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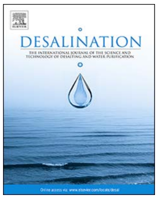

In situ modification of membrane elements for improved boron rejection in RO desalination

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ABSTRACT

The study presents in situ modification of a spiral-wound seawater reverse osmosis (SWRO) membrane elements using sorption of hydrophobic long-chain aliphatic amine molecules as a generic approach to increasing selectivity, in particular, boron removal. Spiral-wound seawater SW30 elements modified using decylamine and dodecylamine showed 2–4 times lower boron passage for the modified elements at the expense of a moderate drop in permeability. Autopsy indicated no change in surface morphology and chemistry, suggesting immobilization of the modifying molecules within the active layer. Overall, the reported in situ modification of the SWRO element resulted in a superior trade-off between permeability and boron passage and no change in salt rejection, as compared to regular polyamide membranes. The enhanced selectivity toward boron5 removal could potentially help eliminate or reduce the costs related to the second pass in sea water desalination.

1. Introduction

RO technology has progressively developed over the last six decades since the first cellulose acetate membranes introduced by Loeb and Sourirajan [1]. Reverse osmosis (RO) is nowadays the main technique used for seawater desalination, potable water reuse, water treatment and other applications. An important milestone in RO technology was the development of the interfacial polymerization technique for producing thin-film composite (TFC) membranes with high salt rejection and high water permeability by Cadotte and Rozelle in the 1970s. RO membranes can reject a wide range of inorganic salts and soluble organic molecules. As an example, modern seawater reverse osmosis (SWRO) membranes can easily achieve NaCl rejection > 99.5% [2]. Other successful applications include brackish water treatment, potable and industrial water reuse, biotechnology, and beverage and dairy production [3].

Unfortunately, despite the high salt rejection, the ability to remove undissociated low-molecular weight (MW) molecular solutes, naturally occurring and human activity-related, is still not satisfactory. An important example is boric acid (MW 62 g/mol). It is a contaminant of some concern for public health, yet it is far more problematic for agriculture and environment. Sea water desalination plants typically have to deploy two or more passes of RO modules, whereby the RO permeate from the first pass is treated in the second pass to reduce the boron concentration in the product water under 0.5 mg/L [4,5]. It is noteworthy that commercial SWRO membranes can only achieve a moderate boron rejection (83–92%) at seawater pH (~7.5–8), for which boron exists primarily in the form of undissociated boric acid [6,7,4]. An improvement in boron passage of RO membrane could save the significant expenses related to for the second pass at desalination plants and motivates search for new ways to enhance boron removal [8,9].

Most commercial RO membranes today are polyamide-based thin-film composites. A typical TFC membrane includes an active polyamide skin layer on top of a polysulfone microporous supporting layer cast on a polyether non-woven fabric. The apparent thicknesses of these three layers are approximately 0.05–0.2, 50, and 100 μm; respectively [10–12] The active toplayer is the main barrier that determines the water permeability and solute separation efficiency of the membrane. It is formed by interfacial polymerization whereby an aqueous solution containing a polyfunctional amine placed on the support layer, reacts with a polyfunctional acid chloride dissolved in another solvent solution at the interface between solutions [3]. The polymerization is usually incomplete and leaves a substantial number of unreacted carboxylic groups with a minor fraction of amine groups [13], thereby, overall, the membrane bears a significant negative acidic charge.

It was previously suggested [7,14] that membrane affinity toward boric acid can be reduced and boron rejection can be improved in two principal ways: (1) reducing *polarity*, i.e., increasing *hydrophobicity* of the selective layer and (2) enhancing *steric exclusion*, i.e., tightening the membrane and reducing its effective pore size. Grafting a tight hydrophobic layer on top of polyamide, which "plugs" or "caulks" largest

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defects in polyamide layer, was proposed as one way to improve the rejection of boron and other contaminants and the permeability-boron rejection tradeoff [7,14,15].

Recently, we reported another simple and attractive method for modification of RO membrane based on these principles, which could noticeably improve removal of boric acid by RO membranes [16]. In this approach the modification is achieved by filtering through the membrane a solution of modifying aliphatic amine molecules. As a result, amine molecules are adsorbed and immobilized within the polyamide, altering the membrane chemistry and improving exclusion of the solutes. The effect of such modification was discussed and confirmed in preliminary experiments in dead-end cells [16]. This study also showed that the induced change could be fairly sustainable, e.g., not reversal of characteristics was observed after overnight wash with water. However, results obtained using dead-end and small flat sheet samples are often not fully representative of the actual performance in commercial modules. The focus of the present study was then on the up-scaling of the modification procedure to genuine commercial spiral-wound RO elements and demonstrating its feasibility and performance improvements in pilot-scale experiments.

2. Materials and methods

2.1. Materials

All chemicals were purchased from Sigma-Aldrich and Acros and used without purification. Deionized water (DW) was used in all experiments. The fully aromatic polyamide (PA) membrane spiral-wound elements SW30-2540 (Dow) of nominal active membrane area 2.8 m^2 were purchased from Dow and stored as recommended by the manufacturer.

