Journal of Membrane Science 459 (2014) 143–156

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Conductive CNT-PVDF membrane for capacitive organic fouling reduction

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ARTICLE INFO

Article history:
Received 7 November 2013
Received in revised form
15 January 2014
Accepted 12 February 2014
Available online 19 February 2014

Keywords:
Ultrafiltration membrane
Organic fouling
Surface charge
Capacitive fouling mitigation

ABSTRACT

Organic fouling of ultrafiltration (UF) membranes results in decreased water flux and increased energy requirements. Modification of UF membrane surfaces is one possible method to mitigate natural organic matter (NOM) fouling, yet to date; most modifications have been passive. In this study, we investigate the use of a carbon nanotube-polyvinylidene fluoride (CNT-PVDF) porous non-Faradaic cathode on top of a UF membrane to actively produce negative surface charges via capacitive charging. The study is divided into three elements: (1) modification of the UF system with the capacitive CNT-PVDF electrodes and determination of the optimal electrode-membrane configuration, (2) analysis of the fouling mitigation mechanism, and (3) evaluation of the practical potential of capacitive fouling reduction. All experiments were completed in the cross-flow configuration. The optimal electrode-membrane configuration for organic fouling reduction was when the permeate first flowed through the porous anode, then the CNT-PVDF cathode, and finally the polyethersulfone (PES) UF membrane. The extent of capacitive fouling reduction was determined to be a function of anode material, ionic strength, and cathode potential. The primary fouling reduction mechanism is the potential-induced cathodic negative surface charges that increase the Derjaguin–Landau–Verwey–Overbeek (DLVO) energy barrier and decrease the collision efficiency of negatively-charged organic matter with the membrane surface. The capacitive system has potential to reduce energy requirements by up to 2-fold as compared to the unmodified UF system when challenged with 10 ppm NOM solutions at low ionic strength.

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1. Introduction

Ultrafiltration (UF) is a promising separation technology for drinking water treatment since it is effective and efficient towards turbidity and pathogen removal at low pressures. Direct ultrafiltration can simplify the conventional drinking water treatment process by eliminating multiple steps such as coagulation, sedimentation, and granular filtration from the process train. The advantages of UF include high product water quality, small footprint, compact modular design, and the ability to handle large fluctuations in feed water quality [1,2] and low pressure UF membrane systems are utilized at drinking water treatment facilities across the world [3,4]. However, a critical issue for all membrane applications is fouling [3] since it increases hydraulic resistance and decreases permeability resulting in increases in operation and maintenance (O&M) costs.

Many studies have identified aqueous natural organic matter (NOM) as one of the most detrimental UF surface water foulants [1,5,6]. The NOM fouling behavior is controlled by many factors including the chemical and physical properties of the organic matter, membrane surface and pore characteristics, and feed solution chemistry [7]. The increase in hydraulic resistance and subsequent permeability decline can be caused by concentration polarization, pore blocking, pore thinning, and cake layer formation on the membrane surface [8]. Mechanistically, organic fouling is attributed to the high interfacial energy of the hydrophobic UF membrane surface when in contact with water that is decreased upon sorption and deposition of organic matter [9,10].

Based on known fouling mechanisms, continuous efforts have been made to reduce UF organic fouling through permanent membrane surface modification. For instance, hydrophilic inorganic Al_2O_3 [11] and TiO_2 [12] nanoparticles and amphiphilic organic copolymers such as polyacrylonitrile-g-poly(ethylene oxide) [13] and poly (2-dimethylaminoethyl methacrylate)-b–poly(methyl methacrylate)-b–poly(2-dimethyl aminoethyl methacrylate) [10] have been utilized as UF membrane additives to yield a more hydrophilic surface that tightly binds a thick water layer, which in turn sterically hinders organic matter attachment. Alternatively, UF membrane surfaces have been modified to increase negative surface charge density that reduces fouling via charge repulsion [14] since aqueous NOM is negatively-charged [15]. For example, Wei et al. modified poly

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http://dx.doi.org/10.1016/j.memsci.2014.02.017
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(ethersulfone) (PES) membranes by an electrophoresis-UV electrolyte monomer grafting process and observed that the grafted membranes exhibited less NOM fouling as compared to the unmodified membrane [16]. Bowen et al. added hydrophilic sulfonated poly(ether ether ketone) to polysulfone casting solutions and observed reduced humic acid fouling as compared to the unmodified membrane [17]. However, an increased membrane negative surface charge density will also result in a concomitant increase in membrane hydrophilicity, thus it is difficult to make a definite mechanistic conclusion on how an increased negative surface charge density reduces membrane fouling [14]. Surface modifications to reduce organic fouling are further complicated because certain functional groups such as carboxylates can form calcium ion bridges between the membrane surface and NOM resulting in lower permeability and less reversible fouling [18].

