



Induced organic fouling with antiscalants in seawater desalination



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HIGHLIGHTS

- Antiscalants were shown to affect membrane zeta-potential and hydrophobicity.
- Polyacrylate and carboxylated dendrimeric antiscalants enhanced organic fouling.
- Polyphosphonate antiscalant had no effect on organic fouling.
- QCM-D and AFM were used to study antiscalant effects on organic fouling.

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ABSTRACT

The effect of exposure reverse osmosis (RO) membrane to antiscalants (AS) on consequent organic fouling during seawater desalination was analyzed. Membrane surface properties (hydrophobicity and zeta potential) were altered upon the conditioning of the membrane with AS during the desalination process. For all AS used, polyphosphonate, polyacrylate, or dendrimeric carboxylated based AS, membrane zeta-potential became less negatively charged over pH range between 3 and 10. Furthermore, the membrane became significantly more hydrophobic when dendrimeric carboxylated and polyacrylate based AS were used and only minor effects were observed for the polyphosphonate based AS. The membrane organic fouling process, tested with different model organic foulants (alginate and BSA), was significantly enhanced in the presence of polyacrylate or carboxylated dendrimeric based AS, which were used to condition the membrane surface. These changes in fouling behavior are likely attributed to the AS effects on RO membrane hydrophobicity and zeta potential after exposure and adsorption to the RO membrane. Force curve measurements using atomic force microscopy (AFM) on membranes and adsorption of the organic foulants on sensors of quartz crystal microbalance with dissipation (QCM-D) monitoring were used to explain the induced adsorption of the model organic foulants by polyacrylate and carboxylated dendrimeric based AS.

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1. Introduction

Fouling of reverse osmosis (RO) membranes used for seawater and wastewater desalination is considered as a main obstacle, which challenges the widespread application of this technology. RO membrane fouling is caused by different agents including inorganic (scaling), colloidal, or dissolved organic matters, [1–3] as well as by microbial biofilm formation (biofouling) [4,5]. Scaling of RO membranes used for seawater desalination is the most serious problem, which could impair plant performance and reduce permeate quality. Scaling reduces permeate flux, increases feed pressure and eventually shortens membrane life [6,7]. Membrane scaling is caused by the precipitation and the accumulation of sparingly soluble inorganic salts present in the feed water, associated with divalent and multivalent ions, which exceed their solubility level, on the membrane surfaces. Major scaling salts are calcium

carbonate (CaCO_3), calcium sulfate ($\text{CaSO}_4 \cdot \text{H}_2\text{O}$), barium sulfate (BaSO_4), strontium sulfate (SrSO_4), silicates, calcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$) and alumino-silicates (Al_2SiO_5). Scaling of RO membranes has a proportional relation with plant recovery; increasing the recovery elevates the concentration of salts in the feed side and therefore, the RO membrane will be more prone to scaling [8]. Different studies suggested that membrane scaling is dependent on several factors including, but not limited to, membrane characteristics, module geometry, feed solution characteristics and operating conditions [9–11]. One of the most commonly used method for controlling scale formation involves adding antiscalants (AS) to the RO feed water [12]. AS are poly-electrolyte polymers used in a multitude of traditional applications. AS have a tremendous importance, which increased their usage in water applications such as cooling and boiling water systems, seawater and wastewater treatment facilities, and oil field operations to prevent inorganic fouling (scaling) [13]. AS play a vital role in keeping the efficiency of the RO plant operation at the highest possible recovery rate; avoiding the usage of hazardous acids; reducing water consumption by safely

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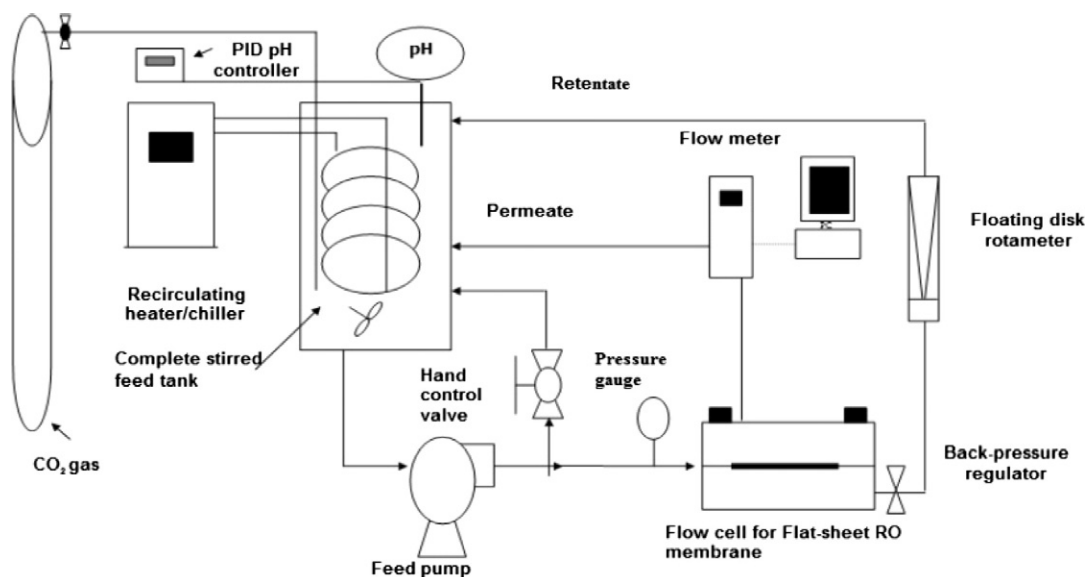


