



# Novel carbon nanotube–cellulose acetate nanocomposite membranes for water filtration applications



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## HIGHLIGHTS

- CNT/CA membranes were successfully prepared for the first time.
- CNTs enhanced permeation by more than 50% with minimal effect on salt retention.
- Permeation rates were found to increase with the decrease in CNT weight contents.
- Pore volume and surface area are investigated and related to membrane behavior.

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## ABSTRACT

Multi walled carbon nanotube/cellulose acetate (CNT/CA) nanocomposite membranes were successfully prepared by phase inversion using acetone as solvent and 20 wt.% deionized water as non-solvent. CNTs were first functionalized by oxidation purification in a strong acidic medium to enhance their dispersion within the polymer matrix. Small amounts of the functionalized CNTs, namely 0.0005, 0.005, and 0.01 wt.% were used to prepare the membranes. The CNTs were randomly oriented and uniformly dispersed within the membranes. Membranes' morphologies were characterized by field emission scanning electron microscopy (FESEM) and nitrogen adsorption. A decrease in the number of macrovoids with increase in CNT content was observed. This was verified by the analysis of pore sizes (differential volumes and surface areas) which were found to also decrease with the increase in CNT content. Nanocomposite membrane permeation rates and salt retention rates were investigated using a 1000 ppm NaCl solution. Permeation rates were found to improve by 54% with a minimal decrease in salt retention (−6%) for the membranes with the lowest CNT content. Further addition of CNTs caused a reduction in permeation rates which is attributed to the decreased porosity and surface area.

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## 1. Introduction

Membrane technology is responsible for more than 53% of the world processes in fresh water production [1]. The first ever reported reverse osmosis (RO) membrane with effective salt retention (98%) was manufactured in 1959 by Reid and Breton [2]. It was a hand cast symmetrical thin film of cellulose acetate (CA) with a water permeation rate less than 0.01 L/m<sup>2</sup>h. About five years later, Loeb and Sourirajan [2] developed a CA asymmetric membrane, with improved salt retention (99%) and water permeation (14.6 L/m<sup>2</sup>h), to become the first high flux asymmetric RO membrane. Since then, improving the performance of CA membranes has been the focus of numerous studies. These have primarily focused on investigating the effect of different additives on membrane morphology and performance. Various investigations

have focused on the effect of different solvents and non-solvents [3–7], while others addressed the effects of pore formers [8–15]. The effect of adding polymer blends [3,5,15–17] was also investigated.

Only a few studies investigated the use of CA membranes for nanofiltration. Among the ones found, permeation rates ranged from 0.06 L/m<sup>2</sup>h·bar all the way to 11.4 L/m<sup>2</sup>h·bar. Permeation measurements were carried out with pressures ranging from 15 to 40 bars, and NaCl concentrations from 1000 to 5000 ppm. Salt retention ranged from 26.08% to 87% [4,5,18,19].

Carbon nanotubes (CNTs) gained considerable attention as additives to desalination membranes following molecular dynamic simulations which established super fast water flow inside them [20–23]. Holt et al. [24,25] investigated the mass transport of water inside nanotubes using micro-fabricated membranes in which arrays of aligned CNTs were surrounded by a silicon nitride matrix. They reported that water flow rates increased by several orders of magnitude as compared to commercial membranes not containing nanotubes. This triggered

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interest in the use of CNTs in desalination membranes. CNTs were added to polymers such as polysulfones, aromatic polyamides, chitosan, polyacrylonitrile, polyethersulfone and are being investigated for filtration applications [26–29].

Choi et al. [26] prepared multi-walled CNT/polysulfone blend membranes using phase inversion, with different nanotube contents. The measured pure water flux increased with the percentage weight (wt.%) increase of the CNT up to a content of 1.5 wt.% beyond which the flux decreased. This was explained by the fact that the increase in CNT wt.% increased the membrane hydrophilicity and pore sizes until the threshold content of 1.5 wt.% above which increasing the amount of CNT resulted in reduced pore sizes leading to lower permeation rates. Qiu et al. [27] used modified CNTs with polysulfones to prepare blend membranes by phase inversion. Measured values for pure water flux showed a similar trend to the previous study, with a decrease beyond a CNT wt.% content of 0.19 wt.%. Shawky et al. [28] prepared CNT/aromatic polyamide nanocomposite membranes with different amounts of CNTs using solvent evaporation. Membrane performance, permeation and retention rates were measured using a 4000 ppm NaCl solution. The results showed that permeation rates decreased with the addition of CNTs. However, salt retention increased significantly from 24% to 76%. This large increase in retention rates was believed to be due to the membrane compactness resulting from strong interactions between the added CNTs and the polymer matrix. Tang et al. [29] prepared CNT/chitosan nanocomposites with different wt.% of CNTs. Pore formers polyethylene glycol (PEG) 6000 and 10,000 were used, and membranes were prepared by solvent evaporation. Measured pure water flux values followed the same trend as the CNT/polysulfone membranes described earlier, exhibiting a decrease beyond 10 wt.% and 1 wt.% CNT contents for the membranes prepared with PEG 6000 and PEG 10,000 respectively. In their study, the maximum observed increase in pure water flux was 4.6 times that of a blank chitosan membrane. The authors argued that the CNTs could have created alternative channels for water passage, thus increasing the flux rates. Majeed et al. [30] prepared an ultrafiltration membrane of different CNT wt.% blended with polyacrylonitrile (PAN) by phase inversion. Pure water flux rates increased by 63% upon the addition of 0.5 wt.% CNT compared to blank PAN membrane, and then decreased again to give the same trend stated before. A suggested explanation to the trend was that the increase in CNT content increased the membranes' hydrophilicity. The enhanced hydrophilicity was, however, compensated for by the increase in the thickness of the top dense layer of the membrane upon the addition of further amounts of CNTs thus resulting in reduced water flux rates. Rahimpour et al. [31] used amine functionalized CNTs with different weight contents to prepare polyethersulfone (PES) based nanocomposite membranes by phase inversion. The best performing membrane in pure water flux measurements was found to be the one with 1 wt.% CNT. Similar to other studies, further addition of CNTs reduced the flux rates. This was explained by the fact that the increase in CNT content increased the membranes' hydrophilicity, until a point at which the high CNT content (2 wt.%) increased the cast solution viscosity, thus slowing down the solvent–nonsolvent demixing process, resulting in small pore sizes and a decrease in water flux rates.

