to disperse large amount of CNTs, the resulting products are stabilized by non-covalent interactions with the polymer molecule (surfactant) [18, 19]. For example, both single-walled carbon nanotubes (SWNTs) and multiwalled carbon nanotubes (MWCNTs) were very effectively dispersed to produce membranes using the nonionic surfactant octylphenol ethoxylate (Triton X-100). Resulted dispersions are very stable to the proper membrane due to the aromatic rings of Triton X-100 p-stack onto the external graphene lattice of the CNTs [20, 21]. Another study demonstrated that high power tip sonication was used to fabricate membranes containing different surfactants mixed with multiwalled carbon nanotubes (MWCNTs) and multiwalled carbon nanotubes functionalized with carboxylic acid groups (MWCNT-COOH) or amine groups (MWCNT-NH<sub>2</sub>) [22]. In addition, the membrane fabricated using MWCNT and Triton X-100 as the surfactant exhibited more than 80% removal efficiency for 11 out of the 12 trace organic contaminants (TrOCs) [23]. A few studies have used the same method (ultrasonic energy) to disperse CNTs (SWNTs and MWCNTs) for preparing a number of membranes using different surfactants [20, 24].

Moreover, among the various adsorbents like zeolite, organoclays, biochar, metal-organic frameworks, and carbon nanotubes for the exclusion of nitrophenolic compounds from aqueous solutions [25–33], CNTs have been

acknowledged as the productive adsorbents for elimination of them. This CNT application can be associated to electrostatic interactions and high surface areas, and the equilibrium time is shorter compared to the other materials. A number of biopolymers have been examined to disperse CNTs and their ability to prepare membranes [34–37]. Furthermore, the CNT performance as an adsorbent significantly enhanced through the modification with polymer materials like chitosan. Chitosan (CHIT) is an abundant biopolymer which has been extensively castoff in numerous applications such as industrial and biomedical [25, 38], enzyme immobilization [26], and water treatment [27–29], as well as used as transporters for controlled drug delivery [30]. These applications can be associated to the existence of quantities of the reactive amino and hydroxyl groups in the molecular chain of chitosan. Therefore, CNTs/chitosan composites, which are developed by imbedding functional groups of the chitosan to CNTs, have been developed to adsorb the pollutions or toxic metals from the wastewaters [31–33, 39].

Chitosan has the ability to disperse CNTs in an aqueous medium, and it can wrap around CNTs separately based on changes in their diameter [40]. A previous study showed that multiwalled carbon nanotubes and the chitosan composite membrane (MWCNT/CHIT) could be highly effective for removing salts from water [41]. This study used MWCNT/CHIT fabricated by depositing MWCNT mixed with chitosan 0.2% (w/v) onto a paper of polyvinylidene fluoride (PVDF). The result revealed effective removal of four inorganic electrolytes (NaCl, Na<sub>2</sub>SO<sub>4</sub>, MgSO<sub>4</sub>, and MgCl<sub>2</sub>) from water by this MWCNT/CHIT membrane.

The aim of this work was to improve the composite NF membrane from CNTs (MWCNT) and chitosan using the evaporative casting method in order to use for desalination process. The morphology, mechanic properties, and hydrophobicity of the composite membrane were characterized. In addition, the water permeability and the rejection performance of the composite membrane to inorganic electrolytes and pH effect of solution were also investigated in this study.

## 2. Materials and Methods

**2.1. Materials.** MWCNT was purchased from Hanwha Nanotech Corporation Ltd, Seoul, South Korea. The outer diameter ranges from 3–10 nm. All other materials used in this study were purchased from Sigma-Aldrich (USA) and used without further purification.

