Induced organic fouling with antiscalants in seawater desalination

Amer Sweity, Zeev Ronen, Moshe Herzberg * 

Albert Katz International School for Desert Studies, Jacob Blaustein Institutes for Desert Research, Zuckerberg Institute for Water Research, Ben-Gurion University of the Negev, 84990, Israel

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.

ARTICLE INFO
Article history:
Received 12 June 2014
Received in revised form 18 August 2014
Accepted 19 August 2014
Available online 14 September 2014

Keywords:
Desalination
Reverse osmosis
Antiscalants
Organic fouling

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.

© 2014 Elsevier B.V. All rights reserved.

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 (CaCO₃), calcium sulfate (CaSO₄·H₂O), barium sulfate (BaSO₄), strontium sulfate (SrSO₄), silicates, calcium phosphate (Ca₃(PO₄)₂) and alumino-silicates (Al₂SiO₅). 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

http://dx.doi.org/10.1016/j.desal.2014.08.018
0011-9164/© 2014 Elsevier B.V. All rights reserved.

* Corresponding author. Tel.: +972 8 6563520; fax: +972 8 6563503.
E-mail address: herzberg@bgu.ac.il (M. Herzberg).
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 a hydrophilic 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 g·l⁻¹ was prepared for further use. Prior to their use, the organic foulant stock solutions were filtered through 0.45 μm 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

![Fig. 1. Cross-flow flat-sheet RO desalination unit used for conditioning RO membranes with AS during desalination of seawater.](image-url)
with a temperature control system, PID pH controller for dosing CO₂ gas, and a data acquisition system. Permeate flow rate, conductivity, and pH were acquired for relevant experiments. A high flux RO flat-sheet membrane SW30 HRLE 400 (Dow Filmtec, USA) was compacted before each experiment with deionized water (DW) at a pressure of 60 bars until the permeate flux attained a constant value, usually after 18–24 h. The rectangular, crossflow, channel membrane unit (without spacer) dimensions were 7.7 cm × 2.6 cm with a channel height of 0.3 cm feed flow rate 751 h⁻¹ corresponding to cross flow velocity of 26.8 cm s⁻¹ and shear rate of 536 s⁻¹. A pressure of 60 bars and a temperature of 25 °C were kept constant during all of the experiments. Following the compaction stage of the RO membrane with DW, feed of seawater was collected from the Palmachim desalination plant (Palmachim, Israel) after passing through all the pretreatment process, except for AS addition. In all the experiments, seawater supplemented with 20 mg l⁻¹ AS (weight of liquid AS per liter of seawater) was desalinated and conditioned the RO membranes for 24 h, prior to the fouling experiments using seawater supplemented with model foulants (control experiment was conducted without AS). General chemical analysis of the commercial AS used in this study is presented in Table 1.

After the conditioning of the RO membranes in each experiment, a model organic foulant was added to the feed seawater (10 l) of the RO unit. The initial foulant (BSA or alginate) concentration at the beginning of the fouling experiment was 20 mg l⁻¹. For the control experiment, the feed seawater used for conditioning the membrane did not include AS. The whole period of the organic fouling experiments was four days. Permeate flux decline was measured every 20 min and pH was kept constant in the range of 6.8 ± 0.2. Also during the fouling experiments (similar to the membrane conditioning step) seawater was supplemented with or without pre-treatment with AS. For each solution, measurements were done twice. During each measurement, each run of the electrolyte solution flow proceeded in two directions (right to left and then left to right). The zeta potential of the RO membranes was calculated from the streaming potentials using the Helmholz–Smoluchowski equation with the Fairbrother and Mastin substitution [34,35]. The hydrophobicity of the RO membrane was deduced from the contact angle analysis method, whereby it is determined by the captive bubble method (OCA, Data Physics). A droplet size of double distilled water with a diameter of 0.4–0.5 mm was introduced onto the RO membrane surface after the antiscalant treatment stage in the RO unit. Duplicated experiments, with five different measurements of contact angle, were carried out for each of the treated membranes to obtain at least 10 measurements of contact angle for each set of conditions.

2.4. Extracting of the organic foulants from the fouled membranes

After each run, pieces of each membrane from different fouling experiments were divided and placed in 20 ml scintillation vials. Then, 5 ml of 0.2% sodium pyrophosphate in mineral salts buffer (10 mM NaCl) was added to enhance desorption of organic material from the membrane surface. The vials were sonicated 10 min to extract foulants, and the extracted suspensions were collected for protein and carbohydrate analysis. Total protein concentration in the extracted suspension was analyzed using the colorimetric quantitative protein determination with the Bio-Rad® protein assay according to Bradford [32]. BSA in the extraction buffer was used as a standard. Polysaccharide content was determined according to Dubois et al. [33] using alginate as a standard. Masses extracted from all the membranes were normalized to the membrane surface area.

