

# Chemical and physical aspects of cleaning of organic-fouled reverse osmosis membranes

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## Abstract

The role of chemical and physical interactions in cleaning of organic-fouled reverse osmosis (RO) membranes is systematically investigated. Fouling and cleaning experiments were performed with organic foulants (alginate and natural organic matter) that simulate effluent organic matter (EfOM) and selected cleaning agents using a laboratory-scale crossflow test unit. Following accelerated organic fouling runs with divalent calcium ions, cleaning experiments were performed at various chemical and physical conditions. The results showed that a metal chelating agent (EDTA) and an anionic surfactant (SDS) were able to clean the fouled RO membrane effectively by optimizing chemical (dose and pH) and physical (time, crossflow velocity, and temperature) conditions during cleaning. The permeate flux was, however, poorly recovered when cleaning was performed with NaOH (pH 11). Interfacial force measurements (by AFM) further confirmed the cleaning results, demonstrating the influence of cleaning agents on reducing the foulant–foulant adhesion force. The results showed that the adhesion force caused by calcium-induced foulant–foulant interaction was reduced significantly with EDTA and SDS cleaning, while substantial adhesion force still remained following NaOH cleaning. It is proposed that an efficient cleaning agent and favorable cleaning conditions could be selected by considering two important mechanisms: *chemical reaction* between cleaning agents and foulants in the fouling layer, and *mass transfer* of chemical agents (from the bulk phase to the fouling layer) and foulants (from the fouling layer to the bulk phase).

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## 1. Introduction

Reverse osmosis (RO) membranes are widely used in drinking water, wastewater, and industrial applications. The use of RO membranes in advanced wastewater reclamation using secondary treated wastewater effluent to produce water for indirect potable use has also increased over the past few years [1,2]. However, a major impediment in the application of RO membrane technology for desalination and wastewater reclamation is membrane fouling.

In advanced water reclamation, secondary effluent from wastewater treatment plants contains dissolved organic matter, commonly known as effluent organic matter (EfOM). When the secondary wastewater effluent is introduced to

the RO membrane processes as feed water, the presence of EfOM contributes to organic fouling [3]. EfOM represents a range of organic compounds, such as polysaccharides, proteins, aminosugars, nucleic acids, humic and fulvic acids, organic acids, and cell components [3]. These complex and heterogeneous compounds can generally be classified into two groups according to their origin: (i) soluble microbial products (SMPs) derived during substrate metabolism in the biological wastewater treatment process and (ii) natural organic matter (NOM) originating from the drinking water source [3,4]. It has been reported that the majority of EfOM in secondary wastewater effluent is made up of SMPs [5,6]. Polysaccharides, one of the major constituents of SMPs [7], have been found to play an important role in the fouling of nanofiltration (NF) and ultrafiltration (UF) membranes [8].

Developing strategies for fouling control has always been a major challenge in membrane research. However, despite

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the many preventive strategies, fouling is inevitable. The long-term solution would be to remove the foulant deposited on membrane surfaces via chemical cleaning [9–14]. Membrane cleaning is performed when there is a significant drop in permeate flux or salt rejection, or when there is a need to increase the transmembrane pressure significantly to maintain the desired water flux [15]. There are five categories of cleaning agents — alkaline solutions, acids, metal chelating agents, surfactants, and enzymes [9,16]. Commercial cleaning products are often mixtures of these compounds, but in most cases the actual composition is unknown. Therefore, many past studies on chemical cleaning are not able to provide useful information to illuminate the mechanisms of chemical cleaning.

In this study, alkaline solution, metal chelating agent, and surfactant are used to clean the organic-fouled membranes. Alkaline solutions clean organic-fouled membranes by hydrolysis and solubilization. Alkaline solutions increase the solution pH, and therefore increase the negative charge and solubility of the organic foulant. For example, when carboxylic functional groups of the organic foulant are deprotonated at alkaline conditions, solubility increases nearly three orders of magnitude [17]. In the presence of divalent cations, such as  $\text{Ca}^{2+}$ , alginate, which is selected in this study to represent the hydrophilic (polysaccharide) fraction of EfOM, forms complexes with calcium ions, resulting in a highly compacted gel network of fouling layer [18,19]. Metal chelating agents, such as EDTA, remove divalent cations from the complexed organic molecules and improve the cleaning of the fouled membrane [20]. Surfactants are compounds that have both hydrophilic and hydrophobic groups, and are semi-soluble in both organic and aqueous solvents. Surfactants can solubilize macromolecules by forming micelles around them [21], and help to remove the foulant from the membrane surface.