**2.2. Preparation of Dispersions.** The chitosan (CHIT) solution was prepared as mentioned in the previous study [41]. MWCNTs (15 mg) were added to the CHIT solution 0.2% w/v (15 ml) for preparing the dispersant using an ultrasonic processor 750 (750 W, ultrasonic digital probe sonicator with a diameter of 10 mm). The sonication was performed at an amplitude of 30% and pulses of 0.5 s “on” and 0.5 s “off,” with a total “on” time of 30 minutes. Vials containing MWCNTs and the CHIT solution (0.2% w/v) were placed in a water bath to reduce temperature changes from the heat

that was generated from this process. The above method was repeated 10 times to produce homogeneous dispersions (150 ml) containing MWCNTs and CHIT and were then diluted up to 250 ml.

**2.3. Preparation of Casting Membrane.** The evaporative casting membrane was fabricated using a custom-made unit and rectangular polyvinylidene difluoride (PVDF) membrane. The dispersion solution (MWCNT/CHIT) was deposited on the surface of the PVDF membrane (6.0 cm × 12.0 cm) and then was evaporated by using a vacuum oven, which typically operated at 35°C for 24–48 hours. Once the dispersant had evaporated, the resulting EC membranes were washed with sodium hydroxide (NaOH) followed by Milli-Q water to remove the remaining acetic acid. The EC membranes (Figure 1) were then dried for 24 hours in a controlled temperature at 21°C and removed from the support membranes (PVDF).

**2.4. Characterization Techniques.** The surface morphology of the EC membrane (Figure 1) was analyzed using field emission scanning electron microscopy (FESEM) (JEOL, Japan). Samples were prepared by putting small pieces of EC membranes on to the SEM's stage using a conductive carbon tape. The small pieces of EC membranes were imaged with gold sputter coating.

The hydrophobicity property was studied by using the contact angle instrument (sessile drop method). Deionized water (2 μl) was dropped on the surface of the membrane and an image was taken. The values of the contact angle were then estimated by constructing triangles on the obtained images.

The mechanical properties of membranes were studied in a controlled temperature at 21°C using a tensile tester. Prior to testing, five sample strips from each EC membrane were examined with a dimension 20 mm by 3 mm with thickness 0.5 measured using a micrometer. The samples were examined using a strain rate of 0.5 mm/min and a gauge length of 10 mm. The tensile strength of each sample was measured as the maximum stress, and Young's modulus was calculated from the slope of the linear part of the stress-strain diagram. Elongation and stress were calculated at the break.

Surface charge of the EC membranes was studied using a SurPASS electrokinetic analyzer. Zeta potential (ZP) was measured using 1 mM KCl of background electrolyte solution, and the pH was adjusted by automatic titration using HCl and KOH solutions.

The permeability towards water of large EC membranes was determined using the cross-flow NF/RO filtration system (CF042 membrane cell), as shown in Figure 2. The experiment was carried out using rectangular pieces (6.0 cm × 12.0 cm) of membranes, which were placed between two halves of the transport cell. A digital flow meter (FlowCal, GJC Instruments Ltd, Cheshire, UK) linked with a PC was used to evaluate the flux flow. Deionized (DI) water was applied to the membrane which was set at a pressure of 22 bar to compact the membranes for nearly 1 h until a

steady baseline flux was achieved. Permeate flux of DI water was estimated at different applied pressures. Resulting data were then used to calculate the water permeability ( $f$ ) of the EC membrane using the following equation:

$$f = \frac{J}{A \cdot \Delta P}, \quad (1)$$

where  $J$  is the volume of the permeate flux,  $A$  is the effective area of the membrane exposed to water (40 m<sup>2</sup>), and  $\Delta P$  is the applied pressure on the membrane (bar).

The measurements of salt rejection were performed using each individual salt solution (NaCl, MgSO<sub>4</sub>, MgCl<sub>2</sub>, and Na<sub>2</sub>SO<sub>4</sub>) of 2 g/L separately and a cross-flow of 100 l/h. The temperature of the feed solution was kept at 20 ± 2°C throughout the experiment using a chiller, while the pH and conductivity were measured by using a conductivity meter. The percentage observed rejection ( $R\%$ ) of the salts is determined from the permeate and feed samples using the following equation [41]:

$$R\% = \left(1 - \frac{C_p}{C_f}\right) 100\%, \quad (2)$$

where  $C_p$  and  $C_f$  are the salt concentrations on the permeate and the feed streams, respectively.

