



## Polyelectrolyte modification of nanofiltration membrane for selective removal of monovalent anions

Ramamoorthy Malaisamy\*, Alain Talla-Nwafo, Kimberly L. Jones

Membrane Laboratory, Department of Civil Engineering, Howard University, 2300 6th St., NW, Washington, DC 20059, USA

### ARTICLE INFO

#### Article history:

Received 27 September 2010

Received in revised form

19 December 2010

Accepted 5 January 2011

#### Keywords:

Nanofiltration

Membrane surface modification

Polyelectrolyte multilayer

Composite membrane

Salt rejection

Membrane selectivity

### ABSTRACT

Nanofiltration (NF) membranes operate with higher flux and lower energy requirements than reverse osmosis (RO) membranes, and exhibit relatively low rejection and selectivity for monovalent ions. In cases where high flux, high selectivity and high monovalent ion rejection are desired, an ideal membrane would exhibit the flux behavior of NF membranes and rejection behavior of RO membranes. Thus, a commercially available NF membrane was modified by layer-by-layer (LbL) assembly of alternating polyelectrolyte thin films in order to increase rejection and selectivity towards monovalent ions, namely  $F^-$  and  $Cl^-$ . Poly(styrene sulfonate) (PSS) was the anionic polyelectrolyte and poly(diallyldimethyl ammonium) chloride (PDADMAC) was the cationic polyelectrolyte. Thin (0.5–8.5) PDADMAC/PSS bilayers were deposited on the substrate membrane. NF experiments were performed in a cross-flow cell with feed solutions of (a) a ternary mixture of sulfate, fluoride and chloride at 100, 500 and 1000 mg/L concentrations and (b) single salt solutions of  $Cl^-$  or  $F^-$ . In the ternary mixture experiment, fluoride rejection increased from 40% (unmodified) to 70% (8-bilayer modified), whereas chloride rejection was reduced from 55% (unmodified) to 20% (8-bilayer modified). The selectivity for chloride over fluoride was 2.7 for an 8-bilayer modified membrane compared to 1 for unmodified membrane. In single salt filtration of fluoride there was no appreciable change in the rejection for the modified membranes, whereas in the filtration of chloride the rejection increased from 30 to 91% upon modification (8-bilayer). The flux decreased by 30% with 8-bilayer modification for all feed solutions. The performance (flux, rejection, selectivity) of the modified membranes was compared to a BW30 RO membrane; under identical operating conditions, the modified membranes exhibit higher selectivity and flux than the commercial RO membrane.

© 2011 Elsevier B.V. All rights reserved.

### 1. Introduction

In drinking water treatment, salt removal is commonly achieved using ion exchange, nanofiltration or reverse osmosis. In some cases, removal of total dissolved solids is desirable; however, it is becoming increasingly important to remove targeted ions from a feed stream in order to reduce the volume of concentrate. For example, removal of an ion such as perchlorate or fluoride from a solution that also contains a commonly occurring ion such as chloride would be difficult with traditional RO membranes. A process to selectively remove a harmful metal or ion while allowing harmless salts to pass would greatly reduce the volume of concentrate for disposal, often considered a major environmental disadvantage to using RO membranes for salt removal.

Common separation techniques such as ion exchange (using resins), electrodialysis, and adsorption (using activated alumina)

are non-selective [1], develop unwanted byproducts [2] and/or suffer from low binding capacity (depending on the composition of the solution) [3]. Membrane separation can address these issues. Nanofiltration (NF) membrane separation in particular, is a very attractive alternative, due to higher fluxes when compared to reverse osmosis (RO). NF is widely utilized in water softening applications [4,5], as well as for pretreatment for RO. Multivalent ions are removed via a combination of charge interaction and size exclusion [6]. NF rejects less than 60% of monovalent ions [7,8], compared to over 90% monovalent ion rejection possible with RO membranes. Reverse osmosis membranes demineralize the water with low or no selectivity for monovalent ions, and suffer low permeate flux, high operating pressure and high energy requirements. Thus, it would be desirable to increase the monovalent ion rejection and selectivity of NF membranes while retaining flux. To this end, some researchers have employed tighter (low flux) commercial nanofiltration membranes [8,9], while some others have modified microfiltration (high flux) membranes into nanofiltration membranes by polyelectrolyte deposition [10,11], thus increasing monovalent ion removal and separation. However, these designs do not enable increased selectivity while retaining high flux behavior.

