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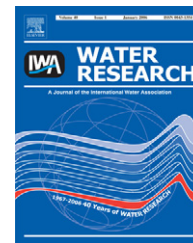
Salt cleaning of organic-fouled reverse osmosis membranes

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ABSTRACT

Cleaning of organic-fouled reverse osmosis membranes with concentrated salt solutions has been investigated. Polysaccharides (alginate and pectin) and Suwannee River natural organic matter were used as model organic foulants. By systematically varying the chemical and physical factors affecting salt cleaning efficiency, we were able to elucidate the processes and mechanisms involved during salt cleaning. Chemical factors investigated included salt dose, salt type, and organic foulant composition, while physical factors included cleaning contact time, crossflow velocity, cleaning solution temperature, and permeation rate. Atomic force microscopy (AFM) was utilized to quantify the reduction in intermolecular foulant–foulant adhesion upon salt cleaning. Our results showed that salt cleaning was quite effective in cleaning reverse osmosis membranes fouled by gel-forming hydrophilic organic foulants, such as alginate and pectin. The proposed mechanism for salt cleaning involves structural changes of the cross-linked gel layer on the membrane surface upon exposure to the salt solution followed by an ion exchange reaction that induces the breakup of calcium-foulant bonds as well as calcium bridging (cross-linking) between foulant molecules. The results obtained from AFM force measurements as well as foulant release experiments confirmed that these chemical reactions were the major mechanisms of salt cleaning. Salt cleaning appears to be an effective cleaning method, and may prove useful for membrane-based advanced wastewater reclamation, where a large fraction of the organic foulants is hydrophilic.

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1. Introduction

The use of reverse osmosis (RO) membranes in advanced wastewater reclamation to treat secondary wastewater effluent for production of water for indirect potable use is now widely recognized as a promising technology to augment water supply. A major challenge for efficient application of RO technology in wastewater reclamation is the phenomenon of organic fouling as secondary wastewater effluent contains a considerable amount of organic foulants (Ma et al., 2001; Shon et al., 2004; Sophonsiri and Morgenroth, 2004). Of particular interest are acidic polysaccharide-like substances due to their gel-forming nature in the presence of divalent cations (Gregor et al., 1996; Davis et al., 2003; Lattner et al., 2003; Her et al., 2004). Divalent cations bind to charged functional groups of these anionic macromolecules to form a compact cross-linked gel layer which results in severe membrane fouling (Ang et al., 2006; Lee and Elimelech, 2006). Despite the vast efforts to reduce fouling, for instance, by improvement of membrane properties, optimization of hydrodynamic

conditions, and pretreatment of feed waters, fouling is still inevitable. Consequently, chemical cleaning to remove the fouling layer on the membrane surface is a necessary process to ensure successful application of membrane technology.

Chemical cleaning involves both chemical and physical interactions. More specifically, two sequential steps take place in membrane cleaning: (i) chemical reaction between the cleaning agent and the foulants in the fouling layer and (ii) mass transfer of the foulants from the fouling layer to the bulk solution, which is controlled by hydrodynamics. The effectiveness of cleaning chemicals strongly depends on the chemical reactivity of the cleaning agents since the second step of mass transfer can take place only after the foulant–foulant interactions have been weakened by the chemical reaction (Ang et al., 2006). It has been demonstrated that effective cleaning agents eliminate or reduce significantly the foulant–foulant adhesion forces that sustain the structural integrity of the fouling layer on the membrane surface (Li and Elimelech, 2004; Ang et al., 2006). For cleaning chemicals which exhibit unfavorable or weak chemical reaction with organic foulants, it is impossible to appreciably improve the cleaning efficiency via optimization of physical cleaning conditions (such as hydrodynamics). Therefore, selection of cleaning chemicals that exhibit favorable chemical reaction with the target substances in the fouling layer is of paramount importance.

Several types of cleaning agents are commonly used for chemical cleaning of organic-fouled membranes, including alkalines, acids, metal chelating agents, surfactants, and enzymes (Tragardh, 1989; Madaeni et al., 2001; Tran-Ha et al., 2005). Among these cleaning agents, metal chelating agents (e.g., EDTA) and anionic surfactants (e.g., SDS) have been proven to be effective in the cleaning of organic-fouled NF and RO membranes (Li and Elimelech, 2004; Ang et al., 2006). However, one important concern regarding these cleaning agents is their adverse impact on the environment when discharged as waste streams. Enzymatic cleaning of organic-fouled membranes, especially for protein-fouled membranes, is expected to be effective and environmentally acceptable. However, the cost of enzymes is prohibitive for large-scale application. Therefore, the development of economically feasible as well as environmentally acceptable cleaning agents that have favorable chemical interactions with gel-forming organic foulants would be of great importance.

In this study, we demonstrate the use of common inert salts (or even seawater) as an effective alternative for the cleaning of RO membranes fouled by gel-forming hydrophilic organic foulants. Systematic bench-scale cleaning experiments were carried out with polysaccharides and natural organic matter as model organic foulants. These experiments were complemented with measurements of foulant–foulant adhesion forces via AFM to identify the mechanisms of salt cleaning. Relating cleaning efficiency to foulant–foulant adhesion forces revealed a remarkable correlation between the cleaning efficiency and the reduction of the adhesion force by the salt solution. The results verified that effective salt cleaning can be achieved by eliminating foulant–foulant adhesion, thereby rupturing the structural integrity of the fouling layer.

