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Potential and performance of a polydopamine-coated multiwalled carbon nanotube/polysulfone nanocomposite membrane for ultrafiltration application

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ABSTRACT

The addition of multiwalled carbon nanotubes (MWNTs) as inorganic fillers is well known to improve membrane performance for water desalination. Most MWNTs are treated by acid treatment to enhance their hydrophilicity before their applications in membranes. However, acid treatment leads to structural damages of the MWNT wall. An alternative way of improving the hydrophilicity of MWNTs is through coating of polydopamine (Pdop), where MWNT wall damage is avoided. In the present study, polydopamine-coating on MWNT is carried out at pH 8.5 and at room temperature (23–25 °C). Different concentrations (0.1–0.5 wt%) of Pdop-MWNTs were incorporated into polysulfone (Psf) membranes fabricated by phase inversion. The results showed that the incorporation of Pdop-coated MWNTs has increased the membrane permeability using BSA solution (1000 ppm) by 19–50% depending on the amount of Pdop-MWNTs in the membrane, and has maintained good rejection performances (99.88%). Moreover, the antifouling properties of the nanocomposite membranes were also improved. Here, the optimum dose was determined to be 0.1 wt% of Pdop-MWNTs. Furthermore, even though the Pdop-MWNT/Psf membranes showed lower permeability than acid-MWNT/Psf membrane, the Pdop-MWNT/Psf membrane obtained higher mechanical strength and would be potentially sustainable for a long term ultrafiltration operation.

Introduction

The use of membranes has become popular over the years for water and wastewater treatment processes [1]. However, the common problem occurring in membrane application is the trade-off between permeability and selectivity of the membranes [2,3]. Furthermore, the high expenses for flushing the membrane as a consequence of the fouling tendency [4] have made people reconsider the efficiency of implementing membrane filtration. Continuous research efforts are carried out to improve the membrane separation and regeneration efficiency by optimizing process parameters or by developing new membranes. In the past few decades, the advent of nanotechnology has sparked many developments in materials science and engineering, including the manufacture of new membranes and materials for separation technologies. Among the nanomaterials, CNTs [5] have gained interest as the main material or as filler material of polymer composites for water and wastewater treatment. CNTs possess many unique properties such as high aspect ratio, small size, very low density, high tensile strength (reportedly more than 100 times that of stainless steel), and excellent thermal and electrical properties [6,7]. Many review papers have been reported in literature on the use of CNTs for desalination, removal of contaminants in drinking water, and other water treatment applications [8–10].

The role of MWNTs as inorganic fillers in the membrane is predicted to enhance the membrane performance [11]. However,

Abbreviations: BSA, Bovine serum albumin; CA, contact angle; CNT, carbon nanotube; DI, deionized water; FTIR, Fourier-transform infrared spectroscopy; H_2SO_4, sulfuric acid; HCl, hydrochloric acid; HNO_3, nitric acid; MWCO, molecular weight cut-off; MWNT, multiwalled carbon nanotube; NMP, N-methyl-2-pyrrolidone; Pdop, polydopamine; PEG, polyethylene glycol; PEO, poly(ethylene oxide); Psf, polysulfone; PVP, polyvinylpyrrolidone; RO, reverse osmosis; SEM, scanning electron microscopy; TEM, transmission electron microscopy; TOC, total organic carbon; UF, ultrafiltration; UV/vis, ultraviolet/visible light.

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Nomenclature

A	membrane surface area (m^2)
C_f	feed concentration (g/L)
C_p	permeate concentration (g/L)
FRR	flux recovery ratio (%)
h	membrane thickness (cm)
J_f	membrane flux using BSA solution (kg/m^2 h)
J_{wc}	membrane flux of the cleaned membrane (kg/m^2 h)
J_{wv}	membrane flux using deionized water (kg/m^2 h)
m	weight of permeate water (g)
P	membrane porosity (%)
R_{ir}	irreversible fouling ratio (%)
R_r	reversible fouling ratio (%)
R_t	total flux loss (%)
W_d	dry weight of membrane (g)
W_w	wet weight of membrane (g)
Δt	permeation time (h)
ρ_{wl}	density (g/cm^3)

their hydrophobicity and inert characteristics create dispersibility problems in many kinds of solvents. Thus, to solve the dispersion problem, several approaches for producing hydrophilic MWNTs in the membrane fields have been developed [12]. Two main approaches are usually carried out to disperse the MWNTs: mechanical process and chemical modification. Mechanical process involves the use of high shearing force through sonication with or without ball-milling or grinding of MWNTs. Chemical modification on the other hand usually involves acid treatment or the use of surfactants to modify the surface properties of MWNTs. The chemical modification approach followed by sonication is usually carried out by most researchers to disperse MWNTs. Surface modification of MWNTs could provide a pathway to the effective mixing of MWNTs in solution or hybrid assemblies [13]. Interestingly, the enhancement in the hydrophilicity of MWNTs is found to improve not only their dispersion ability but also has a positive impact on the membrane performance [14,15]. For example, Phao et al. [16] improved the dispersbility and wettability of CNTs by doping the CNTs with nitrogen (N-CNTs). N-CNTs/polyethersulfone membranes were then fabricated by modified phase inversion process, and the permeability tests showed up to 70% increase in water flux with the use of polyethersulfone membranes incorporated with N-CNTs.