### 3. Results and Discussion

**3.1. Surface Morphology of Membrane.** A previous study reported that a sonication time of 20 min was suitable for MWCNT/CHIT (0.2% w/v) dispersions [41]. Accordingly, all dispersions used to prepare membranes in the current study were fabricated using the same sonication time (20 min) in order to simplify the comparison of their physical properties.

Figure 3(a) shows the scanning electron microscopic image (SEM) of the EC membrane with MWCNT/CHIT. In the surface of the EC membrane, it was found that the MWCNT completely covered by CHIT with no pores was observed in the image. In contrast, Figure 3(b) shows a randomly entangled mat/network of MWCNT. The MWCNTs are not well dispersed through the surfactant (chitosan). These images have a number of differences to that of a MWCNT/CHIT reported in previous studies [24, 41]. Sweetman et al. [42] reported that the surface morphology of membranes varied depending on the dispersant and the type of CNT used. In addition to that, SEM provided significant differences between the surface morphology of composite membranes of SWNTs with the same biopolymer dispersants [20]. Moreover, the EC membrane was prepared by the evaporating method. This indicates that the surface morphologies (Figure 3(a)) of the membrane may be affected greatly by using this method. This suggests that there may have been no loss of biopolymer (chitosan) at the surface of the membrane in the case of the evaporating method comparing to other methods such as the vacuum method, which demonstrated a greater range of surface morphologies in SEM studies [21, 24, 41].

Moreover, a cross-section image (Figure 3(b)) reveals that the structure of the EC membrane has many layers of



FIGURE 1: Images of the developed EC membrane.

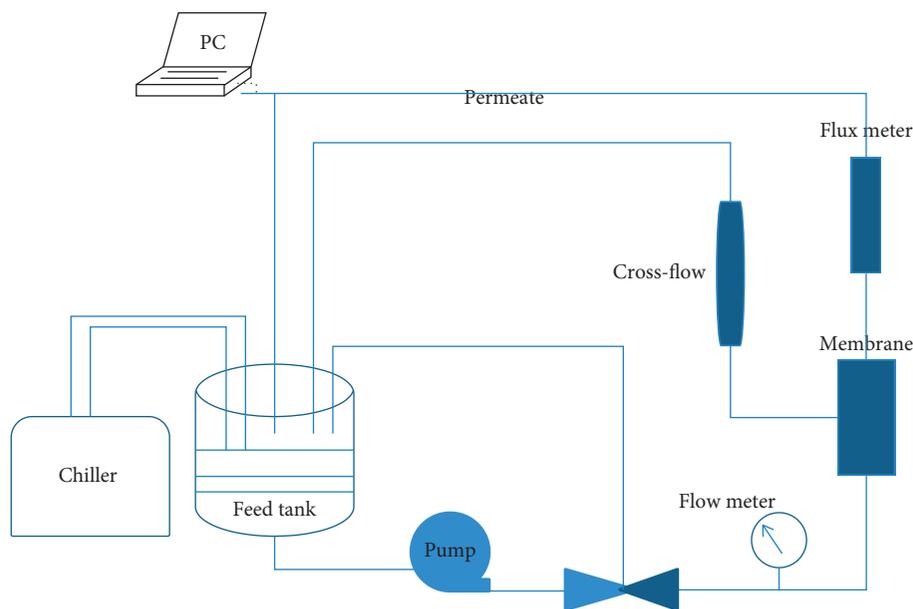


FIGURE 2: Schematic illustration of forward cross-flow filtration system.

MWCNTs, which was aligned with each other with a narrow distance between them. The membrane was found to be similar to those reported recently for other fabricated methods using the same CNT and chitosan ligand dispersant [24, 41].