2. Materials and methods

2.1. Model organic foulants

Alginate was selected as the model organic foulant because acidic polysaccharides, which form gels in the presence of calcium ions, are some of the most recalcitrant organic foulants (Grant et al., 1973). Suwannee River natural organic matter (SRNOM) and pectin were also used as organic foulants to broaden the scope of the study and to better understand the cleaning mechanisms involved. Alginate and pectin are polysaccharides and are both hydrophilic, while SRNOM is humic-like and hydrophobic. The molecular weight ranges of alginate, pectin, and SRNOM are 12–80, 30–100, and 1.5–2.5 kDa, respectively. The alginate (Sigma-Aldrich, St. Louis, MO), SRNOM (International Humic Substances Society, St. Paul, MN), and pectin (Fluka, CH-9471, Buchs, SG, Switzerland) were received in powder form. Each was dissolved in deionized water and passed through a 0.45-μm filter (Millipore, Billerica, MA) to make the stock solutions (2 g/L).

2.2. Salt cleaning solutions

The salt cleaning solutions were prepared by dissolving an inert salt in deionized (DI) water. We used NaCl, $NaNO_3$, Na_2SO_4, KCl, CsCl, and NH_4Cl (Fisher Scientific, Pittsburgh, PA) to determine the effect of salt type on cleaning. The concentration of each salt solution was adjusted prior to the cleaning experiment, with no pH adjustment. In addition, cleaning with real seawater was investigated to determine the possible use of seawater or brine from seawater desalination plants as alternative salt cleaning solutions. Seawater was collected from the Atlantic Ocean near Boston, Massachusetts and was used after filtration through a 0.45-μm filter.

2.3. RO membrane

An aromatic polyamide thin-film composite RO membrane, denoted LFC-1 by the manufacturer (Hydranautics, Oceanside, CA), was used in this study. The LFC-1 membrane is relatively well-characterized and is widely used for brackish water desalination, wastewater reclamation, and drinking water treatment. The membrane is negatively charged at solution chemistries typical to natural and waste waters, with an isoelectric point at about pH 4 (Vrijenhoek et al., 2001). Its hydraulic resistance and salt rejection were determined to be $9.16\ (\pm 0.11) \times 10^{13}\,m^{-1}$ and 98.7–99.3%, respectively.

2.4. Fouling and cleaning experiments

A laboratory-scale crossflow membrane test unit was used for the salt cleaning experiments. The test unit comprised a membrane cell, a high-pressure pump, a feed reservoir, a temperature control system, and a data acquisition system. The system operated in a closed-loop with both permeate and retentate being recirculated into the feed reservoir. Temperature was kept constant during the fouling runs by a temperature controller with a stainless-steel coil submerged in the feed reservoir. Permeate flux was recorded

continuously by a digital flow meter interfaced with a PC. Details on the test unit and operating methods are described in our recent publication (Ang et al., 2006).

The experimental protocol for fouling and subsequent salt cleaning was adapted from that developed in our recent study (Ang et al., 2006). It consists of compaction, an initial baseline performance assessment, equilibration, fouling, cleaning, and a second baseline performance assessment. The operating conditions for the first and second baseline assessments were identical so that the cleaning efficiency could be determined by comparing the pure water fluxes determined before fouling and after cleaning. All fouling runs subjected to salt cleaning experiments were performed at the same fouling conditions in terms of feed solution chemistry (20 mg/L of organic foulant, pH 6.0, 0.5 mM calcium, and 10 mM total ionic strength adjusted by NaCl) and operating conditions (initial flux of 20 μm/s or 72 L/m^{2}h, crossflow velocity of 8.6 cm/s, and temperature of 20 °C). Salt cleaning efficiencies were determined at various chemical (salt concentration, salt type, and organic foulant composition) and physical (cleaning contact time, crossflow shear rate, cleaning solution temperature, and permeation rate during cleaning) conditions. To confirm the reproducibility of the experiments, selected fouling/cleaning runs were duplicated. The fouling rates and cleaning efficiencies obtained from the duplicate runs differed from their corresponding original experimental values by less than 5%.

2.5. Measurements of foulant–foulant adhesion

Atomic force microscopy (AFM) was used to measure foulant–foulant adhesion forces during the retraction of a foulant probe from the fouled membrane surface. The decrease in foulant–foulant adhesion after salt cleaning was determined by comparing adhesion forces in the absence and presence of salt cleaning solution in an AFM fluid cell. The experimental protocol for measuring the foulant–foulant adhesion forces is described in detail in our recent publications (Li and Elimelech, 2004; Ang et al., 2006). Briefly, the procedure involved the following steps: (i) making a foulant probe by gluing a carboxyl modified latex particle (4 μm in diameter) to a commercial tipless SiN cantilever (Veeco Metrology Group, Santa Barbara, CA), (ii) locating the membrane on the AFM dither piezo drive using a disc with the membrane surface oriented upward, (iii) installing the particle probe inside the fluid cell and then mounting the fluid cell on the membrane with an o-ring placed in between to prevent leakage, (iv) rinsing the fluid cell three times with DI water and then three times with the test solution, (v) filling the fluid cell with the organic foulant test solution and allowing the system to equilibrate for 60 min, and (vi) performing the force measurements by repeatedly approaching the colloidal probe to the membrane surface and retracting it. Data obtained during the retraction of the probe from the fouled membrane surface were used to determine the foulant–foulant adhesion forces.