An alternative to passive modification of a membrane surface would be to introduce negative charge or hydrophilicity via an active process such as capacitance e.g., the deposition of carboxylated latex nanoparticles on an electrochemical carbon nanotube (CNT) filter was reduced when a potential of −2 V was applied [19]. The combination of UF and active electrical processes has been of research interest for the past few decades with most previous studies focusing on the process of electro-filtration where an electric field controls the mass transfer of charged solutes by electrophoresis [20]. Nevertheless, the effect of surface charge densities has seldom been discussed even for systems utilizing a conductive electrode membrane. Classical materials utilized as porous conductive electrodes includes metal alloys, metallic ceramics [21], and conductive polymers [22]. More recently, CNT–polymer composites have been utilized as a novel class of conductive materials [23,24], filters [25–28], and hybrid conductive filters [29,30]. These CNT–polymer composites have been fabricated by methods such as surface deposition, covalent cross-linking, and phase inversion. The CNT–polymer composites exhibit tunable electrical conductivity, porosity, and mechanical properties that all may contribute to the development of novel permeable flow-through electrodes. For example, a conductive non-Faradaic CNT-PVDF membrane produced by phase inversion [31] can produce capacitive surface charge with minimal energy requirements and toxic by-products e.g., chlorine or bromine, due to negligible Faradaic current. Thus, one application of the CNT-PVDF membrane would be to actively produce capacitive negative surface charge to reduce NOM fouling. However, due to the large CNT-PVDF pore size and permeability (Table 1), it cannot serve directly as the UF separation membrane, but could be used as a capacitive layer on top of a UF membrane.

Here, the potential of a conductive CNT-PVDF membrane for the capacitive reduction of organic fouling of a PES UF membrane is investigated. First, three different CNT-PVDF electrode-membrane configurations were evaluated to determine the optimal configuration for organic fouling reduction. Next, using the optimal configuration, the mechanism of NOM fouling reduction was investigated by completion of experiments with various anode materials, ionic strengths, and total applied potentials. Finally, the optimal configuration was challenged with solutions mimicking surface water conditions over extended periods to evaluate the potential of capacitive fouling mitigation for practical application to drinking water treatment.

2. Materials and methods

2.1. Chemicals

Suwannee River fulvic acid (SRFA) standard II (2S101F) was purchased from the International Humic Substances Society (St. Paul, MN). Sodium alginate (ALG; medium viscosity) was acquired from MP Biomedicals (Solon, OH). Polyethylene glycols (PEGs) with different number average molecular weights (M_n) were purchased from Polymer Source (Canada). Polyvinyl pyrrolidone (PVP, M_n=40,000 Da), polyacrylic acid (PAA, M_n=8000 Da) sodium salt (40% in water), sodium chloride (NaCl), and sodium hydroxide (NaOH) were acquired from Sigma-Aldrich (St. Louis, MO). PVDF (Kynar® 761) was kindly donated by Arkema (Philadelphia, PA). 1-Methyl-2-pyrrolidinone (NMP, ≥99%) was purchased from Alfa Aesar (Ward Hill, MA). Isopropyl alcohol (≥99.5%) was purchased from VWR International (West Chester, PA). Deionized (DI) water (>18 MΩ) produced by a Nanopure Infinity Ultrapure Water System (Barnstead/Thermolyne) was used to prepare all solutions and rinse all containers.

2.2. Conductive non-Faradaic CNT-PVDF membrane synthesis

The conductive non-Faradaic CNT-PVDF membrane was produced via phase inversion using NMP as a solvent and water as a non-solvent following a previously developed procedure [31]. Briefly, 0.5 g CNTs and 0.1 g NaCl were dispersed in 100 g NMP by probe sonication (Branson, Sonifier S450D) for 15 min at an applied power of 400 W L^{-1}. After the solution had cooled to room temperature, 10 g PVDF (10% w/w NMP) and 1 g PVP (1% w/w NMP) were added to the CNT-NMP solution and mixed for 24 h using an overhead mixer (IKA RW16 Basic) at 200 rpm. The resulting CNT/PVDF w/w ratio is 5%. Then, the casting solution was degased in an ultrasonic bath (Branson 2100) for 60 min and allowed to sit in the dark overnight. For the phase inversion process, the prepared casting solution was spread onto a glass plate with a bar coater of 100-μm thickness using an automated film applicator (Elcometer 4340 Automatic Film Applicator). Immediately after spreading, the glass plate with the casted solution was immersed in DI water at room temperature until the film detached from the plate. All the films were placed in a DI water bath (PolyScience Digital Temperature Controller) at 30 °C for 24 h to remove any residual solvent and then stored in fresh DI water until use.

2.3. Cross-flow ultrafiltration

2.3.1. Cross-flow filtration setup

Ultrafiltration was conducted with a bench scale system using a commercial flat-sheet cross-flow filtration cell (Sterlitech CF042)

Table 1
Properties of the CNT-PVDF, CCP, PES membranes, and mesh spacers.

Materials		Thickness[a] (mm)	Top pore size (mm)	Bulk porosity (%)	Conductivity[a] (S m^{-1})	Contact angle (deg)	Specific surface area (m^2 g^{-1})	Total surface area (m^2)
Electrode	**CNT-PVDF**	0.048	10^{-5}	81.0	3.20×10^{-4}	66.2	16.3	0.781
	CCP	0.203	0.2	50.0	$>8\times10^{-2}$	136	5.54	2.59
Filter	**PES**	0.169	–	66.1	–	60.9	15.9	5.95
Spacer	**Cloth**	0.236	0.3	–	–	–	–	–
	Mesh	0.600	2.0	–	–	–	–	–

[a] Thickness data in this table were the measurement results with a digital micrometer (Fowler Tools and Instruments; 0.00005 in. to 1.0 in.)

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