2.5. Membrane surface properties

Membrane surface zeta potential was measured using a streaming potential analyzer (SurPass Elektrokinetic Analyzer) at 10 mM NaCl solution with or without pre-treatment with AS. For each solution, measurements were done twice. During each measurement, each run of the electrolyte solution flow proceeded in two directions (right to left and then left to right). The zeta potential of the RO membranes was calculated from the streaming potentials using the Helmholz–Smoluchowski equation with the Fairbrother and Mastin substitution [34,35]. The hydrophobicity of the RO membrane was deduced from the contact angle analysis method, whereby it is determined by the captive bubble method (OCA, Data Physics). A droplet size of double distilled water with a diameter of 0.4–0.5 mm was introduced onto the RO membrane surface after the antiscalant treatment stage in the RO unit. Duplicated experiments, with five different measurements of contact angle, were carried out for each of the treated membranes to obtain at least 10 measurements of contact angle for each set of conditions.

Fig. 2. The effect of AS treatment (20 mg/l) on membrane zeta potential and hydrophobicity: polyphosphonate-based (PP), polyacrylate-based (CA) and carboxylated dendrimer (Den) AS were tested. (A) Filmtech-SW30 RO membranes surface zeta-potential plotted as a function of the pH in a background solution of 10 mM NaCl; (B) Captive air bubble contact angle on the surface of Filmtech-SW30 RO membrane. The results present average of five measurements with one standard error, and are significantly different with p-value < 0.05.
2.6. QCM-D measurements

Polyamide coated sensors mimicking RO membrane surfaces were employed in QCM-D, E4 type (Q-Sense, Sweden), for analyzing the effect of AS on organic fouling. All QCM-D experiments were performed under flow-through conditions using a digital peristaltic pump (Ismatec Peristaltic Pump, IDEX) operating in a pushing mode. The flow rate of the working solution in the QCM-D flow cell was 150 μl·min⁻¹. The following solutions were injected sequentially to the QCM-D flow cell: (i) double distilled water baseline for 20 min; (ii) filtered seawater for 20 min; (iii) filtered (0.2 μm) seawater supplemented with 20 mg·l⁻¹ AS for 1 h; (iv) filtered (0.2 μm) organic foulant model solution with a final concentration of 20 mg·l⁻¹ of either BSA or alginate, supplemented with or without AS for 30 min; (v) final concentration of 20 mg·l⁻¹ of either BSA or alginate, supplemented with or without AS for 30 min; (v) finally, steps iii, ii, and i were repeated in a reverse order. When no AS was supplemented, the duration of step (ii) was 80 min. A replicated set of experiments was made for each model organic foulant with polyphosphonate, polyacrylate and carboxylated dendrimer based AS, which was separately injected to the QCM-D. The adsorption kinetic curves were made by Q-Tools software (Q-SENSE, Sweden). This software adjusts the incoming and outgoing electrical currents, regulates the altitude of the oscillation and controls the temperature according to the temperature set. The variations of frequency shift (Δf) were measured for five overtones (n = 3, 5, 7, 9 and 11) and the 7th overtone is presented in the results section. The adsorbed mass of AS to the polyamide sensors was calculated to using the Sauerbrey[36] equation, which describes the linear relationship between frequency and mass: \(\Delta m = \frac{-C_n}{n} \Delta f\) where \(\Delta m\) is the change in mass per area unit (ng·cm⁻²), \(C = 17.7\ ng\cdot s\cdot cm^{-2}\), \(n\) is the overtone number and \(\Delta f\) is the frequency shift (s⁻¹).