Force measurements were performed at five different locations on the membrane surface to minimize data variability due to local membrane surface heterogeneity. Several measurements were taken at each location. From the raw data (i.e., cantilever deflection with respect to cantilever displacement) obtained from each measurement at either the same or different locations, some similar data were selected and averaged. In the absence of multiple jump-off events (Moy et al., 1994), all the raw data were quite similar. When multiple jump-off events took place, comparable data obtained at different locations were averaged. The averaged raw data were converted to force versus distance curves by the method reported by Ducker et al. (1991). The reduction in foulant–foulant adhesion forces determined from AFM force measurements was then compared to the salt cleaning efficiency determined from fouling/cleaning experiments performed using the same salt solution used for AFM force measurements.

3. Results and discussion

3.1. Chemical factors governing cleaning efficiency

The chemical factors investigated include salt concentration, salt type, and organic foulant composition. Fouling experiments were performed using alginate, except when investigating the influence of organic foulant composition, where both alginate and SRNOM were used. Calcium was used to accelerate fouling through the formation of a cross-linked fouling layer on the membrane surface. Other chemical (foulant concentration, feed solution pH, total ionic strength) and physical (initial flux, crossflow velocity, and feed solution temperature) conditions employed during the fouling runs were identical. Because the cleaning experiments were performed at fixed physical conditions, only the influence of chemical factors is reflected in the obtained results.

3.1.1. Salt concentration
Cleaning with different concentrations of NaCl solutions was performed to investigate the influence of salt concentration on cleaning efficiency. Cleaning with DI water was also carried out to serve as a baseline for comparison with the salt cleaning. Flux behavior during the fouling/cleaning runs and the cleaning efficiency determined at different NaCl concentrations are shown in Fig. 1. All flux profiles in Fig. 1a were nearly identical, except for those obtained after cleaning, because each fouling run was performed under identical conditions. Cleaning efficiency increased with increasing NaCl concentration and reached about 90% for the cleaning solution of 50 mM NaCl. It is quite remarkable that an indifferent electrolyte, such as NaCl, is so effective in cleaning the alginate gel layer formed on the membrane surface. Our recent study indicated that the alginate gel layer formed on an RO membrane in the presence of calcium ions was not effectively removed by alkaline cleaning (pH 11) and that a considerable amount of a strong chelating agent or surfactant was needed to obtain over 90% cleaning efficiency (Ang et al., 2006).

Chemical cleaning of fouled membranes is realized through a chemical reaction between the cleaning agents and the foulants, followed by transport of the reaction products away from the membrane surface. Therefore, it is assumed that the salt cleaning data shown above involve a favorable chemical
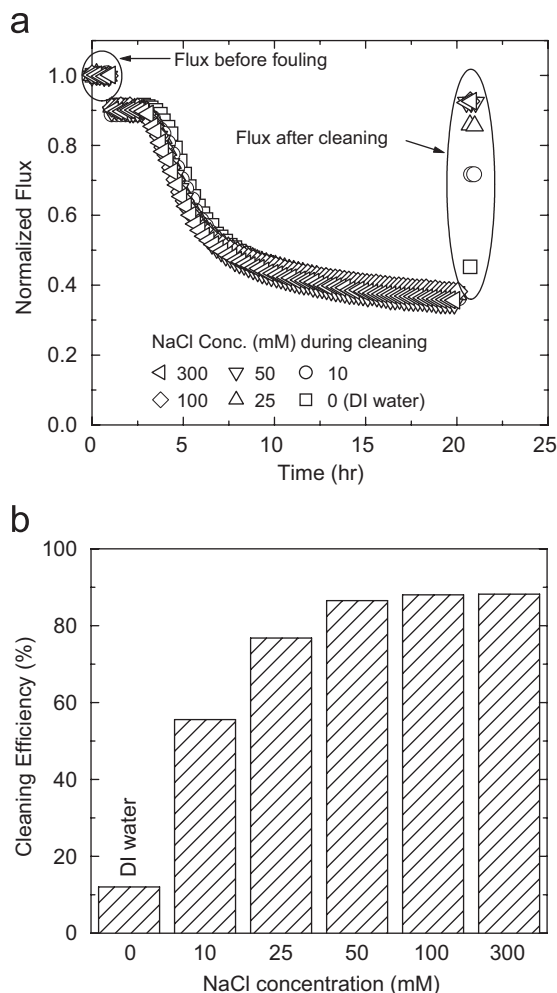
a

b

Fig. 1 – Influence of salt concentration on cleaning of organic-fouled RO membranes: (a) flux behavior during the fouling/cleaning experiments and (b) variation in cleaning efficiency with respect to salt concentration. Conditions for fouling experiments: alginate concentration = 20 mg/L, calcium concentration = 0.5 mM, total ionic strength = 10 mM (i.e., 0.5 mM CaCl$_2$ plus 8.5 mM NaCl), pH = 5.90±0.05, initial flux = 20 µm/s (42.4 gal/ft^2 day (gfd) or 72.0 L/m^2 h), crossflow velocity = 8.56 cm/s, and temperature = 20.0±0.2 °C. Conditions for cleaning experiments: ambient pH, time = 15 min, temperature = 20.0±0.2 °C, crossflow velocity = 42.8 cm/s, and no permeation.

reaction between the salt and alginate gel layer. The increase in cleaning efficiency with increasing salt concentration up to 50 mM implies that this chemical reaction is controlled by the stoichiometry between the salt dose and the amount of alginate gel layer on the membrane surface. The lack of increase in the cleaning efficiency at salt dosages above 50 mM NaCl is attributed to suboptimal physical conditions for effective mass transfer as all cleaning experiments shown here were performed at fixed physical conditions.