**3.2. Mechanical Properties.** Mechanical strength of the membrane is of primary importance in seawater separation mechanisms. The reason beyond that is that the membrane should be able to withstand various pressure loads that were applied and different flow-rates over a long period. Hence, a study of the mechanical features of EC membranes was conducted by employing the tensile testing methodology, and the results obtained are plotted in Figure 4. The plot initially indicates a linear stress vs. strain relationship, which indicates elastic deformation. Still at higher strain levels, little deviations from the linear relationship could be seen, which suggest that the materials have a strong mechanism. The stress vs. strain plot was used to determine mechanical properties such as Young's moduli, toughness, elongation, and tensile strength. Table 1 summarizes the values found for

the EC membrane comparing with other techniques used for the membrane.

In this study, the EC membrane resulting from dispersions in MWCNTs and the surfactant (CHIT 0.2% w/v) showed Young's moduli in the  $1.2 \pm 0.1$  GPa, elongation in the  $10.2 \pm 1.2\%$ , tensile strength in the  $28 \pm 1$  MPa, and toughness in the  $1.9 \pm 0.2$  J/g. The results observed for the elongation is slightly higher to that previously obtained for MWCNT/CHIT [41]. In addition, the mechanical properties of membranes containing biopolymers were much better among other membranes fabricated using MWCNT and low molecular mass dispersants [23]. The reason for the mechanical characteristics of EC membranes to be greater is due to the high molecular weight of chitosan and the method used for preparing membrane in this study. A recent method (evaporative casting method) indicates that the mechanical properties of the membrane made from MWCNT and CHIT 0.2% w/v were significant increased.

**3.3. Contact Angle.** Contact angle is one of the important properties for a material that is used as a filtration membrane

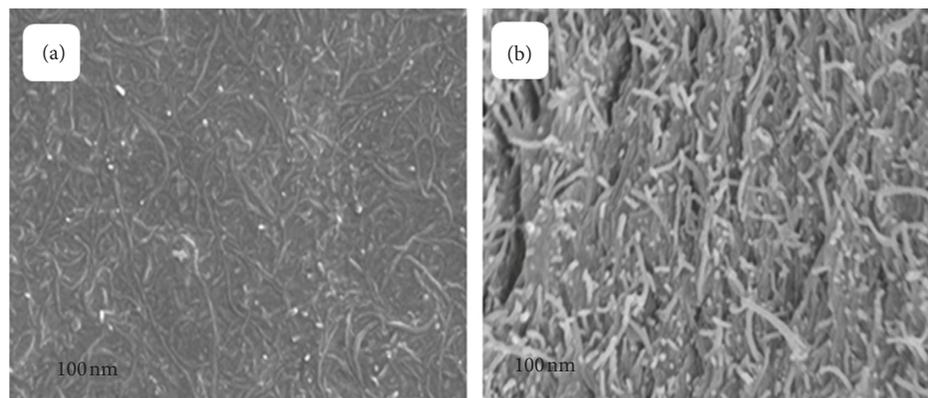


FIGURE 3: SEM of MWCNT/CHIT evaporative cast membrane. (a) Morphology of surface and (b) cross section.

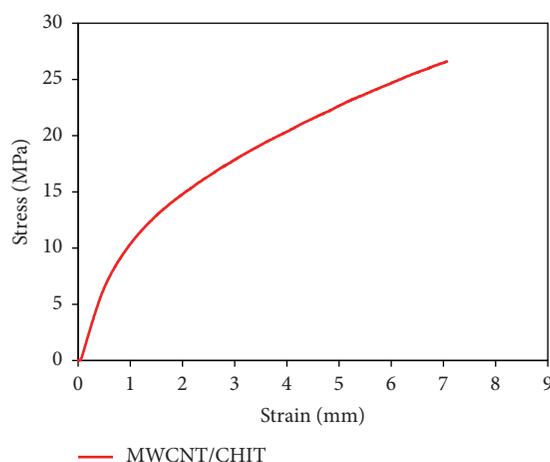


FIGURE 4: The stress vs. strain of MWCNT/CHIT evaporative cast membrane.