Incorporating CNTs in CA polymer membranes for desalination applications has not yet been reported in the literature. A study describing mechanical, thermal, and electrical properties of such nanocomposites was published by Li et al. [32]. The group suggested the presence of strong interactions between the CA polymer and the functional groups on the functionalized graphene walls of the CNTs, mainly hydrogen bonding. This led to enhanced dynamic mechanical properties, improved thermal stability, associated with increased electrical volume resistivity. Enhanced mechanical and thermal stability are desirable properties for membranes for water desalination applications.

The current study investigates the effect of adding functionalized randomly-oriented CNTs on the morphology and performance of CA membranes in water desalination applications. Membrane performance

was characterized by water permeability and salt retention. Different masses of multi-walled CNTs were used in order to produce 0.0005 wt.%, 0.005 wt.%, and 0.01 wt.% CNT/CA membranes. The performances of these CNT-blend membranes are compared with a blank CA membrane devoid of CNTs. Additionally, membrane textural properties (porosity and surface area) were studied and related to the observed performance.

## 2. Experimental

### 2.1. Materials

CA with an average molecular weight of 50,000 Da, and 39.7 wt.% acetyl content (Sigma Aldrich) was used as the polymer matrix. Acetone (Sigma Aldrich, purity  $\geq 99.8\%$ ) was used as solvent, and deionized water as non-solvent. Multi-walled carbon nanotubes with an inner diameter of  $\sim 4$  nm, outer diameter of  $\sim 13$  nm, and length  $> 1 \mu\text{m}$  (Baytubes® C150P, C-purity  $\geq 95$  wt.%) were used as nanofillers. Sodium chloride (Sigma Aldrich, purity  $\geq 99.5\%$ ) and silver nitrate (Sigma Aldrich, purity  $\geq 99.8\%$ ) were used for salt retention determinations.

### 2.2. Membrane preparation

Functionalization of the CNTs was carried out as detailed elsewhere [33] with the aim of improving their interaction with the polymer matrix. CNT functionalization was characterized using a Nicolet 380 FTIR with the KBr pellet method. Functionalized CNTs were added to 15 wt.% CA solution in acetone in the following manner: the nanotubes were dispersed in deionized water by sonication for 10 s, then added gradually to the CA solution with vigorous stirring. Once all the nanotubes were added, the mixture was sonicated for 2 min, then left for 18 h to allow any air bubbles in the solution to dissipate. Different masses of the nanotubes were used in order to obtain mixtures of 0.0005, 0.005, and 0.01 wt.% CNT. The amount of deionized water used was such that all membrane mixtures were 20 wt.% in water (a nonsolvent for CA). The presence of this nonsolvent helps in creating large macrovoids, as reported in [34]. A CA solution devoid of CNTs was also used to prepare a blank membrane (0 wt.%) and was also 20 wt.% in deionized water.

Each of these solutions was cast on a glass substrate, using a casting knife, then directly immersed in a deionized water bath kept at room temperature for phase inversion to take place by solvent/non-solvent demixing. The final thickness of all membranes was  $100 \pm 10 \mu\text{m}$ .

### 2.3. Membrane characterization and testing

A Leo Supra 55 field emission scanning electron microscope (FESEM) was used to characterize the membranes' cross-sections in order to determine the membranes' final thicknesses, CNT distribution and orientation as well as membrane morphology. Pore size distribution and membrane BET (Brauner, Emmett and Teller) surface area were determined by  $\text{N}_2$  adsorption at 77 K using an ASAP 2020-Micromeritics apparatus.

For water permeation and salt retention tests, a 5 cm diameter membrane disk was placed in a test cell (Sterlitech HP4750 stirred cell), which was filled with a 1000 ppm NaCl feed solution. A pressure of 24 bars was applied using  $\text{N}_2$  gas. Permeation rate was calculated using Eq. (1).

$$J = V / (A \cdot t \cdot P) \quad (1)$$

where  $J$  is the permeation rate (in  $\text{L}/\text{m}^2\text{h}\cdot\text{bar}$ ),  $V$  (in L) is permeate volume that passed through the membrane,  $A$  (in  $\text{m}^2$ ) is the total area of the membrane on which pressure is applied,  $t$  is the time taken (in h) for the permeate to fill a certain volume  $V$ , and  $P$  (in bars) is the applied pressure. Salt retention was determined using titration where 1 mL of permeate was titrated with standardized silver nitrate solution

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