The proposed mechanism of salt cleaning is a combination of structural changes of the cross-linked fouling (gel) layer

and ion-exchange reaction (Skjåk-Bræk et al., 1989; Matsumoto and Mashiko, 1990). Structural changes and deformation of the gel layer are attributable to the osmotic pressure difference between the bulk solution and the interior of the gel layer, which usually leads to favorable conditions for gel-network swelling. The ion-exchange between sodium and bound calcium ions results in the breakup of calcium-alginate binding as well as calcium-induced intermolecular bridging. A detailed description of how these mechanisms play a role in salt cleaning of the alginate gel layer on the membrane surface is given later in this paper.

3.1.2. Salt type

To investigate the influence of salt type on cleaning efficiency, various salts were tested at the same conditions employed during the NaCl cleaning. Cleaning with each salt solution was performed at two different concentrations, and the cleaning efficiency was compared with that of NaCl at the same molar concentration (Table 1). At the lower salt concentration (25 mM), cleaning efficiency varied from 62% to 75%, showing the highest cleaning efficiency for NaCl and the lowest for NaNO$_3$. At the higher salt concentration (100 mM), however, cleaning efficiency was comparable with all salts. The distinct difference in the cleaning efficiency at the lower salt concentration is attributed to the difference in the ion-exchange capacity of each salt, a difference that becomes greater at lower concentration. In addition, the ability of each salt to influence the gel-network swelling is also likely to be different. The results shown here suggest that various salts can be used to clean the alginate-fouled membrane by optimizing salt dose, which can be achieved through systematic analysis of the stoichiometry between the salt dose and the foulant amount.

We also tested seawater samples as an alternative salt cleaning solution for the cleaning of alginate-fouled RO membranes. The seawater was diluted to have a similar ionic strength as 100 mM NaCl. The cleaning efficiency of the alginate fouled RO membrane was over 90%, comparable to NaCl and other monovalent salts (Table 1) at the same total ionic strength. This implies that seawater or brines from seawater desalination plants can be effective as cleaning agents for gel-forming organic foulants, like wastewater effluent organic matter (Into et al., 2004).

Table 1 – Cleaning efficiency of various salts

Salt	Cleaning efficiency (%)	
	25 mM	100 mM
NaCl	75.2	88.1
NaNO$_3$	57.4	89.4
Na$_2$SO$_4$	60.1	87.7
KCl	66.5	87.2
CsCl	62.1	88.1
NH$_4$Cl	65.2	87.6

3.1.3. Organic foulant composition

Fouling runs were performed with feed waters containing different mass ratios of alginate to SRNOM, with the total foulant concentration maintained at 20 mg/L. Feed waters with different organic foulant composition will likely form organic fouling layers which are structurally different from one another, thus resulting in different cleaning efficiencies with the same cleaning solution. Following the fouling runs, each cleaning experiment was performed with 100 mM NaCl solution. The flux profiles of these fouling runs and the cleaning efficiencies determined from the subsequent cleaning experiments are presented in Fig. 2.

NaCl was less effective in cleaning membranes fouled by feed waters with higher SRNOM content, even though the flux
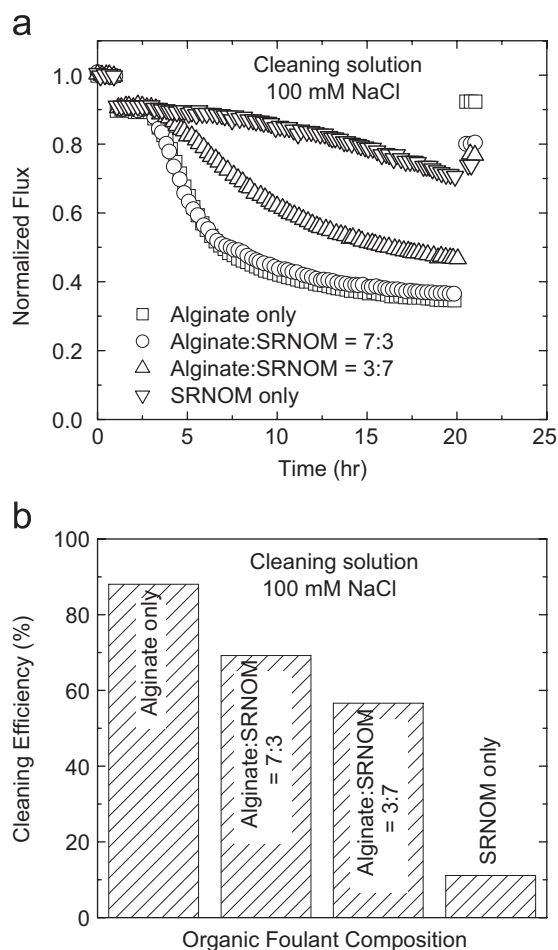