3. Results and discussion

3.1. Effects of AS on membrane surface properties

Both surface charge and hydrophobicity are of major importance to the propensity of the membrane to organic fouling [37]. Both polyphosphonate and polyacrylate based AS were shown in our previous study to alter both the hydrophobicity and surface charge of the SW30 HRLE 400 (Dow Filmtec, USA) membrane, which in turn, likely affect the initial adsorption of organic foulants (Fig. 2) [20]. Polyphosphonate-based AS is shown to alter, to smaller extent, membrane hydrophobicity in comparison to the polyacrylate based AS, though, the effect of exposure a third polycarboxylated dendrimeric based AS on membrane hydrophobicity was similar to the case of exposure of the membrane to the linear polyacrylate. Higher surface hydrophobicities were detected for the polyacrylate (54.3 ± 5.4°) and carboxylated dendrimeric based AS (57 ± 4.7°) than the polyphosphonate based AS (42 ± 4.3°), and seawater without AS (32 ± 1.5°). A similar effect on membrane surface charge was observed for all AS, in which membrane surface zeta potential was elevating to the positive sign, for all cases (Fig. 2). Most likely, an important driving force for adsorption of the polyacrylate and carboxylated dendrimeric based AS to the RO membrane surface is mediated by specific interactions between carboxyl groups of the polyamide surface and backbone carboxyl groups of the polyacrylate and carboxylated dendrimeric based AS bridged with divalent cations, interactions which are accompanied with an entropic gain during the adsorption event [38]. Carboxyl groups, abundant in the polyacrylate and carboxylated dendrimeric AS, are de-protonated at the common working pH range (above 6). De-protonation of polyacrylates to large extent can lead to a high swelling capacity [39]. In conclusion, our results suggest that adsorption of polyacrylates and carboxylated dendrimers to the membrane, mediated by multivalent ions, can lead to a complexed, swollen, and cross-linked fouling deposit with a high fouling potential.

3.2. Effects of AS conditioning on force interaction with CML particles

Retraction force curves analyzed with AFM between RO membranes conditioned with AS (20 mg·l⁻¹) were conducted (Fig. 3). The adhesion forces between CML particle (1 μm diameter) and the RO membrane after conditioning with different AS were measured and the distribution of the adhesion forces of the retraction curves (maximum values) is presented in Fig. 3. By analyzing the force interactions between the RO membrane and a highly charged surface of CML particle with dense layer of carboxyl groups, we try to simulate the effect of conditioning RO membranes with AS on the initial organic fouling process (representing foulant–membrane interaction). A significant difference

![Fig. 3](image-url) Frequency distribution of the adhesion forces between the AFM CML particle probe and the conditioned RO membranes, which mimic foulant–membrane interaction. The background solution was 100 mM NaCl at pH 6.8. Force measurements were performed at 8 different locations on the membrane, with 20 measurements at each location.
between the force distribution of the membranes conditioned with polyacrylate and carboxylated dendrimeric based AS versus the membrane conditioned without AS or with polyphosphonate is presented in Fig. 3. The membranes conditioned with polyacrylate and carboxylated dendrimeric based AS showed a higher adhesion to the CML particle with average forces of 1.2 mN/m ± 0.43 and 1.06 mN/m ± 0.36, respectively versus values of 0.09 mN/m ± 0.08 and 0.16 mN/m ± 0.11 for the membranes conditioned with seawater and polyphosphonate based AS, respectively. Commonly, fundamental approach for delineating organic fouling mechanisms has been carried out in a variety of publications by analyzing force interactions between CML particles and RO membranes with AFM[31,40]. Hence, the adhesion force normalized by the radius of the particle \( F/R \) was found as a good indicator for RO membrane fouling potential with humic acids. \( F/R \) describes the energy per unit area required to separate the particle and the membrane surface to an infinite distance [41]. Probably, the increase in membrane hydrophobicity due to conditioning with either polyacrylate or carboxylated dendrimeric based AS (Fig. 2B) is the main cause for the elevated adhesion analyzed with AFM. This suggestion is supported later by QCM-D experiments and flux decline measurements in the RO system.

