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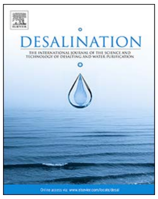

Synthesis and characterisation of MWNT/chitosan and MWNT/chitosan-crosslinked buckypaper membranes for desalination

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ABSTRACT

Novel buckypaper (BP) membranes for nanofiltration application were fabricated from multi-walled carbon nanotubes (MWNT) and biopolymer containing quaternary amine groups (chitosan and chitosan-crosslinked by in-situ amine crosslinking). Characteristics of the BP membranes were systematically characterized in terms of mechanical (tensile strengths varied between 49 ± 4 and 59 ± 3 MPa) and electrical properties (60 ± 1 to 70 ± 1 S/cm), contact angle (76 ± 3° to 102 ± 3°), surface morphology, membrane swelling, pore size, surface charge, solubility, water permeability (ranging from 019 ± 0.01 to 0.87 ± 0.03 $\mathrm{L\,m^{-2}\,h^{-1}\,bar^{-1}}$), and salts rejection (80–95% for $MgCl_2$, 21–63% for NaCl, 18–37% for $MgSO_4$ and 6–14% for Na_2SO_4). These BP membranes were able to sustain up to 18 bar of pressure. Their properties were significantly affected by the type of biopolymer modifiers. The highest water permeability was obtained with the MWNT/chitosan BP membrane, while the MWNT/chitosan-crosslinked membranes showed the best salt rejection performance. In addition, separation performance by these membranes appeared to be governed by the unhydrated radii of these inorganic salts.

1. Introduction

Carbon nanotubes (CNTs) have attracted significant scientific attention in recent years. They are promising materials for the fabrication of functional membrane materials due to their excellent electrical, mechanical, thermal properties and high surface area [1–5]. For example, molecular dynamic simulations of CNTs membranes have demonstrated unexpectedly much higher water permeability comparing to other known porous materials [6,7]. As a result, CNTs matrices have been evaluated for membrane applications. Hinds et al. [8] constructed an array of aligned carbon nanotubes (CNTs) incorporated across a polymer film to form a well-ordered nanoporous membrane structure. They observed a permeation fate of four to five times higher compared to conventional fluid flow calculated by the Hagen–Poiseuille equation. In another study, aligned CNTs in silicon nitride composite membranes were fabricated using chemical vapor deposition by Holt et al. [9]. The CNTs in silicon composite membrane achieved faster gas and water permeation than would be expected. However, preparing aligned CNTs is still limited to small-scale, costly and difficult to reproduce techniques [4,10].

As an alternative to the aligned structure, CNTs can be dispersed in an aqueous solution using sonicator and dispersant and reform to obtain composite thin membrane with fast transport rate and easy to scale-up operation. Recent research has significantly improved the mass transport rate of non-aligned CNTs membranes. For instance, single walled carbon nanotubes (SWNT) with poly(imid siloxane) nano-composite membranes were prepared by Kim et al. [11] and they reported that the mass transport rate of O_2, N_2 and CH_4 increased by increasing SWNTs content in the nano-composite membranes. Polyvinyl alcohol (PVA) was coated with a nonporous hydrophilic polymer and oxidized multi-walled carbon nanotubes (MWNT) nano-composite membranes were fabricated by Wang et al. [12]. Their results showed considerable improvement in the water flux and solute rejection.

Recent investigations have shown that buckypaper (BP) fabricated from aligned arrays of CNTs can have a free volume of up to 70% of the total porous network structure. Potential applications of BP membranes have been explored in several fields including artificial muscles, hydrogen storage, sensors, actuators, for structural reinforcement in polymer composites and in the membrane separation process [13,14]. CNTs BP membranes have high permeability towards water and gases as well as good selectivity between small and large molecules [15,16]. The internal structure of BPs contains small and large pores due to the

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spaces between bundles of CNTs, while the pore size distributions of BPs are controlled by the pores with diameters of 100 nm or above [17]. The sizes of the BP pores are wholly dependent on the arrangements and sizes of the CNTs. BPs can also absorb gas and liquid to 60–70% of their volume because of intrabundle pores and interbundle gaps. This porosity, coupled with high strength, rigidity and exceptional flow rates, suggests that BPs could make outstanding membranes [18].

CNTs have the tendency to aggregate. Thus, a dispersant is required to solubilize for the fabrication of BP membranes. Several studies have used chitosan as a dispersant for preparing a CNTs BP membranes due to their ability to interact with CNTs to form an aqueous solution [19,20]. Chitosan is a polymer of randomly distributed a-(1-4)-linked D-glucosamine and *N*-acetyl-D-glucosamine. Chitosan is commercially made by deacetylation of chitin from the exoskeleton of crustaceans. The degree of deacetylation (DDA) controls the solubility of chitosan in acidic solution, the ability to modification supramolecular structures through hydrogen bonding [21]. Chitosan addition allows for BP membrane preparation using solvent evaporation with a low concentration of organic acid such as acetic acid [22,23]. Several studies have also reported that chitosan can be modified via chemical modifications to create functional derivatives of chitosan [22–25]. These modifications could enhance the mechanical strength, chemical stability, biocompatibility and hydrophilicity of chitosan. For example, the cross-linking of chitosan by dialdehydes [26] or epoxides [27,28] may lead to a denser network structure, enhancing the mechanical properties and improving the resistance of the membrane against acid, alkali and oxidising chemicals.