Fig. 2 – Influence of feed water organic composition on salt cleaning of organic-fouled RO membranes: (a) flux behavior during the fouling/cleaning experiments and (b) variation in cleaning efficiency with respect to feed water organic composition. Fouling experiments were performed with feed waters containing: alginate = 20 mg/L (i.e., alginate only); alginate = 14 mg/L and SRNOM = 6 mg/L (i.e., alginate:SRNOM = 7:3); alginate = 6 mg/L and SRNOM = 14 mg/L (i.e., alginate:SRNOM = 3:7); or SRNOM = 20 mg/L (i.e., SRNOM only). Other fouling conditions were identical to those in Fig. 1. Cleaning experiments were performed with 100 mM NaCl solution. Other cleaning conditions were identical to those in Fig. 1.
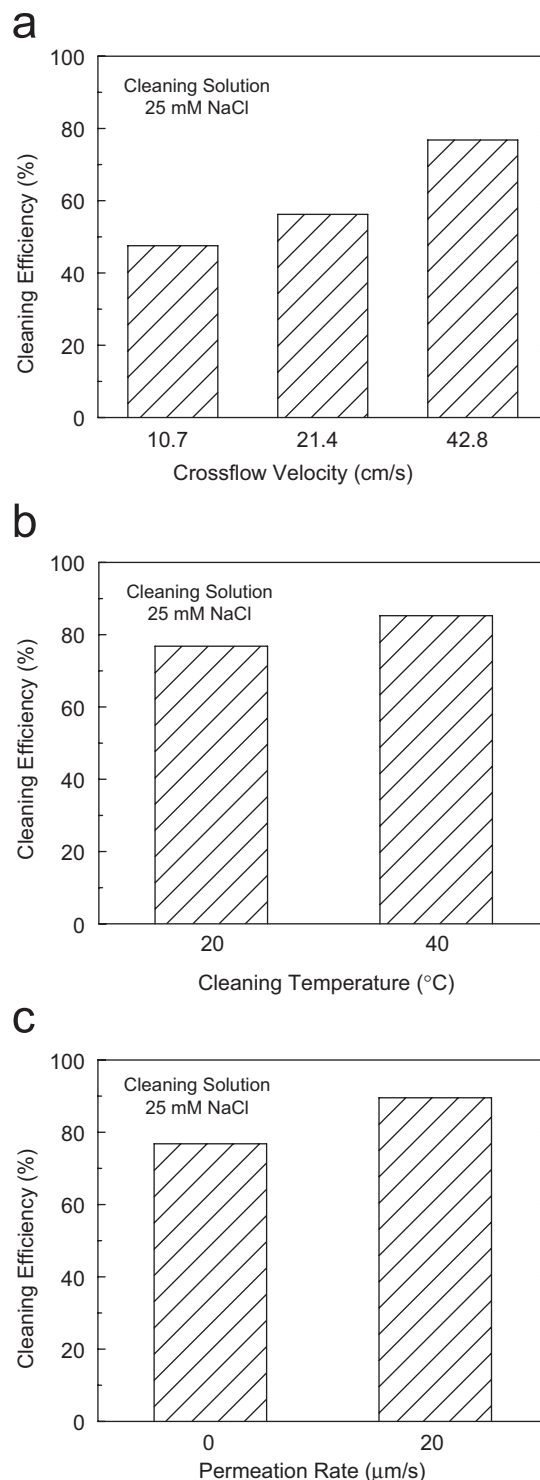

Fig. 3 – Influence of physical conditions on salt cleaning of organic-fouled RO membranes: (a) effect of crossflow velocity, (b) effect of temperature, and (c) effect of permeation rate. Conditions for fouling experiments were identical to those in Fig. 1. Cleaning experiments were performed with 25 mM NaCl solution. Other cleaning conditions were identical to those in Fig. 1.
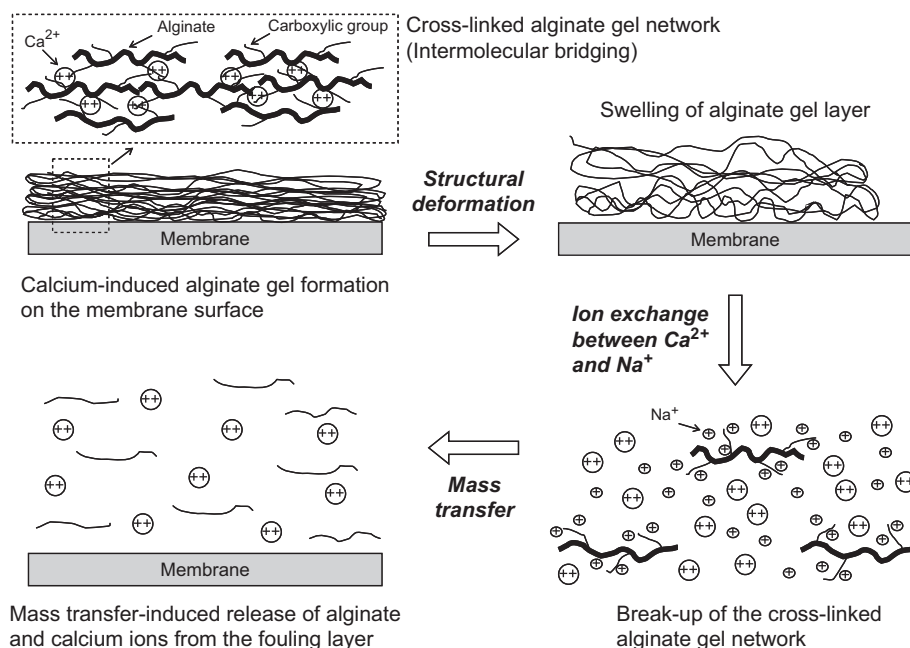
Fig. 4 – Schematic representation for mechanisms of salt cleaning. A cross-linked fouling layer is formed on the membrane surface in the presence of calcium ions, which bind to organic foulants and form bridges between adjacent foulant molecules. During salt cleaning, the alginate gel layer swells and, thus, results in the lessening of the structural integrity of the gel network. Following the weakening of the structural integrity of the gel network, an actual breakup of the gel network takes place as a result of an ion-exchange between Na^+ and Ca^{2+}, which results in the freeing of Ca^{2+} ions and alginate molecules from the cross-linked gel network. A layer-by-layer removal of these reaction products from the fouling layer to the bulk solution takes place through the hydrodynamics/mass transfer.