TABLE 1: Values found for the EC membrane comparing with other techniques used for the membrane.

Membrane	Tensile strength (MPa)	Elongation (%)	Young's modulus (GPa)	Toughness (J/g)	Contact angle (°)	Permeability (L/m <sup>2</sup> ·h·bar)
MWCNT/chitosan*	56 ± 3	5.7 ± 0.	2.9 ± 0.1	2.1 ± 0.3	102 ± 3	0.87 ± 0.03
MWCNT/chitosan-glycerin*	49 ± 4	6.4 ± 2	2.9 ± 0.1	2.2 ± 0.8	80 ± 2	0.61 ± 0.02
MWCNT/chitosan-PEGDE*	59 ± 3	8.1 ± 2	2.7 ± 0.2	2.3 ± 0.2	76 ± 3	0.19 ± 0.01
MWCNT/chitosan	28 ± 1	10.2 ± 1.2	1.2 ± 0.1	1.9 ± 0.2	80 ± 2	0.75 ± 0.1

\*Data for MWCNT/chitosan, MWCNT/chitosan-glycerin, and MWCNT/chitosan-PEGDE are taken from reference [41].

for separation of molecules in aqueous solutions. The information about the nature of the membrane surface such as hydrophobicity can be determined by the contact angle [41]. The contact angles values of the EC membranes ( $80^\circ \pm 2^\circ$ ) reported in Table 1 indicate that the membrane is hydrophilic in nature [20, 23]. The contact angle values reported in the current study are lower to those values reported previously for membranes prepared using MWCNT and the same dispersant ( $102^\circ \pm 3^\circ$ ) [41]. This indicates that lower contact angle of these membranes displayed by the method used in the present study provided more amount of dispersants (CHIT 0.2% w/v) at the membrane surface.

**3.4. Zeta Potential.** Figure 5 shows the membrane-surface charge density of the EC membrane, which is approximately neutral between pH 7 to 8 and it is gradually positive charged below pH 4, while it is negative charged above pH 8. This can be attributed to the deprotonation and protonation of chitosan [41]. This agreed with the behavior observed previously for MWCNT and chitosan as a surfactant, where absorbance was found to be positive charged below pH 4 and significantly negative charged above pH 8 [24, 41]. In addition, the measured membrane-surface charge was lower than to that was analyzed by Zhan et al. [16], due to the functional groups (carboxylic group) present in MWCNT.

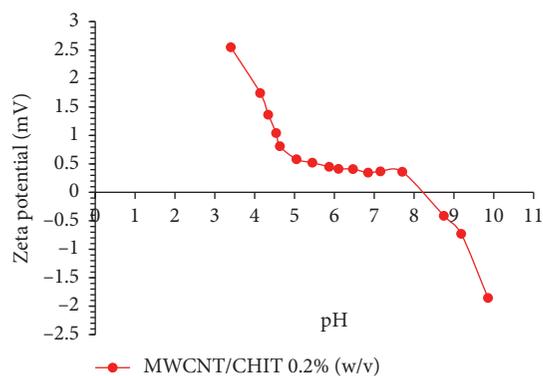


FIGURE 5: Zeta potential of MWCNT/CHIT evaporative cast membrane.

**3.5. Permeability Salt Rejection Study of Membrane.** The discussion in the previous sections illustrates the possibility of incorporating MWCNT and chitosan in order to develop mechanically strong and hydrophilic membranes. These characteristics are essential for membranes with potential use in nanofiltration and microfiltration processes. The next step in investigating the suitability of the membrane for filtration applications was to test the water permeability of the evaporative cast membrane, using the NF/RO system. Water permeability graph for MWCNT/CHIT is illustrated in Figure 6. Plot of the permeate flux against pressure applied indicates a linear relationship for evaporative cast membrane as illustrated in Figure 6. Equation (1) was used to estimate the membrane flux ( $f$ ). The water permeability rate of the evaporative cast membrane (MWCNT/chitosan) was approximately  $0.75 \pm 0.1 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}$ . Resulting value is in good agreement with our previous investigation for the MWCNT/chitosan bucky paper membrane, which was prepared by using the filtration method (our work). In addition, the water permeability of the evaporative cast membrane (MWCNT/Chitosan) was slightly higher than the MWCNT/chitosan-glycerin membrane, while the water permeability of the MWCNT/chitosan-PEGDE membrane was significantly lower than the membrane (MWCNT/chitosan) that was fabricated in this study as shown in Table 1.