3.3. Effects of AS conditioning on fouling of RO membrane with BSA and alginate

The effect of AS on membrane performance, in the presence of model organic foulants, BSA and alginate was tested at AS concentration of 20 mg·l\(^{-1}\). Enhanced fouling experiments were performed with pretreated seawater under controlled pH (6.8 – 7.0) conditions by a controlled dosage of CO\(_2\)(g). Fig. 4A and B shows the effect of AS on BSA and alginate fouling through permeate flux decline due to fouling with these model foulants accompanied with each of the AS being tested. For both the foulants, alginate and BSA, highest rate of permeate flux decline was observed for the fouling experiments accompanied with the polyacrylate and carboxylated dendrimeric based AS. BSA fouling rate was 1.2 and 1.02 l m\(^{-2}\) h\(^{-1}\) for polyacrylate and carboxylated dendrimeric based AS, respectively, and 0.63 and 0.48 l m\(^{-2}\) h\(^{-1}\) for polyphosphonate based AS and seawater, respectively. For the fouling experiments with BSA, the elevated fouling with polyacrylate and carboxylated dendrimeric based AS, is probably due to the higher hydrophobicity induced by AS conditioning the membrane surface as shown in Fig. 2B. The slight increase of fouling by BSA with polyphosphonate may be related to lower repulsion of the membrane conditioned with polyphosphonate, due to its lower zeta potential, also induced by polyphosphonate conditioning (Fig. 2A). For the fouling with alginate, a rapid flux decline is observed for all cases, with, or without AS, at the beginning (1st 50 h) of the fouling experiment. The similar and fast permeate flux decline rate ~7.5 ± 0.5 l m\(^{-2}\) h\(^{-1}\) during the first 50 h of fouling with sodium alginate is likely because of the formation of alginate gel on the membrane surface by the abundant concentration of calcium cations from the seawater used as a feed solution [37]. For alginate fouling, a different pattern of permeate flux decline was observed in the presence of polyacrylate and carboxylated dendrimeric based AS, where the rate of flux decline was relatively constant throughout the 150 h experiment, while either for the polyphosphonate AS or in the absence of AS, flux decline leveled off after ~30 h. The typical alginate gel layers formed on the membranes conditioned with polyacrylate and carboxylated dendrimeric based AS showed a more obvious, thicker layer observed later. Intriguingly, permeate flux decline results correlate
to the higher adhesion forces between the RO membrane and CML probe analyzed with the AFM for these membranes, which were conditioned with these AS. Different complexes between the BSA and either the polyacrylate and carboxylated dendrimeric based AS may have been formed and may also induced membrane fouling [23,42], in addition to the aforementioned effects of gel layer formation by adsorbed AS to the membrane surface [43]. The faster fouling in the presence of polyacrylate and carboxylated dendrimeric based AS, mediated by the presence of divalent cations, could be explained by their high density of carboxyl functional groups fully de-protonated at pH 6.8–7 [44], which contribute to high density of possible chemical bridging between the membrane, the AS, and the foulants. Opposite effect when AS reduced fouling of BSA and humic acid (HA) was shown by Yang et al. [29,30] with a negative impact when AS was over-dispersed. In a Yang et al. study, when the AS was used (polyaspartic acid – PASP), the charge of the fouling colloids became more negative and their size decreased due to formation of a water-soluble complex: BSA–Ca–PASP and HA– Ca–PASP via Ca\(^{2+}\) bridging. It should be mentioned that Yang et al. conducted their experiments under significant lower ionic strength (~10 mM), while our experiments were done with real seawater at ionic strength of ca. 600 mM.

Significant effect of the induced fouling by AS on salt rejection was observed only for the polyacrylate and carboxylated dendrimeric based AS, with both foulants, BSA and alginate (Fig. 4C and D). The results showed lower salt rejection for the membranes that were conditioned with polyacrylate and carboxylated dendrimeric based AS and fouled with either BSA or alginate. Since permeate flux decline was also the highest for these AS and since organic fouling has been reported to have minor or almost no contribution to the “cake enhanced osmotic pressure” (CEOP) phenomenon [40,45], the decrease in salt rejection is probably because of “concentration effect” of the solutes passage in a smaller permeate volume.

In order to provide further analysis on the effect of membrane exposure to AS on organic fouling, in addition to membrane performance, the associated amount of adsorbed fouling layer was analyzed. The adsorbed BSA and alginate were dissolved into 0.2% sodium pyrophosphate buffer solution (see Section 2) and the total protein and polysaccharide content was colorimetrically analyzed [32,33]. As expected and correlated to the flux decline results (Fig. 4C), for the membranes conditioned with polyacrylate and carboxylated dendrimeric based AS, a higher adsorbed BSA was detected compared to the cases of using either polyphosphonate or seawater without AS: 262.3 ± 18.6 and 256.3 ± 14.3 μg·cm\(^{-2}\) versus 196 ± 9.9 and 166.6 ± 21.1 μg·cm\(^{-2}\), respectively (Fig. 5). Similar correlation was obtained between permeate flux decline and the amount of deposited alginate on the membrane: the alginate concentration dissolved from the membranes that were conditioned with polyacrylate and carboxylated dendrimeric based AS was higher than the membranes that were conditioned with either polyphosphonate or seawater without AS: 640.4 ± 48.4 and 633.5 ± 32.2 μg·cm\(^{-2}\) versus 415.4 ± 66.2 and 357.8 ± 48.4 μg·cm\(^{-2}\), respectively (Fig. 5).