decline was much more substantial at the higher mass ratio of alginate to SRNOM. This indicates that the efficiency of salt cleaning is dependent on the type of organic foulants, and that salt cleaning seems more applicable when the major foulants are polysaccharide-like substances (such as alginate) rather than humic-like substances (such as SRNOM). The lower efficiency of salt cleaning for the SRNOM-fouled membrane when compared to the alginate-fouled membranes is attributed to the hydrophobic nature of SRNOM. The swelling of the hydrophobic SRNOM fouling layer on the membrane surface during salt cleaning is expected to be less pronounced when compared to the hydrophilic alginate-fouling layer. This likely results in less diffusion of sodium ions into the fouling layer and, hence, a limited ion-exchange reaction between sodium ions and calcium ions bound to SRNOM. In fact, visual inspection after the cleaning of the alginate-fouled membrane showed the disappearance of the alginate gel layer, while SRNOM deposition on the membrane surface was quite visible after salt cleaning with almost no difference from that observed at the end of the fouling run.

3.2. Physical factors governing cleaning efficiency

The physical factors investigated include cleaning contact time, crossflow shear rate, cleaning solution temperature, and permeation rate during salt cleaning. In an earlier study, we have demonstrated that the cleaning efficiency can be improved noticeably by employing favorable physical conditions for

effective transport of foulants from the fouling layer to the bulk solution after the chemical reaction between the cleaning agent and deposited foulants has weakened the structural integrity of the fouling layer (Ang et al., 2006). In this section, we will verify that salt can be viewed as a favorable cleaning agent for organic-fouled RO membranes, by showing that cleaning efficiency can be improved by optimizing physical cleaning conditions. During the salt cleaning experiments, all chemical factors (salt type, salt concentration, and foulant type) as well as other physical factors, excluding the factor being investigated, were kept constant.

3.2.1. Cleaning contact time
The influence of cleaning contact time on salt cleaning efficiency was investigated. Salt cleaning was performed for 15 and 60 min with two different NaCl concentrations (25 and 100 mM). For the cleaning with 25 mM NaCl, cleaning efficiency increased from 78% to 90% with increasing cleaning contact time from 15 to 60 min; for 100 mM NaCl, 90 and 110% cleaning efficiencies were obtained for 15 and 60 min cleaning times, respectively. These results are in accord with our previous findings showing that, for favorable cleaning agents in terms of chemical reaction, increasing cleaning time enhances the cleaning efficiency (Ang et al., 2006).

3.2.2. Crossflow shear rate
The influence of crossflow shear rate on salt cleaning efficiency was investigated with 25 mM NaCl solution

(Fig. 3a). Cleaning efficiency increased noticeably from 48% to 78% after increasing the crossflow velocity from 10.7 to 42.8 cm/s. An increase in crossflow shear rate enhances the disruption of the fouling layer and the mass transfer of the foulants from the fouling layer to the bulk solution after the salt has weakened the structural integrity of the fouling layer.

3.2.3. Temperature

Salt cleaning efficiencies (at 25 mM NaCl) for runs performed at different solution temperatures are shown in Fig. 3b. We note that, in both cases, the pure water flux after cleaning was determined with DI water, and the temperature was adjusted to 20 °C prior to the baseline performance. An increase in the cleaning solution temperature resulted in an increase in the salt cleaning efficiency. In this case, both the rate of chemical reaction between the salt and the deposited foulants and the transport of foulants from the fouling layer to the bulk solution increased. In addition, at higher temperature, the swelling of the organic fouling layer might have also contributed to the weakening of its structural stability (Clark and Ross-Murphy, 1987; Moe et al., 1992).

3.2.4. Permeation rate

The purpose of having permeation occur through the membrane during cleaning of fouled RO membranes is to investigate the influence of permeation rate on the convective transport of salt into the fouling layer. A permeation rate of 20 μm/s (72 L/m^2 h) was employed during salt cleaning (25 mM), and the results were compared with the cleaning efficiency obtained in the absence of a permeation rate as shown in Fig. 3c. The salt cleaning efficiency increased from 78% to 90% when inducing permeation, implying that the enhanced-convective transport of salt ions into the fouling layer results in more favorable conditions for the weakening of the structural stability of the fouling layer. It should be noted that operation under pressure (and hence permeation) during chemical cleaning of fouled RO membranes is not common in practice.

3.3. Mechanisms of salt cleaning

Membrane cleaning involves both chemical and physical interactions as discussed earlier (Ang et al., 2006). A schematic representation of the specific chemical and physical processes during salt cleaning of organic-fouled RO membranes is shown in Fig. 4. The various processes and mechanisms involved are discussed below.