Salt rejection of EC membranes was investigated using four inorganic electrolyte solutions (NaCl,  $\text{Na}_2\text{SO}_4$ ,  $\text{MgSO}_4$ , and  $\text{MgCl}_2$ ), with a salt concentration of 2 g/l, applied pressure ranging from 3–20 bar, and temperature of  $20^\circ\text{C} \pm 2^\circ\text{C}$ , using a cross-flow NF/RO system. Figure 7 shows that the rejection of four inorganic electrolyte solutions was found to increase as the applied pressure was increased. The rejection order follows that  $R(\text{MgCl}_2) > R(\text{NaCl}) > R(\text{MgSO}_4) > R(\text{Na}_2\text{SO}_4)$ . In addition, the rejection of  $\text{MgCl}_2$  was demonstrated to be significantly greater than other three inorganic electrolyte solutions (NaCl,  $\text{MgSO}_4$ , and  $\text{Na}_2\text{SO}_4$ ). The observed behavior of the EC membrane (MWCNT/CHIT) is in good agreement with previous studies, which showed the similar order of rejection as  $R(\text{MgCl}_2) > R(\text{NaCl}) > R(\text{MgSO}_4) > R(\text{Na}_2\text{SO}_4)$  [41, 43, 44]. Consequentially, the MWCNT/CHIT membranes demonstrated stronger sorption to  $\text{Cl}^-$

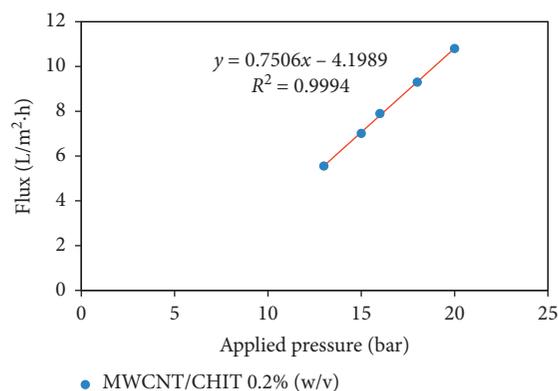


FIGURE 6: Water permeability of the MWCNT/CHIT evaporative cast membrane.

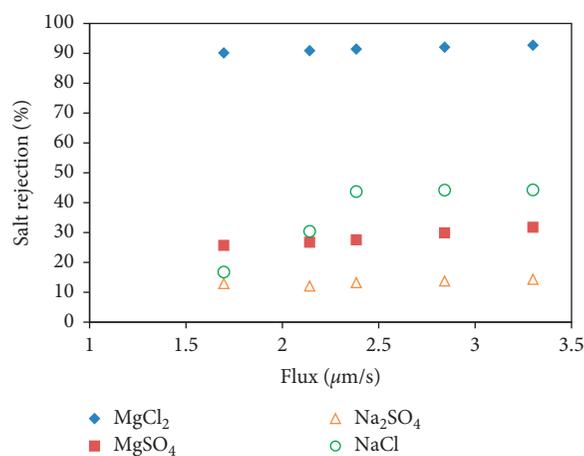


FIGURE 7: Effect of the operating pressure on the rejection performance of the MWCNT/CHIT evaporative cast membrane.

rather than  $\text{SO}_4^{2-}$  ions. This may be related to stronger interaction among the anions in  $\text{MgCl}_2$  and functional groups available on the surface of the EC membrane. In addition, the  $\text{Mg}^{2+}$  ions can interact with anions on the surface of the membrane leading to decrease in the effective surface charge on the membrane [45]. This in turn makes the ions less absorbable on the surface of the EC membranes. This may be because the cation shield affects the membrane repulsive forces on the anions [46].

