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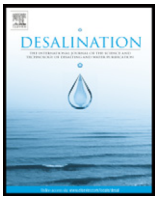

Fouling and rejection behavior of carbon nanotube membranes ☆

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HIGHLIGHTS

- Vertically aligned carbon nanotube (VA-CNT) membranes were fabricated.
- Fouling and rejection of VA-CNT membrane were compared with those of UF.
- The VA-CNT membranes were modified by graft polymerization method.
- The surface modification improves on performances of VA-CNT membranes.

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ABSTRACT

In recent years, there has been a growing interest in nanostructure membranes made of vertically aligned carbon nanotubes (VA-CNT) due to their potential of high water permeability. Nevertheless, membrane fouling is one of the most critical issues in these VA-CNT membranes. Accordingly, this study mainly focused on understanding of membrane fouling of VA-CNT membranes, which were prepared by thermal chemical vapor deposition (CVD) technique. Surface modification by graft-polymerization of methacrylic acid (MA) was attempted to not only retard membrane fouling but also improve solute rejection. The resistance-in-series model was applied to characterize the properties of fouling layers. BSA (bovine serum albumin) was used as the model foulant. Results indicated that the VA-CNT membranes had higher fouling propensity than polymeric membranes. After surface modification, however, irreversible fouling was significantly reduced in the VA-CNT membranes, which was attributed to an increase in hydrophilicity and surface charge. The rejection of BSA by VA-CNT membrane also increased after surface modification, suggesting that the surface charge played an important role in the rejection of charged molecules.

1. Introduction

Recently, carbon nanotube (CNT) membranes have been investigated by many researchers as a novel membrane technology for water treatment [1–3]. When CNTs are used as pores of membranes, they appear to allow fast fluid flow due to their strong hydrophobicity [4–6]. Due to its potential, there are a lot of possible applications: programmable transdermal drug delivery of nicotine [7], biomolecule separation [8], chemical separation [9], DNA translocation [10], water desalination [11], natural protein cannel mimicking and gas separation [12]. Nevertheless, relatively few studies have been done in the development of CNT membranes for water treatment.

There are several issues in the application of CNT membranes for water treatment. One of them is fouling of CNT membranes. Since these membranes are hydrophobic, a rapid membrane fouling is anticipated [13–15]. Another issue is relative low rejection of ions and small organics by CNT membranes. Multi-wall CNTs generally have large inner diameters (3 ~ 10 nm), which are not sufficient to reject ions. Even single-wall CNTs (~1 nm) may not be enough to reject ions [11,16].

Accordingly, this study focused on i) understanding of fouling and rejection of CNT membranes; and ii) resolving these problems by surface modification. A theoretical model was applied to analyze the experimental data. Graft polymerization using methacrylic acid (MA) was also attempted to reduce fouling and increased rejection. The performance of the modified membranes was compared with untreated CNT membrane and commercially-available polymer membranes in terms of fouling properties and solute rejection.

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Table 1
Summary in characterization of UF and VA-CNT membranes.

Category of membranes	Materials	Average pore size (nm)	Density (pores/cm^2)	Membrane thickness (μm)	Wettability (cosΘ)	Roughness (nm)
UF membrane	Polysulfone	6.43 ± 2.49	8.8×10^{10}	0.1 ~ 0.4	0.349	5.77 ± 0.24
VA-CNT membrane	CNT/epoxy composite	4.87 ± 0.87	6.8×10^{10}	200 ± 50	0.012	21.3 ± 5.21

2. Materials & methods

2.1. VA-CNT membranes & UF membranes

The vertical aligned CNT membrane was made by thermal chemical vapor deposition (thermal CVD) [17,18]. At 800 °C, Multi-walled CNT (MWCNT) was grown on substrate Fe/Al_2O_3/Si at the condition, which is C_2H_2 and CH_4 gas flowing. After preparation of CNT forests, they were separated from the substrate and filled by epoxy resin. Epoxy was chosen as appropriate material to fill the space among CNT due to its high mechanical strength required for high pressure membrane filtration. In addition, epoxy is hydrophobic to have high attractive interaction with CNT. After curing with sufficient time, the CNT-epoxy composites were cut by microtome (HM 340 E, MICROM Lab., Germany).

Commercially available ultrafiltration membranes (UE4040, Woongjin Chemical, Korea) were also used for comparison, were kindly supplied by Woongin Chemical Co Ltd (Korea). The membranes were made of polysulfone. The membranes were washed several times with deionized (DI) water and dipped in DI water overnight before use in order to remove surfactant.

2.2. Membrane characterization

2.2.1. Structure of membranes

Table 1 shows fundamental characteristics of membranes, which were measured by various methods. The CNT/epoxy composites were examined using field emission scanning electron microscope (FE-SEM, S-4700, Hitachi, Japan). The size of the outer and inner diameter of CNTs was measured using scanning electron microscopy (HC200-Cu, Electron microscopy sciences, USA) and transmission electron microscopy (TEM, JEM-2100, JEOL, Japan). The average of diameter was analyzed by TEM images. In addition, microstructure and pores of the VA-CNT membrane surface were analyzed by TEM (H7600, Hitachi, Japan), which was prepared by the ultra-microtome (UC6, Leica, Germany).