Fig. 1. Cross-flow flat-sheet RO desalination unit used for conditioning RO membranes with AS during desalination of seawater.

operating at high permeate recovery; using fewer chemicals; producing less concentrate; reducing energy costs, and reducing the downtime caused by frequent membrane cleanings [14,15]. Moreover, AS have low molecular weight, in the range of 1000–3500 g/mol [16]. All the previous advantages placed AS in a high rank to be recommended as a best pretreatment choice in comparison to different chemicals including acids. Commercially available AS fall into four major groups: polyphosphates, polyphosphonates, polyacrylates and carboxylated dendrimeric polymers [13]. One of the main disadvantages of AS was reported to enhance membrane fouling [17–19]. Also, it has been shown that some cationic flocculants used for the pretreatment stages can particularly react with some types of negatively charge AS and form adhesive gel like fouling layer. By dosing a small amount of AS, the chemical composition of the feed water modifies due to the polyelectrical effect of these chemicals. Previously, we showed that AS adsorption to RO membrane surface strongly affects subsequent fouling behavior by altering the physico-chemical surface properties of the membrane and serving as a conditioning film for further organic- or bio-fouling [20]. Fine colloidal and dissolved organic compounds, including proteins, polysaccharides, and natural organic matter (NOM) found in natural water can pass all the pretreatment stages of the desalination process, interact with other pretreatment chemicals including AS, and subsequently foul the RO membranes.

Organic fouling mechanisms of RO membranes involve the initial deposition of organic foulants on the membrane surface (foulant–membrane interaction) followed by subsequent growth of a dense fouling layer (foulant–foulant interaction) that adversely influences membrane performance and efficiency [21]. Organic fouling is influenced by (i) membrane characteristics (structure and chemical properties including surface charge and hydrophobicity); (ii) feed solution chemistry (divalent cations, ionic strength, and solution pH); (iii) foulant composition and properties (molecular weight and polarity); and (iv) operating conditions at the membrane surface including hydrodynamics and permeate flux [22,23]. Accordingly, organic fouling is induced by a variety of parameters, among others are the presence of divalent cations, elevated ionic strength, low pH, hydrophobic fouling compounds, elevated surface charge (away from the membrane isoelectric point), concentration polarization, elevated surface roughness, and increase in permeate flux [24–27].

Up to date, relations between organic foulants and AS in seawater desalination were not investigated. Some AS and dispersants enhanced organic fouling through adsorption of humic acids onto the membrane

surfaces [28]. Controversially, it was reported that bovine serum albumin (BSA) fouling could be greatly reduced by using AS in desalination of brackish water [29]. Also, it was shown that organic fouling may be mitigated under appropriate conditions such as optimal AS dosage [30].

The overall goal of this work was to investigate AS effects on RO organic fouling in seawater. In this work, it was shown that AS were adsorbed to the polyamide RO membrane surface active layer and therefore, RO membrane surface properties were altered. RO permeate flux decline was tested when two model organic foulants (alginate and BSA) were added to the feed seawater with different AS including polyphosphonates, polyacrylates and carboxylated dendrimeric based AS. Moreover, results from quartz crystal microbalance with dissipation (QCM-D) and atomic force microscopy (AFM) provided explanation for the cases when organic fouling was enhanced.

2. Materials and methods

2.1. Model organic foulants

Alginate and BSA have been selected as model organic foulants. Alginate represents polysaccharides with a hydrophilic nature, while BSA is a hydrophobic foulant. The molecular weights of BSA and alginate were 66.5 kDa and 10–60 kDa, respectively. The model foulants were purchased from Sigma-Aldrich (St. Louis, MO) and were received in a powder form. For the alginate and the BSA, both were dissolved in seawater and a stock solution of $2 \text{ g} \cdot \text{l}^{-1}$ was prepared for further use. Prior to their use, the organic foulant stock solutions were filtered through $0.45 \mu\text{m}$ hydrophilic filters (Millipore, Billerica, MA).

2.2. RO unit and membrane preparations

The RO laboratory unit (Fig. 1) comprised a membrane cross-flow cell, high-pressure pump, feed water reservoir of 10 l, chiller equipped

Table 1
Organic carbon (DOC), nitrogen, phosphorous and ammonium content (mg/l) in an AS solution of 10 mg (liquid) AS per liter of deionized water.

Type of AS	DOC	Total N	Total P	NH_4^+
Neutralized polyacrylate	2.19	0.1	3.8	0.1
Neutralized polyphosphonate	1.46	1.4	7.3	0.2
Polycarboxylated dendrimer	5.6	0.3	0.3	0.1

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