2.2. Reverse osmosis setup

In situ modification of a spiral wound membrane element and the filtration experiments were carried out in a pilot unit described schematically in Fig. 1. The setup included a 200 L feed tank, a 2540 membrane element mounted in a stainless steel pressure vessel (M-1), a high pressure pump with an auxiliary feed pump, a feed pressure gauge (PI-1) and a control valve with a pressure gauge located in the concentrate line (PI-2). The water fluxes were monitored using flow meters installed in the feed and permeate lines. The water temperature was kept constant using a heat exchanger (HE-1) and monitored with a thermometer. The system was operated in a closed loop returning the permeate and concentrate back to the feed tank. The feed tanks could be fully drained via drainage valve D-1 to replace the feed solution between testing and modification.

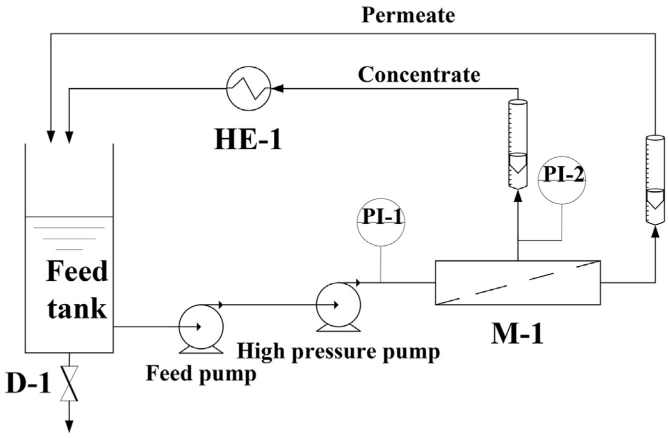

Fig. 1. A schematic drawing of the RO pilot system.

Table 1
Molecules used in the modifications and their characteristics.

Name/designation	Mw $[g/mol]$[a]	MPA $[\mathring{A}^2]$[a]	Volume $[\mathring{A}^3]$[a]	LogP[a]	Solubility, $[mM]$[b]
Amylamine/C5	87.16	20.14	108.02	1.14	∞
n-Octylamine/C8	129.24	21.37	159.01	2.48	15.5
Decylamine/C10	157.30	26.49	192.98	3.37	3.5
Dodecylamine/C12	185.35	26.90	226.98	4.25	0.42

[a] http://www.chemicalize.org, MPA is the minimal projected area, logP – is octanol-water partitioning coefficient.

[b] ECOSTAR - Ecological Structure Activity Relationships (ECOSAR) Predictive Model [17].

2.3. Membrane testing

The filtration tests were performed on an RO pilot system schematically shown in Fig. 1. A SW30-2540 RO element was mounted in the housing and initial performance was tested as follows. First, the membrane was compacted at 20 bar for 2 h and the pure water (DW) permeability was measured at feed pressure 40 bar and concentrate flow 500 L/h. DW then was replaced with a solution of 15,000 ppm NaCl and 5 ppm boron (as boric acid) at pH 7–7.3 and the performance, including NaCl and B rejection and volumetric flux, was tested at feed pressure 40 bar, keeping the recovery in the range 13–16%.

Thereafter, the membrane was treated using solutions of one of the aliphatic amine molecules at 4 different concentrations 0.1, 0.5, 1 and 2 mM. Table 1 lists the molecules used in the modification experiments. For each element the modifying solutions of a specific amine were applied consecutively, starting from the lowest concentration (0.1 mM) up to the highest one (2 mM). After each solution, the system was washed with DW and performance of the membrane was tested again as explained above. Tables S1–S4 in Supplementary material lists the conditions of operation, including recovery, permeate and concentrate flow rates.

Permeate and feed samples were collected and measured every 30 min before modification and after washing stage followed the modification. The permeability was determined as follows:

$$L_p = \frac{V}{tA(P-\pi)} \tag{1}$$

where V is the permeate volume collected over time t, A the membrane surface area in the element (2.8 m^2), P the applied transmembrane pressure difference, and π is the osmotic pressure difference which was calculated using the van't Hoff equation using NaCl concentration in the feed and permeate determined from electric conductance. Boron concentration was measured using inductively coupled plasma (ICP) analyzer (iCAP 6000 Series, Thermo Scientific). The passage P and rejection $R = 1 - P$ of salt and boric acid were calculated using the relation.

$$P = C_p/C_f, \tag{2}$$

where C_p and C_f are the permeate and feed concentrations, respectively.

2.4. Surface Characterization

After tests, the modules were cut open and membrane samples were taken from different parts of the module for surface characterization. Attenuated total reflection (ATR) FTIR spectra (average of 40 scans at 4 cm^{-1} resolution) were recorded on a Nicolet 8700 FTIR spectrometer (Thermo-Electron corporation) using a Miracle ATR attachment with a one-reflection diamond-coated KRS-5 element (Pike).

The contact angle was measured by the sessile drop method using a Kruss contact angle analyzer. Every measurement was repeated and averaged for at least 7 drops on each membrane sample. Surface morphology was examined on a Zeiss Ultra-Plus scanning electron microscope (SEM). Prior to imaging the membrane samples were dried in