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Nanocarbon-based membrane filtration integrated with electric field driving for effective membrane fouling mitigation

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ABSTRACT

Membrane filtration provides an effective solution for removing pollutants from water but is limited by serious membrane fouling. In this work, an effective approach was used to mitigate membrane fouling by integrating membrane filtration with electropolarization using an electroconductive nanocarbon-based membrane. The electropolarized membrane (EM) by alternating square-wave potentials between +1.0 V and −1.0 V with a pulse width of 60 s exhibited a permeate flux 8.1 times as high as that without electropolarization for filtering feed water containing bacteria, which confirms the ability of the EM to achieve biofouling mitigation. Moreover, the permeate flux of EM was 1.5 times as high as that without electropolarization when filtrating natural organic matter (NOM) from water, and demonstrated good performance in organic fouling mitigation with EM. Furthermore, the EM was also effective for complex fouling mitigation in filtering water containing coexisting bacteria and NOM, and presented an increased flux rate 1.9 times as high as that without electropolarization. The superior fouling mitigation performance of EM was attributed to the synergistic effects of electrostatic repulsion, electrochemical oxidation and electrokinetic behaviors. This work opens an effective avenue for membrane fouling mitigation of water-treatment membrane filtration systems.

1. Introduction

Currently, approximate 800 million people in the world lack access to hygienic drinking water, and this number will increase to approximately 4 billion by 2030 as estimated by the World Health Organization (WHO) and the World Water Council (WWC) (WHO, 2007; WWC, 2007). There is an urgent need for water purification technologies that satisfy escalating worldwide demand for clean water. Membrane filtration has received considerable interest for water treatment applications due to its capability to provide higher quality water without chemical additives and byproduct compared with other technologies (Shannon et al., 2008). In particular, membranes constructed from nanomaterials have opened a fascinating avenue for filtration performance as well as affordable and convenient application (Liao et al., 2014; Pendergast and Hoek, 2011).

Recently, interest in nanocarbon-based membranes (NCMs) as a new family of innovative membranes has been rapidly grown among various research fields, especially water treatment (Han et al., 2013; Huang et al., 2014; Li et al., 2007; Srivastava et al., 2004). Due to the molecularly smooth, hydrophobic surface and unique morphology of nanocarbons, NCMs usually offer a flux rate that is orders of magnitude higher than other membranes with comparable pore size (Falk et al., 2010; Huang et al., 2013; Liu et al., 2012; Noy et al., 2007). On the other hand, NCMs have been found to be efficient in removing a wide range of ions, organic contaminants, pathogens and nanoparticles from water via size-exclusion and/or adsorption (Brady-Estévez et al., 2010; Liang et al., 2010; Roy et al., 2012; Sun et al., 2012). Moreover, constructing NCMs on ceramic substrate can not only provide the required physicochemical stability, but also are capable of maintaining an excellent filtration performance for practical applications (Fan et al., 2015). Although fascinating permeability and selectivity have been obtained by using NCMs, membrane fouling is still a major obstacle that limits the application of membrane filtration (including NCMs) in water treatment. Due to the ubiquitous presence of waterborne pathogens and natural organic matter (NOM) in natural water, membrane fouling usually occurs during filtration as a result of NOM accumulation and/or bacterial adhesion and multiplication. These disgusting fouling phenomena deteriorate

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membrane permeability and increase energy consumption, which necessitates frequent and costly treatments for membrane performance recovery and even membrane replacement.

It is noteworthy that nanocarbons typically exhibit significant electrochemical properties and corrosion resistance under bias application. According to existing reported works, electrochemical assistance can significantly improve contaminant adsorption to electropolarized nanocarbons (Li et al., 2011). Furthermore, some adsorbed substances may be electrochemically oxidized or even mineralized with only nontoxic "electrons" as the reaction mediator (Gao and Vecitis, 2011; Liu and Vecitis, 2012; Nakayama et al., 1998; Vecitis et al., 2011a). Charged substance motility, originating from electrostatic, electrophoretic and electroosmotic forces in electric fields or on electrode surfaces, have been confirmed (Hong et al., 2008; Istanbullu et al., 2012; Kang et al., 2011). Electrochemical cleaning and recovery of fouled nanocarbons has been achieved via electrostatic repulsion coupled with gas bubble generation (Hashaikeh et al., 2014; Sun et al., 2013). The reported electrochemical behaviors and processes of electropolarized nanocarbons suggest that electropolarization maybe a feasible method for fouling mitigation in NCMs during filtration processes.

To verify the feasibility of the above hypothesis, an NCM was prepared by coating ceramic hollow fiber substrate with interconnected carbon nanotubes (CNTs/ceramic membrane). Effects of electropolarization including anodic, cathodic and alternating polarization on membrane fouling mitigation for either biofouling or organic fouling were investigated using electropolarized CNTs/ceramic membranes in a custom-made cross-flow module. Filtration experiments with both bacteria and natural organic matter in feed water were also performed. Moreover, the underlying mechanisms for membrane fouling mitigation under electropolarization were discussed by observing bacterial viability and amount of bacteria/natural organic matter on the CNTs/ceramic membrane surface.