One of the well-known functionalization techniques is through acid treatment of MWNTs. Nitric and sulfuric acid or a combination of both are usually utilized for acid treatment since it is easy to implement in the laboratory and industrial settings [17]. The acid treatment leads to oxidation of the MWNT walls, wherein the introduction of the oxygen-containing groups such as carboxyl, carbonyl, and phenol groups increases the hydrophilicity of the MWNTs [18]. However, this acid treatment is prone to breakage of the MWNT wall structure [19]. Additionally, the structural integrity of nanocomposite could be decreased due to the presence of carboxylic groups on the MWNT surface [20]. Moreover, the use of aggressive acids could have potential impact to the surroundings during the chemical modification process and its disposal. Thus, it is desired to find alternative approaches for improving the hydrophilicity and dispersibility of MWNTs.

One of the recent advances is the use of Pdop coating on materials for improving their wettability [21]. Pdop, a biorepeated polymer of dopamine monomer, has amine and hydroxyl groups [22,23], which can increase the hydrophilicity of the coated material [24,25]. Reports indicated improved membrane performances such as permeability and antifouling properties after the addition of a Pdop film on the membranes [26–28]. Karkhanechi et al. [29] modified a RO membrane with Pdop and found an improved anti-fouling property of the composite membrane, which was mainly attributed to the bactericidal property of the protonated amine groups of Pdop. Furthermore, Pdop which has similar properties with the adhesive secretion of mussel is reported to increase the mechanical strength of the coated materials [30]. Huang et al. [31] investigated the coating effect of Pdop on the mechanical properties and wettability of electrospun nanofibers. They reported an increase of 100–300% in tensile strength and Young's modulus without sacrificing the flexibility of the membrane as Pdop promotes bonding of the nodes of the fibers. Furthermore, an increase in hydrophilicity was observed for the hydrophobic Psf nanofibers. Considering its hydrophilic characteristic and high mechanical strength, Pdop shows a potential as a coating material to MWNTs to improve their hydrophilicity without damaging the wall structures of the MWNTs and at the same time enhancing the strength of the MWNT structure. A recent study reported an enhanced separation performance and anti-fouling capability of Psf membrane when incorporated with Pdop/CNTs for forward osmosis application [32].

In this study, MWNTs were coated with Pdop to improve their dispersibility and to provide an antifouling behavior. First, the optimal Pdop coating time on MWNTs was investigated. Pdop-MWNTs were then used as fillers for Psf membranes and their permeability and antifouling properties were investigated for ultrafiltration application. The permeability and mechanical strength of Pdop-MWNT/Psf membranes were also compared to those of acid-MWNT/Psf membranes for their ultrafiltration performance.

Materials and methods

Materials

Pristine MWNTs (HANOS CM 95) with a length of 10–50 nm, and outer and inner of diameters ±10 nm and ±4 nm, respectively, were purchased from Hanwha Nanotech Company, Republic of Korea. Polysulfone (Udel P-3500 LCD, 75–81 kg/mol) as a polymer matrix was bought from Solvay, Belgium. Dopamine hydrochloride ($C_8H_{11}NO_2{\cdot}HCl$, 189.6 g/mol), Tris–$C_4H_{11}NO_3$, 121.14 g/mol, poly(-ethylene oxide) (PEO, 100 kDa), PVP (55 kDa), PEG (35 kDa), and BSA (67 kDa) were provided by Sigma–Aldrich, USA. Various solutions such as NMP, HNO_3, and H_2SO_4 were received from Daejung (Republic of Korea). For membrane filtration, a 0.2 μm Anodisc (Cat No. 6809-5022) and 0.45 μm glass microfiber filter (Cat No 1822-047) was used, which was purchased from Whatman GmbH Dassel, Germany (Whatmann International Ltd). DI water was produced from Ultra Water Purification System (Ultra 370 Series aqua max Younglin Company, Republic of Korea).

MWNT functionalization

Polydopamine coating of MWNT

In brief, 15 mM of Tris was added to 200 mg of dopamine-HCl solution in 100 ml of DI water (2 g/L) [33]. The mixture was left in ambient air for 1 min to produce polydopamine. The color of the mixture became darker indicating the oxidation of dopamine (i.e., self-polymerization) and it started to change to polydopamine [34]. Then, 100 mg of pristine MWNTs was added and stirred in a stirrer cell (Model HS15-26P, Misung Company, Republic of Korea) to let the coating process occur (room temperature: 23–25 °C)