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High performance and antifouling vertically aligned carbon nanotube membrane for water purification

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ABSTRACT

A vertically aligned carbon nanotube (VA CNT) membrane created from the successful fusion of nanotechnology and membrane technology has been stated to be a next generation membrane due to its fast water transport and antimicrobial properties. Although previous studies of the VA CNT membrane reported the potential for fast water transport or desalination by molecular dynamics simulation, this study is the first to report on the feasibility of using the VA CNT membrane for water purification. The VA CNT membrane (4.8 nm of pore diameter and 6.8×10^{10} #/cm^2 of pore density) was fabricated and its flux, rejection performance, and membrane biofouling tendency were evaluated in comparison to the commercial ultrafiltration (UF) membrane. The VA CNT membrane appeared to have a water flux approximately three times higher than the UF membrane and water transport approximately 70,000 times faster than conventional no-slip flow. This higher flux was peculiarly observed in water, the most hydrophilic solvent, while other solvents showed that permeate flux decreased with higher viscosity. The rejection property of the VA CNT membrane as examined by the MWCO measurement was similar to the commercial UF membrane. Additionally, the VA CNT membrane showed better biofouling resistance with approximately 15% less permeate flux reduction and 2 log less bacterial attachment than the UF membrane. This study reports the high potential of the VA CNT membrane with antifouling property in the water purification process.

1. Introduction

Water scarcity has emerged as one of the most serious global challenges which threatens over one-third of the world's population [1]. Membrane technology used for water treatment has been consistently developed to alleviate the water scarcity problem [2]. However, this membrane technology has some drawbacks such as high energy consumption and membrane fouling [3]. Although energy consumption has been decreased over the past decade, the membrane based water treatment is still an energy-intensive technology. For example, although reverse osmosis (RO) membrane energy consumption for desalination has decreased from 8.0 kWh/m^3 to 3.4 kWh/m^3, it is still higher than the theoretical limit of 1.06 kWh/m^3 (assuming 35,000 mg/L of seawater with the typical 50% recovery) [2,3]. Additionally, membrane fouling such as crystalline fouling, organic fouling, colloid fouling, and biofouling results in low efficiency of membrane performance, eventually leading to high operating and maintenance costs [4–6].

Various approaches to reduce energy consumption and prevent membrane fouling have been researched. One approach to develop the high performance membrane is limited to using conventional polymer membranes due to the 'trade-off' phenomenon between permeability and selectivity [7,8]. Another approach is to make an antifouling membrane where the surface is modified to be more hydrophilic, smoother, and more negatively (or neutrally) charged [9]. In addition, the act of embedding antibiotics in the active layer of membranes has been studied [10,11]. To satisfy both approaches, a novel membrane that combines nanotechnology and membrane

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technology has been suggested [12,13]. Among various nanomaterials, carbon nanotubes (CNTs) have been utilized due to their fast water transport and antimicrobial properties. These properties are required in order to make a high performance membrane with antifouling property [14–16].

Among various kinds of CNT membranes, vertically aligned (VA) CNT membrane has been studied remarkably. Previous studies of the VA CNT membrane investigated analysis flow properties [17–19] or evaluated the feasibility for desalination technology by molecular dynamics (MD) simulation [20,21]. The pore diameters of VA CNT membrane reported in previous studies were much larger than 1 nm (hydrated radius of Na^+ ion: 0.716 nm, Cl^- ion: 0.664 nm [22–24]). Since it is obviously difficult to remove salt ions due to their size, they are not enough for the desalination process. Despite the difficulty of using the current VA CNT membrane for the desalination process, the VA CNT membrane may be useful in the water purification process where the UF membrane is required.

The objective of this study is to evaluate the performance of fabricated VA CNT membranes in terms of flux and rejection compared to commercial UF membranes with a similar pore size. Pore size, pore density, hydrophilicity, and surface roughness of the fabricated VA CNT membranes are measured by TEM images, SEM images, a contact angle analyzer, and atomic force microscopy, respectively. The flux and rejection of VA CNT membranes are evaluated by utilizing various solvents and diverse nanoparticles, respectively. Furthermore, the biofouling tendency of the VA CNT membrane is performed in a lab-scale cross-flow membrane system.

2. Materials and methods

2.1. Synthesis of VA CNT membranes

VA CNTs were synthesized onto a Si wafer from a Fe catalyst using the water-assisted thermal chemical vapor deposition method [25,26]. An 18 nm thick aluminum sheet was used as a buffer layer between the Si wafer and the Fe catalyst to prevent catalytic diffusion. The temperature of the furnace was ramped up 810 °C in 1 min. High-purity acetylene and Ar gas were inserted into the furnace as the carbon precursor and carrier gas, respectively. During the VA CNTs' growth process, a small and controlled amount of water vapor acts to promote and preserve catalytic activity [27]. The grown VA CNTs were analyzed by FE-SEM (field emission scanning electron microscope, S-48000, Hitachi, Japan).