The VA-CNT membrane thickness was measured using a micrometer. The effective area of CNT membrane was measured by imaging of CNT membranes and using area calculation program (Dinocapture, Dino Lite, Taiwan). A wettability of both membranes was measured by contact angle meter (a Krüss DSA 100 goniometer, Krüss GmbH, Germany) using sessile drop method. Membrane surface roughness was measured using SPM (scanning probe microscope, XE-100, Park system, USA).

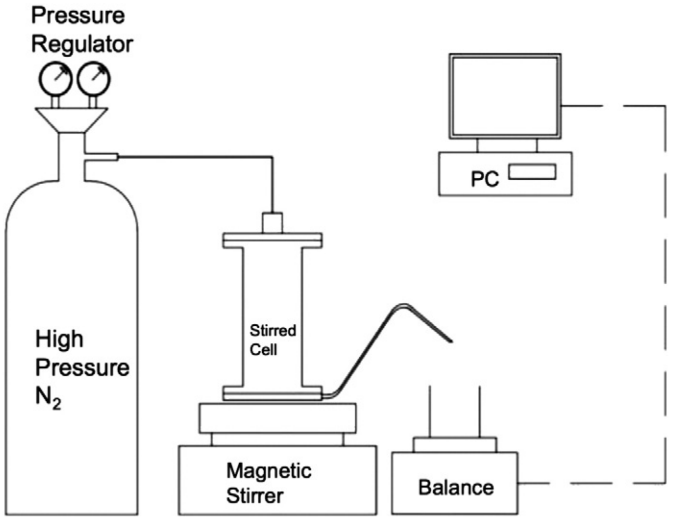

Fig. 1. Schematic diagram of dead-end stirred cell filtration system.

2.2.2. Surface characteristic of membrane

Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR; Nicolet spectrophotometer 5700, Thermo Electron Corp., MA) was used for obtaining chemical and elemental information of membrane surface. In order to analyze the quantitative elemental composition of membrane surfaces, X-ray photoelectron spectroscopy (XPS) was used.

2.3. Fouling characteristic

2.3.1. Resistances in series model

To analyze the characteristics of membrane fouling, the resistance-in-series model was applied [19]:

$$J_o = \frac{\Delta P}{\mu(R_m + R_{ir} + R_r)} \tag{1}$$

where, J_o is a pure water flux, μ is the dynamic viscosity, R_m is the membrane resistance, ΔP is the trans membrane pressure, R_{ir} is the irreversible fouling resistance, and R_r is the reversible fouling resistance.

2.3.2. Filtration system

The experiments were performed in batch mode using a stirred cell as shown in Fig. 1. The stirred cell (model 4750, Steriltech™, USA) was made of stainless steel. The diameter of the stirred cell was 49 mm and the working volume was 300 ml. The stirred cell was specially designed to test small membranes having an effective area less than

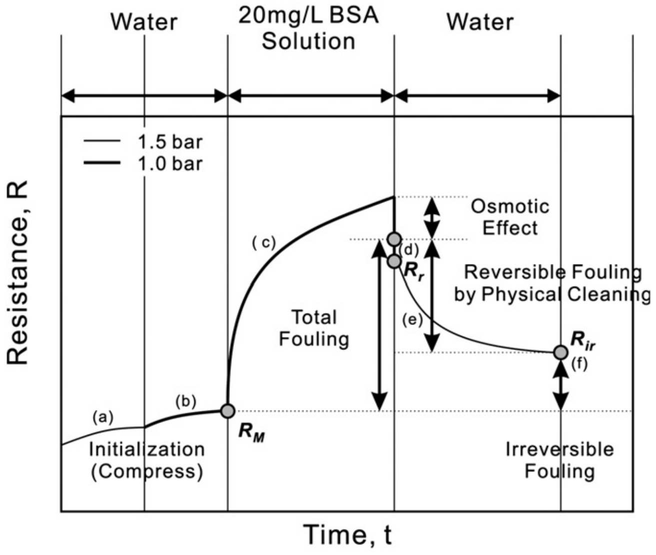

Fig. 2. Filtration protocol for accelerated fouling steps: (a) to minimize compaction effects, DI water was passed through the membrane at the TMP of 1.5 bar for 15 min, (b) initial water permeability at 1 bar, (c) after the cell was emptied, 20 mg/L BSA was filled and the 1 bar was re-pressurized, and the filtration was continued until 25 g and 2.5 g of permeate were collected, UF and CNT respectively. (d–e) the cell was emptied and refilled with DI water. And then, washing the membranes at high stirred speed (physically wash) for 30 min, (f) the water permeability was again measured using DI water.