Atomic force microscopy (AFM) has recently been used to quantify intermolecular forces in membrane research [22–24], as it is able to measure interaction forces in liquids at pico- or nano-Newton level. Li and Elimelech [25] have recently demonstrated that foulant–foulant interactions could be determined by performing force measurements using a carboxylate-modified latex colloid probe in an AFM fluid cell. The technique has been used to quantify the fouling behavior of a nanofiltration membrane by humic acid as well as the cleaning efficiency by several chemical cleaning agents. The study showed a good correlation between the measured adhesion force and the fouling and cleaning behaviors.

The objective of this paper is to systematically study the physical and chemical aspects of cleaning of organic-fouled RO membranes, with emphasis on cleaning of an RO membrane fouled by acidic polysaccharides. AFM was used to study the interaction forces between the foulant in the bulk solution and the foulant accumulated on the membrane surfaces. The results from the bench-scale crossflow fouling/cleaning experiments and the relevant adhesion force

profiles from AFM force measurements were used to explain the cleaning mechanisms involved.

## 2. Experimental

### 2.1. Organic foulants

The organic foulants chosen as representative hydrophilic and hydrophobic EfOM were sodium alginate (Sigma-Aldrich, St. Louis, MO) and Suwannee River natural organic matter (SRNOM) (International Humic Substances Society, St. Paul, MN), respectively. Sodium alginate was extracted from brown seaweed. Based on the manufacturer, the molecular weight of the sodium alginate ranges from 12 to 80 kDa. Other characteristics of SRNOM, including molecular weight and mass fraction of hydrophobic NOM, can be found elsewhere [26,27]. Both organic foulants were received in a powder form, and stock solutions (2 g/l) were prepared by dissolving each of the foulants in deionized (DI) water. Mixing of the stock solutions was performed for over 24 h to ensure complete dissolution of the foulants, followed by filtration with a 0.45  $\mu\text{m}$  filter (Durapore, Millipore, Billerica, MA). The filtered stock solutions were stored in sterilized glass bottles at 4 °C.

### 2.2. Chemical cleaning agents

The chemical cleaning agents used were NaOH (pH 11.0) as an alkaline solution, certified grade disodium ethylenediaminetetraacetate ( $\text{Na}_2\text{-EDTA}$ ) as a metal chelating agent, and certified grade sodium dodecyl sulfate (SDS) as an anionic surfactant. These cleaning agents are the most common compounds in commercial cleaning products for organic-fouled membranes [9,16]. The NaOH, EDTA, and SDS were purchased from Fisher Scientific (Pittsburgh, PA) and used with no further purification. The stock chemical solutions were prepared freshly by dissolving each chemical in deionized (DI) water. Cleaning with DI water served as a baseline. The pH of the EDTA and SDS cleaning solutions was adjusted with 1.0 M NaOH as needed.

### 2.3. RO membrane

The relatively well characterized thin-film composite LFC-1 (Hydranautics, Oceanside, CA) was used as a model RO membrane. The average hydraulic resistance was determined to be  $9.16 (\pm 0.11) \times 10^{13} \text{ m}^{-1}$ . The observed salt rejection was 98.7–99.3% — determined with a 10 mM (584 mg/l) NaCl feed solution at an applied pressure of 300 psi (2068.5 kPa) and a crossflow velocity of 8.1 cm/s. Membrane samples were received as dry large sheets, and were cut and stored in DI water at 4 °C. The membrane has been reported to be negatively charged at solution chemistries typical to natural and waste waters, with an isoelectric point at about pH 4 [28].

