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Improving the performance of polyamide reverse osmosis membrane by incorporation of modified multi-walled carbon nanotubes



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ABSTRACT

Polyamide reverse osmosis membranes incorporating carboxy-functionalized multi-walled carbon nanotubes (MWNTs) were prepared by interfacial polymerization of metaphenylene diamine and trimesoyl chloride. The pristine MWNTs were pre-treated with mixed acids before being modified with diisobutryl peroxide to enhance their dispersity and chemical activity. The prepared nanocomposite membranes had a 100–300 nm skin layer and the modified MWNTs were embedded within the skin layer, which was confirmed by scanning electron microscopy and transmission electron microscopy. The surface of the nanocomposite membrane was shown to be more negatively charged than bare polyamide membrane. It was shown that with an increase in the carbon nanotube loading in the membrane, the membrane morphology changed distinctly, leading to a significantly improved flux without sacrificing the solute rejection. Meanwhile, the nanocomposite membranes showed better antifouling and antioxidative properties than MWNT-free polyamide membranes, suggesting that the incorporation of modified MWNTs in membranes is effective for improving the membrane performance.

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1. Introduction

Reverse osmosis (RO) processes are economical for the production of potable water from brackish water or seawater. These processes have several advantages over traditional production methods, such as high permeation flux, ease of operation, minimal chemical addition, and low energy requirement [1,2]. Currently, over half of the 15,000 desalination plants worldwide are using RO processes, and the growth of RO desalination capacity is expected to continue [3–5].

Although many RO plants have been established by now, research effort to increase the membrane flux is still needed. Based on this demand, the present major researches focus on developing and fabricating high-flux membranes. Several reviews covering different aspects of thin film composite (TFC) RO membranes have been published previously [6–9]. Most of these researches concentrated on either the optimization of membrane fabrication processes or the exploitation of new monomers and additives. For example, an aqueous solution composed of poly(vinyl alcohol) and a buffer solution was used in post-treatment during the preparation of TFC membranes to improve their physical properties (e.g., improved resistance to abrasion) and to enhance flux stability

[10,11]. Additionally, Zhou et al. [12] fabricated RO membranes with excellent performance (both flux and rejection) using newly synthesized functional monomers (e.g., m-phenylenediamine-5-sulfonic acid and 5-chloroformoxy-isophthaloyl chloride). In our previous work [13], phase transfer catalysts, alcohols, and phenols were added to metaphenylene diamine (MPD) solution during membrane formation. The presence of these additives changed the micro-structure of the separation layer, and the performance of the resultant composite membrane can be improved to some extent. However, empirical evidence suggested that increasing the water permeability of these RO membranes further without sacrificing selectivity is quite challenging [14].

Even enhanced water flux is preferable in membrane application, however, fouling is a more severe issue needed to be addressed. Lots of strategies have been proposed to develop antifouling RO membranes in recent years, including the selection of new monomers, improvement of fabrication process, surface modification of RO membrane by physical and chemical methods as well as the hybrid organic/inorganic RO membrane [15].

With the advancement of nanotechnology nowadays, porous nano-materials may be produced as a new class of additives, especially zeolite [16–21] and carbon nanotubes [22–27], and this is expected to provide a chance to further improve the performance of RO membranes. Mixed matrix membranes were developed to take advantage of the tempting properties of nano-materials [28,29] and this method was successfully

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introduced to the area of RO membranes by Jeong et al. [21], who used zeolite nanoparticles in the preparation of mixed matrix membranes and managed to double the water flux of RO composite membranes without affecting the salt rejection. In addition, according to Kalra's simulation [23], due to the super-hydrophobic and tubal structure of carbon nanotubes, the water flux can be enhanced by orders of magnitude if the carbon nanotubes are incorporated into mixed matrix membranes [24]. Before long, these simulation predictions were tested in experiments by Holt et al. [24], who used a silicon nitride matrix, and Hinds et al. [25], who used a polymer matrix. Yu et al. [26] prepared vertically aligned CNT membranes and declared that the prepared membrane showed unparalleled gas permeability and could be used to separate larger molecules from smaller ones. However, these membranes are still not suitable to desalinate sea water because it is quite difficult to produce CNTs with a diameter smaller than that of a water molecule. Even so, aligned CNT membranes have been predicted to be the most promising so far for increasing the water permeability without sacrificing the rejection [1]. This motivated us to incorporate CNTs into the separation layer of polyamide composite membrane prepared by interfacial polymerization to shorten the water transport route. In our previous report [27], the acidifying MWNTs were incorporated in the polyamide layer of RO membranes with a slightly improved dispersion, resulting in a prominent increase in water flux but an accompanying decrease in salt rejection. Amini et al. [30] fabricated novel thin film nanocomposite (TFN) forward osmosis membranes using functionalized MWNTs, which have an obvious impact on the hydrophicity, morphology and forward RO performance of the polyamide/MWNTs membrane. Very recently, Dumée et al. [31] fabricated ultra-thin membranes on top of porous CNTs buckypapers and showed a new approach for exploiting CNTs in membrane applications.