\* Corresponding author. Tel.: +1 202 806 6583; fax: +1 202 806 5271.

E-mail addresses: [mramamoorthy@howard.edu](mailto:mramamoorthy@howard.edu), [malaisamy@gmail.com](mailto:malaisamy@gmail.com) (R. Malaisamy).

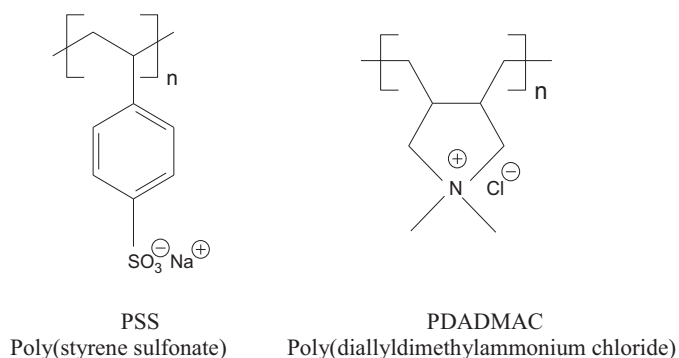


Fig. 1. Structure of polyelectrolytes used in this study.

This study was built on the hypothesis that chemical modification of an existing high flux polymer composite nanofiltration membrane will result in a high flux membrane with increased monovalent ion rejection and increased selectivity. A few reports are available in the literature on the surface modification of nanofiltration membranes, including redox-initiated graft polymerization [12–14], surfactant modification [15], ion implantation [16] and electrostatic self-assembly of polyions [17]. These processes can be useful under specific circumstances, however there are other techniques that are less desirable due to laborious processes and cost: plasma polymerization [18], interfacial polymerization [19], ATRP [20], spin coating [21], UV initiated grafting [22], and plasma grafting [23]. The method chosen for this study is layer-by-layer (LbL) electrostatic self-assembly, or polyelectrolyte multilayer (PEM) deposition technique. This technique was chosen due to its ability to control thickness of the thin films in nanometer scale, charge density, composition of the active layer and ion rejection [24–29]. NF270 was identified as the substrate nanofiltration membrane due to its relatively high salt ( $\text{SO}_4^{2-}$ ) rejection (90%) as well as a high permeate flux ( $125 \text{ L}/(\text{m}^2 \text{ h})$ ), reportedly prepared by interfacial polymerization of polyamide on microporous polymer substrate [30–33].

In this study, a NF270 membrane was modified by the LbL electrostatic deposition of poly (diallyldimethylammonium chloride) (PDADMAC) and poly (styrene sulfonate) (PSS) (Fig. 1) with various numbers of alternating layers. Single and mixed salts of sodium chloride and sodium fluoride with 100, 500 and 1000 mg/L concentrations were employed as feed and the percentage rejection of the monovalent ions and their selectivity were determined using a cross-flow configuration. Surface electrical, chemical and wettability characterizations of the membranes were performed in order to address the confirmation and reproducibility of the modification, as well as to interpret the results.

Fluoride exists in trace amounts in almost all ground waters throughout the world [34]. Local anthropogenic activities such as application of fertilizers or aluminum smelting, and natural processes such as leaching out from mineral containing (host) rocks such as basalt, syenite and shale cause increasing levels of fluoride in the ground water [35–37]. In the United States about 200,000 people consume water with fluoride levels over the maximum contaminant level (MCL) of 4 mg/L [38] set by the US Environmental Protection Agency. Presence of fluoride in drinking water can cause dental fluorosis, skeletal fluorosis and other adverse health effects based on the level and period of exposure [39]. The World Health Organization (WHO) suggests an optimum concentration range of 0.5–1.5 mg/L, and the USEPA has set a secondary MCL of 2 mg/L.

