



# Design of ultrathin nanostructured polyelectrolyte-based membranes with high perchlorate rejection and high permeability



Oishi Sanyal<sup>a</sup>, Anna N. Sommerfeld<sup>b</sup>, Ilsoon Lee<sup>a,\*</sup>

<sup>a</sup> Department of Chemical Engineering and Materials Science, Michigan State University, East Lansing, MI 48824, USA

<sup>b</sup> Department of Mechanical Engineering, Michigan State University, East Lansing, MI 48824, USA

## ARTICLE INFO

### Article history:

Received 27 January 2015

Received in revised form 11 March 2015

Accepted 12 March 2015

Available online 17 March 2015

### Keywords:

Perchlorate rejection

Permeability

Layer-by-layer assembly

Polyelectrolyte multilayer membranes

## ABSTRACT

The presence of perchlorate in drinking water sources is an issue of overwhelming concern in United States. Commercial reverse osmosis (RO) membranes show high rejection of perchlorate ions but with very low water permeability. We propose the modification of commercial nanofiltration (NF) membranes by layer-by-layer (LbL) assembly in order to enhance the ion rejection of these membranes to the same level as commercial RO membranes, but with much higher permeability. Poly allylamine hydrochloride (PAH) and poly acrylic acid (PAA) were the two polyelectrolytes used for surface modification. We found that, when both these polyelectrolytes were deposited on a NF 90 membrane at a pH of 6.5 and cross-linked with glutaraldehyde, we were able to achieve around 93% perchlorate rejection at a pressure of 5 bar with 10 ppm feed concentration. This was almost equal to the rejection offered by SW 30 membrane and higher than a BW 30 membrane under the same conditions of pressure and feed concentration. Most importantly, the modified membranes had 1.5 times the permeability of BW 30 membrane and 6 times that of SW 30. These membranes, therefore, had much superior permselectivity than the commercial membranes. In fact, this was one of the highest values of permselectivity reported so far for a PEM-based RO membrane targeting monovalent ion removal. Only 3 bilayers, with an overall thickness of just 20 Å, were sufficient to achieve such a high rejection. The mechanism of ion rejection by these modified membranes was based on size-based exclusion rather than charge-based separation.

© 2015 Elsevier B.V. All rights reserved.

## 1. Introduction

In 1997 high levels of perchlorate were found in the drinking water supplies of the state of California. Ever since then, a number of other states within United States reported the presence of perchlorate in the groundwater as well as surface water supplies [1]. Recognizing the threats it poses to the environment and the health of millions of people, perchlorate has been added to the contaminants candidates list (CCL) as well as unregulated contaminant monitoring rule (UCMR) [2]. Perchlorate salts like ammonium perchlorate are used as oxidizers for missiles and munitions [3] which makes perchlorate ion an ubiquitous groundwater contaminant in areas close to NASA or other military settlements [4]. When taken in at higher than recommended levels, it interferes with iodide ion thereby impairing the hormone secreting abilities of the thyroid gland. Studies have shown that iodine deficiency in case of pregnant women can lead to lower IQ levels in their babies [5]. Improved methods of perchlorate detection have shown the

presence of perchlorate in at least 26 states all over United States [1]. The Colorado River which provides water for drinking as well as irrigation to almost 30 million people, has been known to be one of the most perchlorate-contaminated sites of the country [4]. Developing effective perchlorate removal strategies is therefore in urgent need.

As of now, the US EPA does not have any strict regulatory limits for perchlorate but according to recent reports they have initiated the process of regulating perchlorate to a uniform level throughout the nation under the Safe Drinking Water Act [3]. Various states like California, Massachusetts, Maryland, etc. have set their own individual standards between 1 and 2 µg/l [6]. Reports have indicated that as many as 11 million people in United States have been consuming drinking water with perchlorate concentration higher than 4 µg/l [6].

So far, the clean-up of some of the perchlorate contaminated sites has involved several billions of dollars. In 2014, the Nevada division of EPA allocated 1.1 billion dollars to a trust for cleaning up the perchlorate contamination in Lake Mead. This contamination originated from the manufacture of jet fuels by Ker McGee Chemical Company (KMCC) and it eventually led to the creation

\* Corresponding author.

E-mail address: [leeil@egr.msu.edu](mailto:leeil@egr.msu.edu) (I. Lee).

of largest perchlorate plume in the nation [7]. Reports indicate that this perchlorate plume showed concentrations as high as 18,000 ppm prior to the cleanup, especially in areas closer to the industrial site [8]. In 2012, DOD and several other companies had to invest 50 million dollars for the cleanup of the perchlorate contaminated sites of Rialto, California [5]. Similar cleanup ventures were also taken up by NASA following the shutdown of several perchlorate-contaminated wells in Pasadena, California [9]. It is therefore quite clear that while developing the most viable treatment technique is essential, the latter also needs to be cost-effective in order to be actually implemented.