In this work, multi-walled carbon nanotubes (MWNTs), which were grafted with abundant long chains of aliphatic acid to greatly facilitate the compatibility of MWNTs in the polyamide layer, were used to improve several properties of RO membranes. In view of the chemical inertness of the pristine MWNTs and the difficulty of dispersion, the MWNTs were chemically modified before being embedded into the membranes. The chemically modified MWNTs could be readily dispersed and could serve as a negatively charged one-dimensional molecular tunnel in the membranes. The separation performances of the membranes were investigated, and the improved antifouling and antioxidative properties of the membranes were demonstrated.

2. Experimental

2.1. Materials

The pristine MWNTs (length 1–5 μm , diameter 20–40 nm and inner diameter 5 nm, purity 95%) were manufactured by Nanotech Port Co. Ltd, Shenzhen, China. Sulfuric acid, nitric acid, and n-hexane were purchased from Fisher Scientific, Canada. 1, 3-Phenylenediamine (MPD) and trimesoyl chloride (TMC) were obtained from Sigma-Aldrich Chemical Company, USA; sodium chloride (NaCl) was purchased from EMD Chemicals Incorporation, Germany. All these chemicals were of analytical grade and were used directly. The polysulfone support membrane (molecular weight cut-off $\sim 30,000$ Da, thickness 52 μm , pure water flux 229 $\text{L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$ at the applied pressure of 1 bar and the temperature of 25 $^{\circ}\text{C}$) was supplied by the Development Center for Water Treatment Technology, Hangzhou, China.

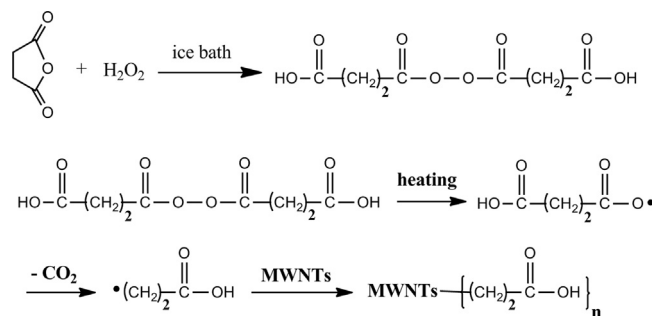


Fig. 1. Chemical scheme for preparing carboxylic MWNTs.

2.2. Preparation and characterization of modified MWNTs

Pristine MWNTs were first treated with mixed acid ($\text{H}_2\text{SO}_4/\text{HNO}_3=3/1$, v/v) by reflux at 80 $^{\circ}\text{C}$ for 6 h and then filtered with microfiltration membranes (pore size 0.2 μm , Whatman). The MWNTs were then rinsed repeatedly with deionized water until it was acid free, dried in a vacuum oven at 70 $^{\circ}\text{C}$, and then dispersed in dimethyl formamide (DMF) and reacted with diisobutyl peroxide (synthesized using butanedioic anhydride and hydrogen peroxide in an ice bath for several hours) in the reflux device at 80 $^{\circ}\text{C}$ for 10 days. They were then washed with an adequate amount of DMF, and carboxylic MWNTs (MWNTs-COOH) were obtained by reduced pressure filtration. Finally, the functionalized MWNTs were dried in the oven [32]. The chemical scheme for preparing carboxylic MWNTs is shown in Fig. 1.

The morphologies of MWNTs and modified MWNTs were directly observed by scanning electron microscopy (SEM, JSM-5610LV). The structure was characterized by infrared radiation (IR, Bruke-Vector 22) and Raman spectroscopy (LabRAM HR UV) at 632.8 nm.

2.3. Preparation of RO membrane with modified MWNTs

Certain amount modified MWNTs were first dispersed in 100 mL MPD aqueous solution (2%, w/v), under ultrasonic treatment, and then the polysulfone substrate membrane was immersed in the solution for 30 s. The membrane was pulled up slowly from the MPD solution and excess diamine solution was removed from the membrane surface. The polysulfone substrate was then covered with moderate volume of TMC solution (0.1%, w/v) in n-hexane for 10 s to induce a thin polymer layer on the substrate by the interfacial reaction. The newly formed composite membrane was post-treated in an oven at 60 $^{\circ}\text{C}$ for 20 min and then stored in NaHSO_3 solution (1 wt%) to prohibit microbial growth. Note that the membrane marked as 0.1% referred to the membrane prepared with an aqueous solution in which the content of carboxylic MWNTs with respect to $\text{DMC}+\text{H}_2\text{O}$ was 0.1%.

2.4. Characterization of RO membrane with modified MWNTs

The surfaces and cross-sections of the nanocomposite membranes were observed under SEM (JSM-5610LV) and transmission electron microscopy (TEM, JEM-1230, JEOL). An Anton Paar (Graz, Austria) SurPASS streaming potential instrument was used to measure the zeta potential on the membranes. Measurements were conducted with a 10 mM NaCl electrolyte solution over a range of pH values (from 2 to 9) using an automated titration unit. The Fairbrother–Mastin approach was used to transform the potential-versus-pressure data into zeta potential.

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