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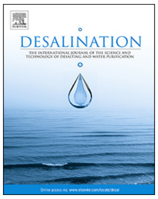

Salt rejection behavior of carbon nanotube-polyamide nanocomposite reverse osmosis membranes in several salt solutions

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ABSTRACT

The present paper describes the desalination performance of reverse osmosis (RO) membranes of multi-walled carbon nanotube-polyamide complex (CNT-PA) and commercial polyamide membranes in NaCl, $MgCl_2$, $MgSO_4$ and Na_2SO_4 aqueous solutions. The permeate flux, salt rejection, and salt flux were determined in a cross-flow experiment. The CNT-PA and commercial RO (PA) membranes (SWC5, Nitto Denko Co.) showed 96.0% and 99.7% salt rejection, respectively, for 0.2% NaCl aqueous solution at 0.7 MPa. The calculated salt flux was $0.38\ g \cdot m^{-2} \cdot h^{-1}$ (CNT-PA) and $0.07\ g \cdot m^{-2} \cdot h^{-1}$ (SWC5). The salt rejection increased with increasing running pressure and decreasing salt concentration. The zeta potential measurement of CNT-PA demonstrated that it is negatively charged due to the presence of CNT. Accordingly, it showed salt rejection performances against the four salt solutions ($Na_2SO_4 > MgSO_4 > NaCl > MgCl_2$) that differed from that of the usual PA membranes ($Na_2SO_4 > MgSO_4 > MgCl_2 > NaCl$). These data are explained based on the Donnan model (CNT-PA) and steric hindrance pore model (SWC5), except for the case of chlorides under low-flux or high ionic strength conditions, where the diffusion and molecular size exclusion of the salts dominate over their mas-transport. Positron annihilation lifetime spectroscopy (PALS) enabled the estimation of the pore diameters of these membranes: 0.55 nm (CNT-PA) and 0.58 nm (SWC5).

1. Introduction

Worldwide industrialization and the explosive population increase have caused serious problems concerning water. For example, it is estimated that > 1.1 billion people do not have access to clean drinking water and 2.6 billion have little or no sanitation [1,2]. The desalination of saline water (i.e., brackish water, sea-water and wastewater) by reverse osmosis (RO) membranes is a very important technology for producing large amounts of clean water [3,4]. Remarkable progress has been made in the fabrication of such membranes, but challenges remain regarding the production of reliable RO membranes with anti-fouling properties, high mechanical strength, high tolerance to chlorine attack, and minimal thickness of the membrane's barrier layer to provide a high flux [5,6].

'Fouling' is contamination of the membrane by organic and inorganic matter [7–9]. In an analysis of an RO membrane taken from a seawater desalination plant on the northern coast of the Canary Islands, after 4 years of operation [9], the fouling layer consisted of particulate matter embedded in an apparently amorphous matrix that was unevenly distributed over the membrane surface, with the greatest accumulation in the valley area. The inorganic foulants consisted mainly of calcium carbonate, calcium sulfate, strontium sulfate, barium sulfate, calcium fluoride and calcium phosphate, whereas the main organic substances were proteins, polysaccharides and humic compounds, attributable to biofouling [11]. Organic fouling and biofouling, alone or in combination, induce the most serious problems in RO and nanofiltration (NF) membrane operations [11,12]. Foulants formed on a membrane increase the filtration resistance, and therefore higher pressure (and a larger amount of energy) is required to produce the same amount of pure water as that produced before the fouling. For the reduction of fouling on RO membranes, pretreatments such as chlorination, ozonation, UV radiation, or other methods are generally required prior to RO processes [10].

Several attempts have been made to improve the fouling resistance of RO and NF membranes. RO membranes, modified by a radical grafting of acrylic and vinyl monomers, were found to be completely

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regenerated by cleaning (rinsed first with base [pH = 12] and then with acid [pH = 2] for 1 h each) after fouling [13]. An RO membrane modified by polyelectrolyte [poly(sodium 4-styrenesulfonate) and poly (allylamine hydrochloride)] was shown to suppress the fouling by bovine serum albumin (BSA) [14]. Another RO membrane, modified by polyvinyl alcohol, showed improved fouling resistance to model foulants (BSA, sodium dodecyl sulfate [SDS], dodecyltrimethyl ammonium bromide [DTAB]) in addition to enhanced stability against chlorine [15]. The anti-fouling characteristics of RO membranes modified by 2-hydroxyl methacrylate-*co*-perfluorodecyl acrylate copolymer films against sodium alginate was improved [16].

We developed a high-performance reverse osmosis (RO) nanocomposite membrane using multi-walled carbon nanotubes (MWCNTs) and fully aromatic polyamide (PA) [17,18]. The membrane was successfully prepared by interfacial polymerization in a simple process. The effect of the MWCNTs on the chlorine resistance, antifouling and desalination performances of the nanocomposite membranes was studied, and the results indicated that a suitable amount of MWCNTs in PA, i.e., 15.5 wt%, not only improved the membrane performance in terms of permeate flow and antifouling, but also improved the chlorine resistance of these membranes. It was also reported that the incorporation of 0.1 wt% of MWCNTs to PA also improved the antifouling [19]. We also demonstrated efficient antifouling and low protein adhesion of MWCNT/PA membranes by combining experimental and theoretical studies [20].

Also, the ultrathin, flexible and highly water-permeable nanostructured amorphous carbon-based membranes were prepared by plasma high-power impulse magnetron sputtering [21]. This membrane (hereafter abbreviated as the a-C [amorphous carbon] membrane) has shown beneficial characteristics that make it a potential alternative to the current polymeric technology used in RO processes.