3.3.1. Gel layer swelling and ion exchange

As depicted in Fig. 4, the alginate gel layer formed on the membrane surface swells during salt cleaning, which results in the lessening of the structural integrity of the gel network. Gelled complexes frequently undergo marked irreversible swelling when transferred from buffer to neutral salt solutions and back to buffer (Yoshida and Thies, 1967). Wang and Spencer (1998) found that the crosslink density of the alginate gel was reduced as the ionic strength (KCl) increased. The reduction of crosslink density results in the increase of the
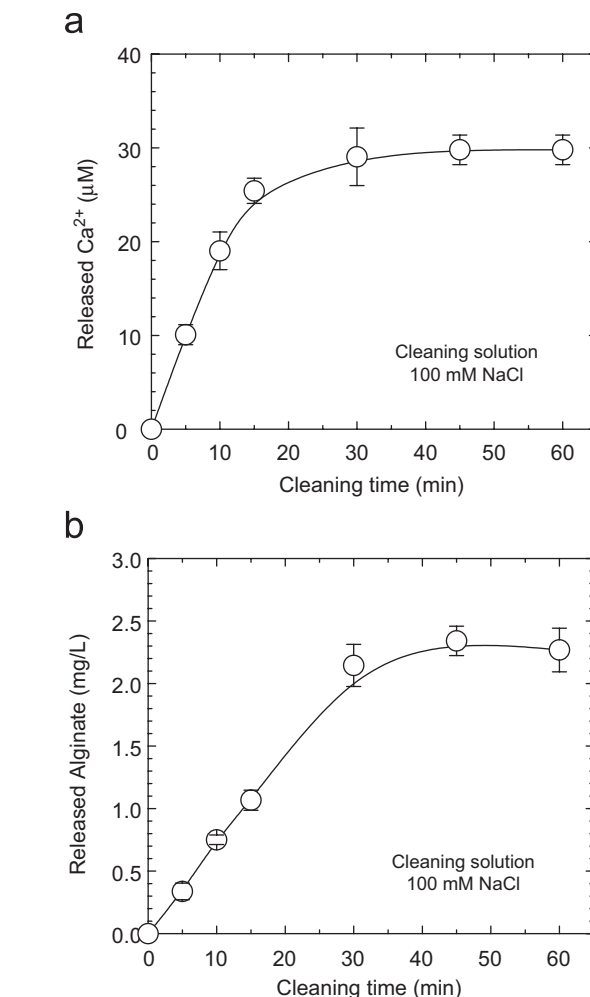
Fig. 5 – Release of (a) calcium ions and (b) alginate molecules from the fouling layer to the bulk cleaning solution during salt cleaning with respect to cleaning time. Measurements of calcium and alginate concentrations were performed several times during the cleaning using a calcium selective electrode along with a reference electrode and TOC analyzer, respectively. Error bars indicate one standard deviation.

chain length inside the gel structure and, thus, an increase of network swelling (de Kerchove and Elimelech, 2006a, b). Following the swelling of the cross-linked alginate gel layer, ion-exchange reaction between Na$^+$ (when NaCl is used as cleaning salt) and Ca^{2+} (bound to alginate) takes place, resulting in the breakup of the alginate gel network (Skjåk-Bræk et al., 1989; Matsumoto and Mashiko, 1990; Nillson, 1992). Analogous to conventional ion exchange processes, the steps involved in NaCl cleaning of alginate gel layer are (i) diffusion of Na$^+$ ions into the alginate gel layer and (ii) breakup of Ca^{2+}-alginate bonds by exchanging the calcium with sodium, thereby freeing the alginate molecules to transport away from the lessened fouling layer. By measuring both Ca^{2+} and alginate concentrations in the bulk solution several times during cleaning with 100 mM NaCl, it was verified that the amount of Ca^{2+} ions and alginate molecules released from the fouling layer increased with respect to
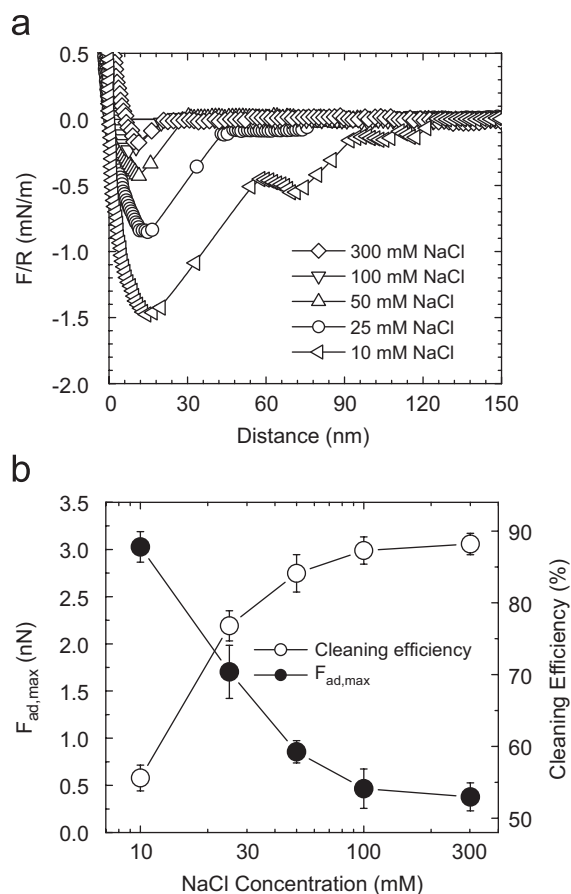
a