The World Health Organization also reports that in the United States, aquifers prone to seawater intrusion have been found to contain chloride at concentrations ranging from 5 to 460 mg/L [40]. Chlorides are very soluble in water and are easily leached from

various rocks into soil and water by weathering. The chloride ion is highly mobile and can then be transported to larger bodies of water. Additionally, chloride in water may be considerably increased by treatment processes in which chlorine or chloride is used [41].

For chloride, both the WHO and the EPA recommend a secondary MCL of 250 mg/L [40,42]. Although chloride and fluoride are regulated through secondary standards, most treatment plants attempt to meet secondary standards and remove these ions.

## 2. Materials and methods

### 2.1. Materials

Composite polyamide (PA) nanofiltration membranes (NF270) were obtained from FilmTec Corporation, Minneapolis, USA and used as the control membrane and also as the substrate for modification. These nanofiltration membranes have a wide pH tolerance for continuous operation from pH 3 to 10, and maximum temperature and pressure at 45 °C and 41 bars, respectively [31]. Poly (styrenesulfonic acid) sodium salt ( $M_w$  70,000), poly (diallyldimethylammonium chloride) ( $M_w$  100,000–200,000), sodium chloride, sodium fluoride and sodium sulfate were purchased from Aldrich Chemical Company, USA. Deionized water (Milli-Q, conductivity of 18.2 MΩ cm) was used for membrane rinsing, preparation of polyelectrolyte solutions and the feed.

### 2.2. Modification of polyamide nanofiltration membrane surface

Prior to modification, the NF270 NF membranes were soaked in water for a minimum of 3 h, replacing the water every hour, and then rinsed with water. The membrane was carefully cut into a suitable size to be used in the membrane cell and mounted on a custom designed holder with the active surface facing up and held tightly to expose the effective membrane area. The electrostatic deposition was initiated by adding an aqueous solution of 0.02 M PDADMAC in 0.5 M NaCl, and allowing this solution to be in contact with the membrane for 3 min (step 1). The membrane surface was then rinsed with milli-Q water for 1 min (step 2) before being exposed to an aqueous solution containing 0.02 M PSS in 0.5 M NaCl for 3 min (step 3). The membrane was then rinsed for 1 min (step 4). The completion of these four steps results in the development of 1-bilayer of PDADMAC/PSS thin film. This process was repeated “*n*” times to obtain membranes modified with “*n*” bilayers, (PDADMAC/PSS)<sub>*n*</sub>. In order to improve charge density on the surface of the films, NaCl at 0.5 M concentration was used as a support electrolyte in PDADMAC and PSS solutions [43]. The pH of PDADMAC and PSS are  $6.0 \pm 0.5$  and  $4.7 \pm 0.5$ , respectively.

### 2.3. Membrane characterization

The surface chemical functionality of the unmodified and modified NF270 membranes was obtained with an ATR-FTIR spectrometer (Nicolet Magna 560, Nicolet Instrument Corp., Madison, WI). Clean, dry membrane pieces were mounted on the ATR germanium crystal and 128 IR scans were performed at a resolution of  $4 \text{ cm}^{-1}$  at an incident angle of 45°. The IR penetration depth for this incident angle is 0.1–1 μm. A baseline was obtained initially without the sample on the crystal, and was subtracted for each membrane sample.

A goniometer (Phoenix 150, from Surface & Electro-Optics Corporation, South Korea, supplied by Scientific Gear LLC, VA) was utilized to evaluate the hydrophilic/hydrophobic nature of the membrane by means of water contact angle of the unmodified and modified membranes. The instrument is equipped with a CCD camera, a sample stage and a syringe holder. The instrument was initially calibrated using a standard supplied by the manufacturer.

Download English Version:

<https://daneshyari.com/en/article/642791>

Download Persian Version:

<https://daneshyari.com/article/642791>

[Daneshyari.com](https://daneshyari.com)