#### 2.4. Crossflow membrane test unit

Fouling and subsequent cleaning experiments were performed with a laboratory-scale crossflow test unit. The membrane test unit consists of a membrane cell, pump, feed reservoir, temperature control system, and data acquisition system. The membrane cell was a rectangular plate-and-frame unit, containing a flat membrane sheet placed in a rectangular channel of dimensions 7.7 cm long, 2.6 cm wide, and 0.3 cm high. Both permeate and retentate were recirculated back to the feed reservoir. Permeate flux was registered continuously by a digital flow meter (Optiflow 1000, Humonics, CA) interfaced with a computer. A floating disc rotameter (King Instrument, Fresno, CA) was used to monitor the retentate flow rate. The crossflow velocity and the operating pressure were adjusted using a bypass valve (Swagelok, Solon, OH) in conjunction with a back-pressure regulator (US Paraplate, Auburn, CA). Temperature was controlled by a recirculating chiller/heater (Model 633, Polysciences) with a stainless-steel coil submerged in the feed water reservoir.

#### 2.5. Fouling and cleaning experiments

The experimental protocol developed for fouling/cleaning is shown in Fig. 1. The membrane was first compacted with DI water for 12 h until the permeate flux became constant, followed by the initial baseline performance for 2 h. Following the initial baseline performance, the membrane was stabilized and equilibrated with a foulant-free electrolyte solution for 4 h. After attaining a stable flux, the initial flux and the crossflow velocity were adjusted to the values used for the subsequent fouling runs. The chemistry of feed solution and operating conditions adjusted in this stage were similar to those used for the ensuing fouling runs. Fouling was then initiated by adding organic foulants (i.e., alginate, SRNOM, or both alginate and SRNOM) to the feed water to achieve the desired organic concentration. Fouling runs were carried out for 17 h. At the end of fouling, the solution in the feed

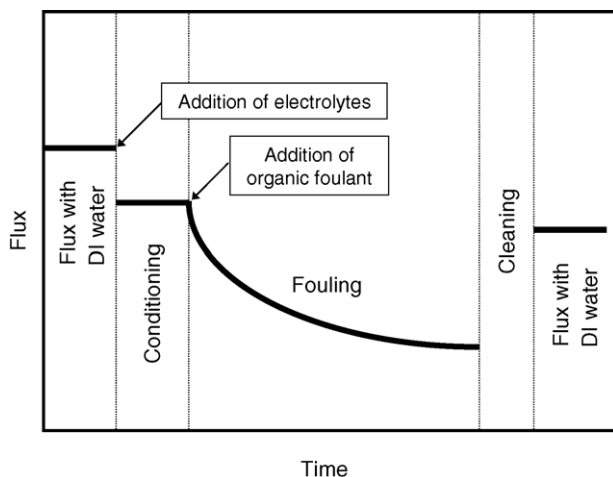


Fig. 1. Experimental protocol for the fouling/cleaning runs.

reservoir was disposed and cleaning of the fouled membrane was performed by adding the chemical cleaning solution to the feed reservoir. At the end of the cleaning stage, the chemical cleaning solution in the reservoir was emptied, and the reservoir and the membrane cell were rinsed with DI water to flush out the residual chemical cleaning solution. Finally, the cleaned RO membrane was subjected to the second baseline performance with DI water for 2 h to determine the pure water flux again. The operating conditions (i.e., initial flux, crossflow velocity, and temperature) at this stage were identical to those applied during the initial baseline performance, so as to determine the cleaning efficiency by comparing the pure water fluxes determined before fouling and after cleaning. To confirm the reproducibility of determined cleaning efficiency, selected fouling/cleaning runs were duplicated. Results showed that fouling rate and cleaning efficiency obtained from the duplicate runs were always within less than 5% difference. Throughout all the fouling/cleaning stages, the feed water in the reservoir located on top of a magnetic stirrer was mixed vigorously to ensure complete mixing of the feed water and cleaning solution.