b

Fig. 6 – Relating salt cleaning efficiency to intermolecular foulant-foulant adhesion forces: (a) effect of salt concentration on eliminating intermolecular foulant–foulant adhesion force and (b) correlation between maximum adhesion force and cleaning efficiency with respect to salt concentration. Force measurements were performed with samples identical to those used in cleaning experiments for direct comparison. Error bars in Fig. 6b indicate one standard deviation.
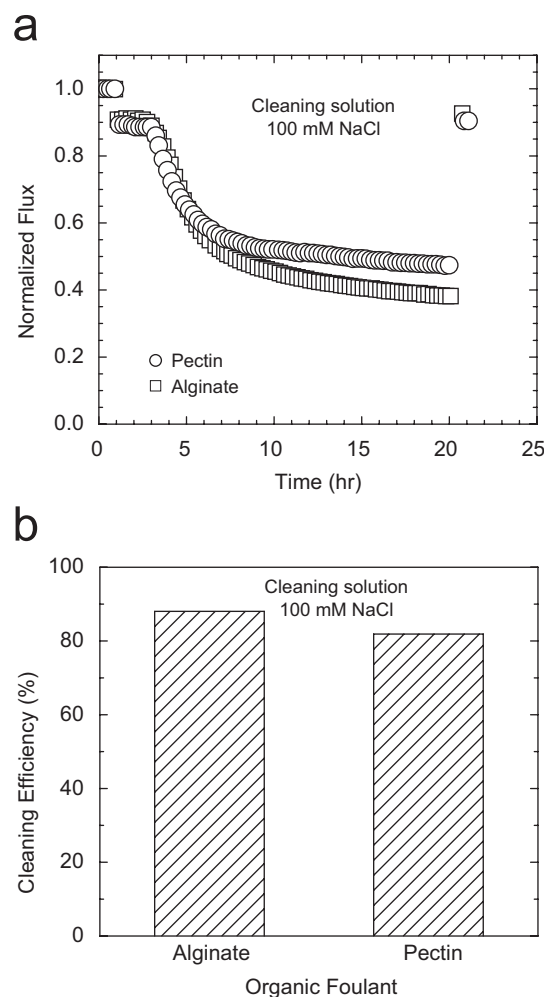
a

b

Fig. 7 – Salt cleaning of fouled RO membranes by different gel-forming organic foulants (i.e., alginate and pectin): (a) flux behavior during the fouling/cleaning experiments and (b) variation in cleaning efficiency with respect to foulant type. In both cases, foulant concentration was 20 mg/L. Cleaning experiments were performed with 100 mM NaCl solutions. Other conditions for fouling/cleaning experiments were identical to those used in Fig. 1.

cleaning time as shown in Fig. 5. It is important to note that the rate and degree of both deformation/swelling and break-up of the alginate gel network vary depending on the salt type and dose, as demonstrated by the different cleaning efficiencies in Table 1.

3.3.2. Salt cleaning eliminates foulant–foulant adhesion

We have recently demonstrated that organic fouling rate and cleaning efficiency are related to the intermolecular foulant-foulant adhesion forces, which can be quantified by the AFM colloid probe technique (Li and Elimelech, 2004; Ang et al., 2006; Lee and Elimelech, 2006). In these studies, the foulant–foulant adhesion was eliminated or decreased significantly in the presence of a cleaning solution containing favorable cleaning agents. As shown in Fig. 6a, the foulant–foulant adhesion force decreased dramatically as the concentration of the NaCl cleaning solution increased. The cleaning efficiencies determined from the membrane cleaning experi-

ments were compared to the foulant–foulant adhesion forces measured in the presence of the same cleaning solutions used in the cleaning experiments (Fig. 6b). The increase in cleaning efficiency correlates quite well with the decrease in the measured foulant–foulant adhesion force, which decreased as the salt concentration increased.

3.3.3. Verification with another gel-forming organic foulant

We have used pectin to verify the effectiveness of salt cleaning on other gel-forming organic foulants. Like alginate, pectin is an anionic polysaccharide that forms gel in the presence of calcium ions. Fouling and cleaning experiments were performed based on the same protocol described previously. A cleaning solution of 100 mM NaCl was used. Flux-decline behaviors during alginate and pectin fouling as well as cleaning efficiencies were compared in Fig. 7. It is shown that salt cleaning is also effective

(over 80% cleaning efficiency) in cleaning pectin-fouled RO membranes.

4.   Conclusion

Common inert salts can be used as an effective alternative for the cleaning of RO membranes fouled by gel-forming hydrophilic organic foulants. Based on the results from the fouling/cleaning experiments and the AFM force measurements, it is proposed that gel layer swelling and ion-exchange reaction are the major mechanisms involved during salt cleaning. A remarkable correlation between the cleaning efficiency and the reduction in the intermolecular foulant-foulant adhesion upon salt cleaning was obtained and further supported by the results from the foulant-release experiments. By optimizing the chemical and physical conditions during salt cleaning, cleaning efficiency could be improved noticeably. Our results indicate that salt solutions of common inert salts or even seawater or brines from desalination plants, with possible pre-treatment, can be used as an economically feasible and environmentally acceptable cleaning alternative for cleaning RO membranes during wastewater reclamation.

Acknowledgements

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