3.4. The effect of AS conditioning on BSA and alginate adsorption to polyamide: QCM-D analysis

The effect of conditioning polyamide surface with AS on BSA and alginate adsorption was elucidated in a QCM-D flow cell using polyamide coated quartz crystals. Fig. (6A&B) shows the frequency shift during the entire QCM-D run, changes in the chemical species in the water as well as changes of the adsorbed mass on the sensor surface were reflected by the shifts in the resonance frequencies of the quartz crystal sensor coated with polyamide. In order to provide accurate measurement, after acquiring a stable baseline with double distilled water step (1), filtered seawaters were injected as a background solution in step (2). The decrease in the frequency during the injection of the seawater as background solution in step (2) is due to viscosity changes of the solution at the interface as well as due to the adsorption of cations that exist in seawater to the polyamide sensor surface. In step (3), seawater with or without different AS (20 mg·l\(^{-1}\)) was injected to condition the polyamide surface. In this step, a minor shift in the frequency was observed when the seawater was supplemented with polyacrylate (CA) and carboxylated dendrimer (Den) due to adsorption of AS, while no changes were observed when the seawater supplemented with polyphosphonate (PP) AS or seawater alone has been used for this type of analysis. Changes in the mass on the sensor in step (3), which are likely attributed to the addition of AS to the seawater, according to Sauerbrey equation, were the highest for the sensors that were exposed to polyacrylate (CA) and carboxylated dendrimer (Den): 4.2 ± 0.6 and 4.9 ± 0.8 ng·cm\(^{-2}\) respectively. The changes in mass on the sensors that were exposed to seawater alone (SW) and polyphosphonate (PP) were 0.43 ± 0.1 and 2.8 ± 0.4 ng·cm\(^{-2}\), respectively. Consequently, the surfaces conditioned with polyacrylate (CA) and carboxylated dendrimer (Den), were preferable for adsorption of BSA and alginate during step (4) of injection BSA or sodium alginate (20 mg·l\(^{-1}\)) dissolved in similar pre-filtered seawater. Significantly higher decrease of the frequency shifts was observed for both cases of BSA and alginate adsorption (Fig. 6A&B), when the sensors were conditioned with polyacrylate (CA) and carboxylated dendrimer (Den) compared to conditioning with polyphosphonate (PP) and seawater alone (SW).

Step (5) shows the washing step of the organic fouling layer by injecting the same background solution that was used in steps (3) and (4) (with AS but in the absence of BSA or alginate). In step (5), loosely adsorbed BSA and alginate molecules were desorbed and a stable fouling layer remained on the surface. Later, steps (6) and (7) included washing of the fouling layers with seawater followed by double distilled water. The last two steps show significantly higher desorption of both BSA and alginate fouling layers from surfaces conditioned with polyphosphonate (PP) and seawater alone (SW), observed by the higher increase in the associated frequency shifts compared to conditioning with polyacrylate (CA) and carboxylated dendrimer (Den). The QCM-D results suggest that the presence of polyacrylate (CA) and carboxylated dendrimer (Den) causes a higher extent of irreversible fouling compared to the presence of the polyphosphonate (PP) and seawater alone (SW). The QCM-D results corroborate with both the AFM and the RO flux decline results, providing important evidence for the side effects of polyacrylate (CA) and carboxylated dendrimer (Den) based AS on organic fouling.
4. Concluding remark

This paper shows the enhancement of organic fouling process when polyacrylates and carboxylated dendrimer based AS were used. The observed organic fouling behavior is explained by changes in the RO membrane surface properties including hydrophobicity and zeta potential attributed to exposure of the membrane surface to AS followed by AS adsorption to the RO membrane. Proper AS development and selection is necessary for RO desalination processes in order to minimize side effects of fouling of the RO membranes. In addition, alternative pretreatment methods for scale prevention need to be adopted in order to minimize the usage of AS.

Acknowledgments

This research study was funded by the Israel Governmental Authority for Water and Sewage (Contract number 4500445438) and by Jacob Blaustein Institutes for Desert Research, Albert Katz International School for Desert Studies (AKIS) in Ben-Gurion University of the Negev. This paper shows the enhancement of organic fouling process when polyacrylates and carboxylated dendrimer based AS were used.

References


[11] S. Shirazi, C.J. Lin, S. Doshi, S. Agarwal, P. Rao, Comparison of fouling mechanism by QCM-D sensors with water only (SW) and with seawater supplemented with 20 mg-I⁻¹ of polyacrylate (CA), carboxylated dendrimer (Den), and polyphosphonate (PP) based AS.