Although the salt rejection and permeate flux for sodium chloride (NaCl) solution of our RO nanocomposite membranes (hereafter abbreviated as CNT-PA membranes) and a-C membranes have been clarified [17,19,21], the further investigation of the salt rejection and permeate flux against several salt solutions such as magnesium chloride ($MgCl_2$), magnesium sulfate ($MgSO_4$), and sodium sulfate (Na_2SO_4) is required in order to fully determine the fundamental characteristics of the membranes and toward the application of the membranes at practical desalination plants. The present paper focused on the desalination characteristics of CNT-PA membranes for four salt solutions (NaCl, $MgCl_2$, $MgSO_4$, Na_2SO_4) in comparison with those of commercial RO membranes and lab-synthesized plain polyamide (PA) membranes.

2. Experimental

2.1. Membranes and materials

The laboratory-made plain PA membranes and CNT-PA membranes were prepared by interfacial polymerization between MWCNT-dispersed *m*-phenylenediamine (MPD) and trimesoyl chloride (MEC) on a porous polysulfone (PSf) substrate as described in our previous report [17]. Three pieces of plain PA membrane were prepared in separate experimental runs and used in the water permeation and desalination experiment (hereafter they are designated as PA-L1, PA-L2 and PA-L3, respectively). Commercially available RO (PA) membranes (SWC5; Nitto Denko, Japan and HDAR; GE, USA) were also used. The values of static water contact angle of CNT-PA, lab-synthesized PA and SWC5 were 40°, 50° and 30°, respectively [17]. The amorphous carbon membrane (a-C) was formed on a porous polymer substrate by plasma high-power impulse magnetron sputtering [20]. Salt solutions were prepared by dissolving reagent-grade chemicals (sodium chloride [NaOH], magnesium chloride [$MgCl_2$], magnesium sulfate [Mg_2SO_4], sodium sulfate [Na_2SO_4]) into de-ionized water. The salt concentration was 0.2% (2000 ppm) in each salt solution.

2.2. Water permeation and desalination tests

Water permeation and salt rejection performance of the membranes were evaluated by laboratory scale cross-flow filtration system shown in Fig. S1. Circular membranes with an effective surface area of 3.46 cm^2 were placed in a transparent polymethyl methacrylate (PMMA) cross-flow cell. The cross-flow tests were carried out using the transmembrane pressure of 0.7 MPa while maintaining the feed water flux at 500 mL/min along the surface of the membrane.

For permeated water, the flux (J) and salt rejection (R) were determined. The flux J ($Lm^{-2}h^{-1}$) at a given pressure (in MPa) was estimated using observed permeate volume per unit time according to Eq. (1):

$$J = \Delta V / A\Delta t \tag{1}$$

where ΔV is the permeate volume over time (Δt) and A is the effective membrane surface area (3.46 cm^2). The electrical conductivity of the feed and permeate water was measured by a conductivity meter (LAQUAact ES-7; Horiba Scientific, Japan). The salt rejection (R) was estimated according to Eq. (2):

$$R = (1 - C_p/C_f)100 \tag{2}$$

where C_p and C_f are the salt concentrations of permeate and feed water, respectively. The observed values of J and R were practically changed with time, especially at the beginning of the experiment. The J and R values were determined after they became stable (it required several weeks to observe stable values, in some cases).

For the evaluation of the membrane performance, the salt flux J_s ($g\,m^{-2}\,h^{-1}$) defined by Eq. (3) was evaluated. Large permeate flux and small salt flux are preferable for the membrane.

$$J_s = J \cdot C_p \tag{3}$$

2.3. Positron annihilation lifetime spectroscopy (PALS) measurement

PALS measurement was carried out at room temperature (20° ± 1 °C) using a PALS200A system (Fuji Imvac Co., Japan). The incident positron energy was 1 keV, and the time resolution of the spectrometer was < 300 ps. Sample membranes measuring 15 mm × 15 mm were used. Four samples were loaded simultaneously on the sample holder. In each experimental run, Kapton film (standard) was loaded on one of four parts of the sample holder; the membrane samples were loaded on the remaining three parts (three samples could be examined in each experiment, at maximum). All the spectra were analyzed in three lifetime components and a pore-size estimation was performed using the software (PALS-2 data analysis) included in the PALS system; this analysis is essentially based on the method established by the AIST (National Institute of Advanced Industrial Science and Technology) group [22].

3. Results and discussion

3.1. Water permeation and desalination of the PA membrane (SWC5) and CNT-PA membrane

The observed permeate flux (J), salt rejection (R) and salt flux (J_s) of the SWC5 membrane for 0.2% salt solutions (NaCl, $MgCl_2$, $MgSO_4$ and Na_2SO_4) are plotted as a function of transmembrane pressure (0.3–0.9 MPa) in Fig. 1. The J value increased monotonically with increasing transmembrane pressure for all of the salt solutions (Fig. 1a). Each curve shows the threshold pressure (x-intercept at $J = 0$), which corresponds to the osmotic pressure. In the case of the 0.2% NaCl solution (hereafter abbreviated as NaCl), for example, the osmotic pressure is estimated to be 0.17 MPa using the equation of $\pi V = 2nRT$, where π, V, n, R and T denote the osmotic pressure (atm), the volume of solution (L), the dissolved amount of NaCl (mol), the gas constant and