This study reports the fabrication and characterisation of three BP membranes prepared from MWNTs and biopolymer dispersants namely chitosan, chitosan-glycerin (CHIT-glycerin) and chitosan-polyethylene glycol diglycidyl ether (CHIT-PEGDE). Water flux and rejection characteristics of these BP membranes were investigated under different experimental conditions. Key parameters that control the optimization of these BP membranes were also systematically examined.

2. Experimental

2.1. Materials

Unfunctionalised thin MWNTs (Nanocyl™ 3100) were obtained from Nanocyl, Belgium. All MWNT samples had 95% purity and were used without any further purification. Low molecular weight chitosan with a deacetylation degree of 82% and a viscosity of 200–800 cP (1% in 1% acetic acid) was obtained from Sigma-Aldrich. Glacial acetic acid with 99.7% purity was purchased from Asia Pacific Specialty (APS) Chemicals Limited, Australia. Glycerin was obtained from Sigma-Aldrich, United States. Polyethylene glycol-diglycidyl ether (PEGDE) (Mn ~ 526) was obtained from Sigma-Aldrich and they were used for crosslinking chitosan. On the other hand, NaCl, $MgCl_2$, and Na_2SO_4 were purchased from Sigma-Aldrich. Anhydrous $MgSO_4$ was purchased from Scharlau, Spain. HCl, methanol and ethanol were bought from Ajax Finechem Pty Ltd., Australia. The filter for MWNT dispersions comprised of rectangular pieces of polyvinylidene fluoride (PVDF) from Millipore (Ireland) in the form of a hydrophobic commercial membrane with a nominal pore size of 0.22 μm. Another hydrophobic PTFE membrane filter with pore sizes 5.0 μm was also purchased from Millipore (Ireland) and used to remove any particulates from the chitosan solution. All the solutions and dilutions in this study were prepared using Milli-Q® water (resistivity of 18.2 MΩ cm).

2.2. BP membrane preparation

2.2.1. Preparation of chitosan crosslinking BP membranes

The chitosan solutions were prepared by dissolving 6 g of chitosan (0.2% w/v) in 3 L of an aqueous solution containing 1% (v/v) acetic-acid. The solutions were heated for 3 h at 80 °C and stirred for 24 h until the chitosan dissolved completely. The solutions were then left overnight to cool at 21 °C. The homogenous solutions were filtered through a 5.0 μm hydrophobic PTFE membrane to remove any undissolved chitosan particles. The final homogenous solution after filtration was divided into three groups.

(i) Chitosan: This was prepared with the homogenous chitosan solution (0.2% w/v) without any additives.
(ii) Chitosan-glycerin: This was prepared with the homogenous chitosan solution (0.2% w/v) and 0.8 g of glycerin (20% chitosan mass).
(iii) Chitosan-PEGDE: This was prepared with chitosan (0.2% w/v) and 0.8 g of PEGDE (20% chitosan mass). Each of these two solutions was heated for 2 h at 50–70 °C, stirred 24 h and left overnight to cool at 21 °C.

MWNTs (15 mg) were added to 15 mL of each chitosan, chitosan-glycerin and chitosan-PEGDE solutions and mixed by sonication for 30 min. The above procedure was repeated 10 times to produce 150 mL of the MWNT dispersion solution. Each dispersion solution was diluted up to 250 mL and then filtrated through hydrophobic PVDF filter paper (142 mm, pore size 0.22 μm) using a vacuum pump at 30–40 mbar. The top of the filtration system (custom-built transport cell unit) was covered with aluminum foil to avoid evaporative loss. The large BP membrane produced on the filtration sheet was placed to dry between absorbent paper sheets with small, flat glasses at the top and left for 24 h at 21 °C. The dry BP membrane was then peeled from the filtration sheet.

2.3. Characterisation techniques and instrumentation

The following instrumentation methods were adopted to analyse and characterise different properties of the BP membranes.

2.3.1. UV–vis-NIR spectroscopy

The absorption of all dispersion solutions (MWNT/chitosan, MWNT/chitosan-glycerin and MWNT/chitosan-PEGDE) was examined from 300–1000 nm using a Cary® 500 UV–vis-NIR spectrophotometer. All above dispersion solutions (0.1 mL) were diluted in a small vial (20 mL) by Milli-Q water (15 mL). The dispersion solutions were taken into a quartz cuvette (1-cm path length) and spectra were measured at estimated 21 °C.

2.3.2. Electrical conductivity

The electrical resistance of three BP membranes was measured at room temperature (21 °C and 45% RH) through using the two-point probe method [29]. All BP samples were prepared via cutting them into small thin strips of 4 mm × 30 mm. Thicknesses of all samples were also determined with a Mitutoyo Digital Micrometer, and width was estimated by optical microscope. The membrane strips were then placed on glass slides using double-sided tape. Both Silver paint (SPI-paint 05002-AB) and copper tape (3 M #1181 electrical tape) were used to ensure low contact resistance. The sample-electrode contacts were located under standard compression (10^5 Pa) by using bull clips. Another glass slide was clasped over the membrane using bull clips to be sure continuous connection during the analysis.

An arbitrary waveform generator (Agilent 33220A) was utilize to apply a stepwise DC-voltage ramp from − 0.1 to + 0.1 V. The current (I) and voltage (V) responses were estimated using a digital multimeter (Agilent 34410A). Measurements were restated for at least five channel lengths from 0.5–3 cm. Electrical resistance as a function of changed length was measured using Ohm's law. This was repeated minimum of five different lengths for each sample to determine the resistance.

2.3.3. Contact-angle measurement

The hydrophobicity of membrane is commonly determined by