There are several wastewater treatment options available for the remediation of perchlorate, like fluidized bed biological reactor treatment, membrane-based processes like reverse osmosis (RO) and nanofiltration (NF), ion-exchange, ultraviolet laser reduction, etc. [3]. In this paper, we mainly focus on the pressure-driven membrane-based processes for removing perchlorate. Different research groups have tried out ultrafiltration (UF), nanofiltration (NF) as well as reverse osmosis (RO) membranes to assess their efficiency in reducing perchlorate [10–16]. Being a monovalent ion, perchlorate can be most effectively removed by a RO membrane [17]. However due to the inherently dense structure of the membrane, the latter offers a very low water flux. This makes RO a highly energy-intensive process with a low energy recovery percentage. Nanofiltration (NF) membranes require a much lower transmembrane pressure compared to RO but their monovalent ion rejection is not sufficiently high [18]. Our research focusses on the surface modification of commercial NF membranes in order to enhance their monovalent ion rejection capabilities to the level of RO membranes without significantly lowering down their permeabilities. These highly perm-selective membranes have the potential to replace the existing RO membranes and thereby reduce the energy/electricity costs involved in the RO process. The surface modification technique used in our research is the Layer-by-layer (LbL) assembly which involves the alternate deposition of oppositely charged polyelectrolytes (PE) on a surface [19]. This aqueous based thin film deposition technique was pioneered by Iler [20] and much later, in 1992 Decher et al. [21,22] brought to light the tremendous versatility of this technique. Over the last two decades this thin film deposition technique has found wide applications in the fields of sensors [23,24], fuel cells [25,26], gas barrier films [27,28], drug delivery [29,30] and membranes [18,31,32]. The wide choices of polyelectrolytes available, the deposition conditions used during the process and the number of bilayers are some of the tuning parameters that help in optimizing the performance of membranes [18].

PEM membranes have been widely employed to reject divalent/multivalent ions [33–38]. Comparatively fewer research groups have worked on the application of polyelectrolyte multilayer (PEM) membranes to typical RO applications involving the rejection of monovalent ions [39–44]. In order to fabricate PEM-based RO membranes, an approach commonly taken by a number of research groups is to modify a porous UF membrane using a considerably large number of PE bilayers. In most of these cases a high rejection value was reported but the permeabilities dropped down to values even lower than commercial RO membranes. A parallel approach was taken by Malaisamy et al., to make salt rejecting membranes by modifying a commercial NF 270 (Dow Filmtec, MI) membranes with just a few bilayers of polyelectrolytes [45]. A high value of permeability was attained; however the percentage removal of the target ion, i.e. fluoride ion was not as high as a commercial membrane. Overall, a good balance between high permeability and high rejection has not been achieved so far. In our work we used the NF 90 membrane (Dow Filmtec, MI) as the base membrane and PAH and PAA as the surface modifiers. We worked on optimizing the LbL process in terms of number of

bilayers and pH used for depositing the multilayers. The most optimized system was then compared with the commercial RO membranes in terms of permeability and perchlorate rejection. To our knowledge, this is the best combination of high permeability and high rejection of monovalent ions, as shown by a PEM based RO membrane, based on what has been reported in literature so far. Besides, the application of PEM based membranes for the removal of perchlorate ions has not been tried out before.

## 2. Experimental section

### 2.1. Materials

The nanofiltration membranes (NF 270 and NF 90) as well as the reverse osmosis membranes (BW 30 and SW 30) were purchased from Filmtec, Dow Chemical Company (Midland, MI). Potassium perchlorate salt, poly (acrylic acid sodium salt) ( $M_w$  15,000, 35 wt.% solution in water) and poly (allylamine hydrochloride) ( $M_w$  900,000) were purchased from Sigma Aldrich. Glutaraldehyde (50 wt.% solution) was obtained from Electron Microscopy Sciences (Hatfield, PA). All aqueous solutions were prepared using deionized (DI) water ( $>18.2$  M $\Omega$ ) supplied by a Barnstead Nanopure Diamond-UV purification unit equipped with a UV source and a final 0.2  $\mu$ m filter. Unless specified otherwise all procedures were carried out at room temperature.

### 2.2. CF 042 cross flow membrane system

A CF 042 cross flow unit (Sterlitech, Kent, WA) with an effective surface area of 42 cm<sup>2</sup> was employed as the membrane module. This type of cross flow cell has a rectangular geometry, the flow channel being 3.62" in length, 1.8" in width and 0.09" in depth. A positive displacement pump (Hydra-cell M03, Wanner Engineering, Minneapolis, MN) was used to deliver the feed from a conical 5-gallon feed tank. A variable speed drive (Emerson, St Louis, MO) was attached to the pump which controlled its speed. A part of the feed stream was directed back to the feed tank via a bypass valve. A back-pressure regulator was used to control the transmembrane pressure across the membrane module. The retentate stream was recycled back to the feed tank and the retentate flow rate was measured by a Site Read Panel Mount Flowmeter (Blue-White, Huntington Beach, CA). The permeate stream was collected and weighed on a measuring balance and the flow rate was determined gravimetrically. The temperature of the solution inside the feed tank was maintained at room temperature by a digital chiller (Polysciences, Warrington, PA). All the components of the cross-flow setup were obtained from Sterlitech (Kent,

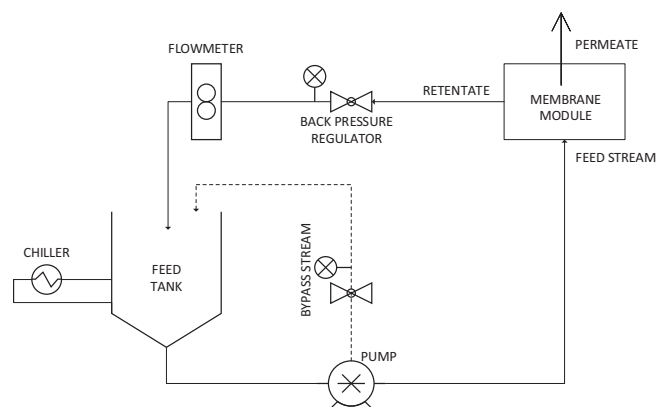


Fig. 1. Schematic representation of Sterlitech CF 042 cross flow system.

Download English Version:

<https://daneshyari.com/en/article/640642>

Download Persian Version:

<https://daneshyari.com/article/640642>

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