**3.6. Effect of pH on Salt Rejection.** The rejection of NaCl and  $\text{MgSO}_4$  was studied on the MWCNT/chitosan EC membrane at  $20 \pm 2^\circ\text{C}$  at the pH range from 3 to 10. The pressure was kept at 15 bar to obtain the same permeate flux for studying the effect of pH on the salt rejection as presented in Figure 8. The EC membrane had high salt rejection for both salts when the feed solution became acidic, and NaCl and  $\text{MgSO}_4$  were 61 and 27%, respectively. In addition, the salt rejection gradually decreases for both solutions till they reach steady state after pH 9 for NaCl and beyond pH 8 for  $\text{MgSO}_4$ . These phenomena show that, it could be attributed to the protonation of free amino groups in chitosan [41]. Based on the previous literature reports which stated

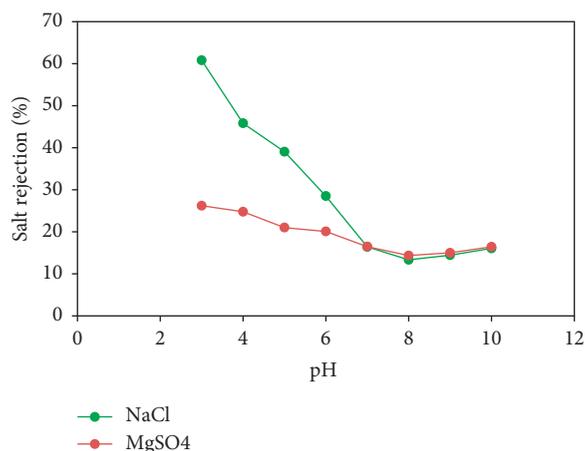


FIGURE 8: Effect of the pH on the rejection performance of the MWCNT/CHIT evaporative cast membrane.

that the amino groups ( $\text{NH}_2$ ) on the chitosan structure can be protonated at low pH, resulting the  $\text{NH}_3^+$  groups, which are mainly responsible for significantly increasing the exchange between anions and negatively charged surfaces [47, 48].

#### 4. Conclusion

In the present study, a nanocomposite membrane multi-walled carbon nanotube (MWCNT)/chitosan fabricated by using evaporative casting (EC) method, which effectively elucidates the correlation between permeability and selectivity, was prepared. The simultaneous increase in flux and the high salt rejection ability factor suggested that the amalgamation of MWCNTs could bring about the packing of hydrophilic chains in the matrix, provided that internal nanochannels exist for enriched water permeation through the nanoscale opening of the MWCNTs. The addition of MWCNTs into the chitosan significantly improves crystallinity and tensile strength. A comprehensive study for properties of this membrane was investigated. The EC membrane has high mechanical properties whose tensile strength was  $28 \pm 1$  MPa. In addition, it provided an excellent salt rejection at high acidic media for NaCl than  $\text{MgSO}_4$ . Additionally, the incorporation of the MWCNT/chitosan composite also primes to the principally enriched mechanical property of chitosan composite membranes. Also, the composite MWCNT/chitosan may play more significant roles in a wide application, such as separation of biomedical products, wound dressings, and the model for mass transport of the biological membrane.

#### Data Availability

The data used to support the findings of this study are included within the article.

#### Conflicts of Interest

The authors declare that they have no conflicts of interest.

#### Acknowledgments

The authors are grateful to King Abdulaziz City for Science and Technology, Riyadh, Saudi Arabia, for the financial support of this work and the facilities in its labs. In addition, the authors would like to extend their thanks to Mr. Abdulrahman Algiahah for helping with the scanning electron microscope image.

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