2. Materials and methods

2.1. Fabrication of CNTs/ceramic membrane

Ceramic hollow fiber substrates were fabricated via a two-step method of dry-jet wet-spinning (Fig. S1) and sintering process. The spinning dope was prepared by adding 5.0 g TiO_2 powder into a mixture of polysulfone and 1-methyl-2-pyrrolidinone (NMP) with a ratio of 1:9 (w/w, 10 g). Immediately after degasification, the spinning suspension was extruded through a tube-in-orifice spinneret (outer diameter 1.2 mm and inner diameter 0.7 mm). Water was chosen as the bore fluid. The flow rates for spinning suspension and bore fluid were 25 mL h^{-1} and 10 mL h^{-1}, respectively. The air-gap was maintained at 2 cm. Then, the prepared hollow fiber precursor was calcined at 800 °C for 30 min in air to remove the organic polymer binder (polysulfone) and sintered at 1200 °C for 4 h in air to obtain the final ceramic hollow fiber substrate.

CNTs were first carboxylated in a H_2SO_4/HNO_3 solution (3/1, v/v) at 80 °C for 6 h, after which the oxidized CNTs were uniformly dispersed into a 0.5 wt% polyacrylonitrile (PAN)/N,N-dimethylformamide (DMF) solution by ultrasound for 30 min. Then, a vacuum-filtration process was applied to coat the CNTs onto the ceramic hollow fiber substrate. Finally, the prepared membranes were heated at 250 °C for 3 h in air, followed by PAN pyrolysis at 1000 °C in a hydrogen atmosphere. After PAN pyrolysis, the membrane was cooled down to 400 °C in the hydrogen atmosphere and then to room temperature in air.

2.2. Characterization of CNTs/ceramic membrane

Membranes morphologies were observed by field-emission scanning electron microscope (FESEM, Hitach S4800, Japan). Pore sizes of the prepared NCM were estimated by separation with molecular polyethylene glycol (PEG, 400–8,000,000 Da, size ranging from 1 to 75 nm) and polystyrene microspheres (PS, 89.4–954.7 nm). Mechanical strength was evaluated by three point bending test on a mechanical test system (Instron 3345, USA) with stain rate of 1 mm min^{-1}. Porosity of the CNT layer in CNTs/ceramic membrane was determined by microscopic image analysis method (Masselin et al., 2001; Sun et al., 2007; Wang and Wang, 2006). Electroconductivity of the CNTs/ceramic membrane was measured with a four-point probe conductivity meter (RTS-8, 4 PROBES TECH, China).

2.3. Fouling mitigation tests on CNTs/ceramic membrane under electropolarization

Water permeability and fouling mitigation tests were performed on the prepared membranes in a custom-made electrochemical membrane module. The membrane module was fabricated by assembling five hollow fiber membranes into a polypropene tube of 1.2 cm outer diameter and 5 cm length. Both ends of the module were sealed by expoxy (thickness of each end: 1.5 cm), which ensured a membrane area of 10 cm^2. The performance of CNTs/ceramic membrane was evaluated under different potentials using a electrochemical system (CHI-660A) with CNTs/ceramic membrane as the working electrode, a Ti mesh as the counter electrode, and a Ag/AgCl (saturated KCl) electrode as the reference electrode. The distance between working electrode and counter electrode was 0.5 cm. Three types of polarization forms were performed in the tests including anodic polarization at $+1.0$ V, cathodic polarization at -1.0 V, and alternating polarization at ± 1.0 V with pulse width value of 60 s (Fig. S4). During the filtration processes, feed water was pumped into the membrane reactor at a constant cross-flow rate (0.2 m s^{-1}) by a peristaltic pump. A constant trans-membrane pressure of 0.1 bar was maintained on the membrane by a vacuum pump. The permeate water was collected and monitored by an analytical balance (Sartorius BP221S, Germany), which was used to calculate the permeate flux.

Escherichia coli (*E. coli*) were chosen as the target organisms to evaluate the membrane performance for biofouling mitigation. The bacteria were cultured into freshly sterilized Luria-Bertani (LB) broth at 37 °C overnight on a rotary shaker with 150 rpm under aerobic conditions, after which the cells were harvested by centrifuging at 10,000 rpm for 10–15 min and washed with sterile physiological saline solution by resuspension/centrifugation processes for three times. Finally, the bacteria were resuspended in 10 mmol L^{-1} NaCl solution with approximately 10^7 colony-forming units per milliliter (cfu mL^{-1}).

Humic acid (HA) was chosen as a source of natural organic matter (NOM) to evaluate membrane performance for NOM fouling mitigation. HA (Sigma-Aldrich, St, Louis, MO, USA) aqueous solution with initial concentration of 10 mg L^{-1} was introduced into the membrane module. The electrolyte (NaCl) concentration was 10 mmol L^{-1}. The hydrodynamic diameter of HA aggregate was measured on a nanoparticle analyzer (Malvem nano-ZS90, UK). The effluent sample was collected and analyzed for total organic carbon (TOC) content using a TOC analyzer (TOC-V_{CPH}, Shimadzu, Japan).

In comprehensive antifouling experiments, feed water containing 10 mg L^{-1} HA and 10^3 cfu/mL *E. coli* was pumped into the membrane module under electropolarization. The electrolyte was 8 mmol L^{-1} NaCl and 2 mmol L^{-1} $CaCl_2$. Effects of alternating potential and pulse width on fouling mitigation were evaluated. Both