Fig. 1 shows the schematic of the manufacturing of the VA CNT membrane. Synthesized VA CNTs were transferred from a Si wafer to a tape (Fig. 1(a)) and then are directly fixed onto the bottom of the cast. As shown in Fig. 1(b), epoxy resin (Epon 828, Miller-stephenson Inc., CA) filled up the vacant areas of the VA CNTs under vacuum (about 0.1 bar). Epoxy was selected due to the simple structure that can penetrate VA CNTs vacancy. After the epoxy-VA CNTs matrix hardened, it was cut by a microtome (HM 340 E, MICROM Lab., Germany) at 40 °C under a halogen lamp to make a homogeneous VA CNT membrane (Fig. 1(c)).

2.2. Characterization of VA CNT membrane

The manufactured VA CNT membrane was characterized by measuring the pore size, pore density and thickness as well as by analyzing the membrane surface properties (i.e. hydrophilicity and roughness). The pore size was determined using the average values of the synthesized VA CNTs' inner diameter. The inner diameter of the VA CNTs was measured by TEM (transmission electron microscopy, JEM-2100, JEOL, Japan) after dispersion into NMP (N-methylpyrrolidone) and then drying on the grid (HC200-Cu, Electron microscopy sciences, USA). Pore density and surface morphology were analyzed by TEM (LIBRA 120, Carl Zeiss, Germany) and the sample was made about 20 nm of thickness by an ultramicrotome (MTX, RMC, USA). The pore size and pore density were determined by measuring 100 CNTs from more than 50 TEM images. Thickness was measured by utilizing the electronic micrometer (Schut Geometrical Metrology, Groningen, Netherlands). The effective area of the VA CNT membrane was about 0.1 cm^2 as calculated by the image program (Dinocapture, Dino Lite, Taiwan). A commercial UF membrane (UE4040, Woongjin Chemical, Korea) was selected to compare with the VA CNT membrane since both pore sizes were similar. The pore size, pore density and surface morphology of the commercial UF membrane were analyzed by FE-SEM.

Membrane surface properties such as hydrophilicity and roughness were measured by the contact angle analyzer (DSA 100, KRÜSS, Hamburg, Germany) with the captive bubble method [28,29] and a scanning probe microscope (SPM; SPA-400, Seiko Instrument, Japan), respectively. At least five measurements were made for both the contact angle analysis and the SPM measurement to examine reproducibility, where the average value with standard deviation was reported. Surface morphology of the VA CNT membrane was analyzed by FE-SEM. Additionally, mechanical strengths of both the VA CNT membrane and the UF membrane were measured using a universal testing machine (Lloyd LR-10K). The dumbbell specimens were prepared using the ASTM standard D638 (Type V specimens dog-bone shaped samples). The gage length and cross-head speed were 15 mm and 10 mm min^{-1}, respectively.

2.3. VA CNT membrane performance

Membrane performance experiments such as flux measurement and rejection test were conducted in the dead-end membrane filtration system pressurized with N_2 gas (Fig. S1, SI).

Prior to the performance evaluation of the VA CNT membrane, control experiments were carried out to examine whether a solvent penetrates through the CNTs on the VA CNT membrane. Two control samples were prepared (Fig. S2, SI). One sample was made of only epoxy resin, which is the filler of the VA CNT membrane and whose shape was the same as the VA CNT membrane. The other was the one-side blocked VA CNT membrane made by cutting only the top part of the epoxy-VA CNTs matrix by the microtome in the fabricating process of VA CNT membranes. In this case, one side of the VA CNT membrane was opened and the other side was presumed to be blocked with partially protruded capped VA CNTs and epoxy resin. SEM-EDS analysis was provided to elucidate whether CNT caps protruded from the membrane surface. The ratios of C/O were as follows: VA CNT membrane sample (8.4), one-side opening sample (5.5), and epoxy resin sample (4.8) in decreasing order (Table S1, SI). The larger C/O ratio of the one-sided opening sample than that of the epoxy resin sample indicates that the capped nanotubes of the one-side opening samples partly protruded from the surface of the one-sided opening sample. Although the capped nanotubes partly protruded from the surface, no flux was observed under harsher conditions (20 bar for 18 h) (cf. water flux was measured under 2 bar for 5 min). In addition, SEM analysis was performed to examine if the gaps between CNTs were well filled in the VA CNT membrane; no gap between VA CNT and epoxy resin was observed in the VA CNT membrane (Fig. S3, SI). These results show that the solvent dominantly flowed through the CNTs on the VA CNT membrane.

Permeate flux of the VA CNT membrane was obtained by measuring the weight of the permeate for 5 min and comparing