Cleaning efficiency varies with respect to the conditions applied during cleaning, namely, type of cleaning agent, cleaning solution pH, cleaning agent dose, cleaning time, crossflow velocity during cleaning, and cleaning solution temperature. Furthermore, cleaning efficiency, even at fixed cleaning conditions, is also influenced by the conditions applied during fouling. For a systematic investigation on the role of chemical and physical interactions in cleaning of fouled membranes, it is necessary to isolate cleaning conditions from the influence of fouling conditions, thus focusing solely on the influence of cleaning conditions on cleaning efficiency. Therefore, all the fouling runs subjected to cleaning experiments were performed at the same fouling conditions in terms of feed solution chemistry (i.e., pH 6.0, 0.5 mM calcium, and 10 mM total ionic strength adjusted by varying NaCl concentration) and operating conditions (i.e., initial flux of 20  $\mu\text{m/s}$ , crossflow velocity of 8.56 cm/s, and temperature of 20 °C); these conditions yielded similar flux decline profiles. This implies that each cleaning is applied to an identical organic fouling layer since the same organic fouling layer produces identical resistance to permeate flow and, hence, the same flux profiles. A few fouling runs were performed with feed waters containing different organic foulants (i.e., SRNOM or mixture of alginate and SRNOM); however, the fouling and cleaning conditions were the same as above, thus allowing to investigate the influence of foulant composition on cleaning efficiency.

During the fouling experiments, calcium was used for two reasons. First, calcium was used to accelerate fouling of the charged organic foulant, leading to a substantial flux decline, which was needed to differentiate the cleaning efficiency determined at various conditions. Based on our previous findings [20,25], it was shown that calcium ions specifically bind with carboxylic functional groups of organic foulants (i.e., NOM and acidic polysaccharides) and form bridges between

adjacent foulants. This results in the formation of a cross-linked fouling layer at the membrane surface, thus producing substantial resistance to permeate flow. In addition, calcium-induced organic fouling is one of the major causes for severe flux decline and known to be most recalcitrant since natural and waste waters contain substantial amounts of calcium.

## 2.6. AFM adhesion force measurements

Atomic force microscopy (AFM) was used to measure the interfacial force between the foulant in the bulk solution and the foulant in the fouling layer on the membrane. The force measurements were performed with a colloid probe, modified from a commercialized SiN AFM probe (Veeco Metrology Group, Santa Barbara, CA). A carboxylate-modified latex (CML) particle (Interfacial Dynamics Corp., Portland, OR) was used as a surrogate for the organic foulants, because organic foulants (alginate and SRNOM) carry predominantly carboxylic functional groups. To make a colloid probe, a CML particle of diameter 4.0  $\mu\text{m}$  was attached by Norland Optical adhesive (Norland Products Inc., Cranbury, NJ) to a tipless SiN cantilever. The colloid probe was cured under UV light for 20 min.

The AFM adhesion force measurements were performed in a fluid cell using a closed inlet/outlet loop. The solution chemistries of the test solutions in the fluid cell were the same as those used in the bench-scale fouling/cleaning experiments. The fluid cell was first rinsed with 6 ml of DI water and 6 ml of the test solution, before injecting another 6 ml of test solution. Once all the air bubbles had been flushed out of the fluid cell, the injection would stop and the outlet was closed. The membrane was equilibrated with the test solution for 60 min before force measurements were performed. The force measurements were conducted at three to five different locations, and 15 measurements were taken

at each location. Because the focus of this study was on the foulant–foulant interaction (adhesion), only the raw data obtained from the retracting force curves were processed and converted to obtain the force versus surface-to-surface separation curves. The force curves presented were the averages of all the representative force curves obtained at the different locations. The detailed procedures of using AFM in conjunction with a colloid probe to determine the intermolecular adhesion forces in membrane fouling/cleaning can be found in our recent work [25].

## 3. Results and discussion

### 3.1. Chemical aspects of cleaning

The chemical aspects of cleaning – cleaning solution type, cleaning solution pH, and cleaning agent dose – have been systematically investigated to find out the favorable cleaning conditions in terms of chemical reaction between the cleaning agent and foulants. In addition, the influence of fouling layer composition on cleaning efficiency is examined with feed waters containing both alginate and SRNOM with different mass ratios. Cleaning experiments presented in this section were performed at fixed physical conditions so that only the chemical aspects of cleaning could be investigated.

#### 3.1.1. Effect of cleaning solution type

The cleaning efficiency with different cleaning solutions – NaOH (pH 11), SDS, and EDTA – is compared in Fig. 2. DI water was also used to serve as a baseline for comparison with the cleaning solutions. Because fouling runs prior to each cleaning experiment were performed under identical conditions, the flux behavior of each run was almost identical, except the pure water flux obtained after cleaning. Therefore,

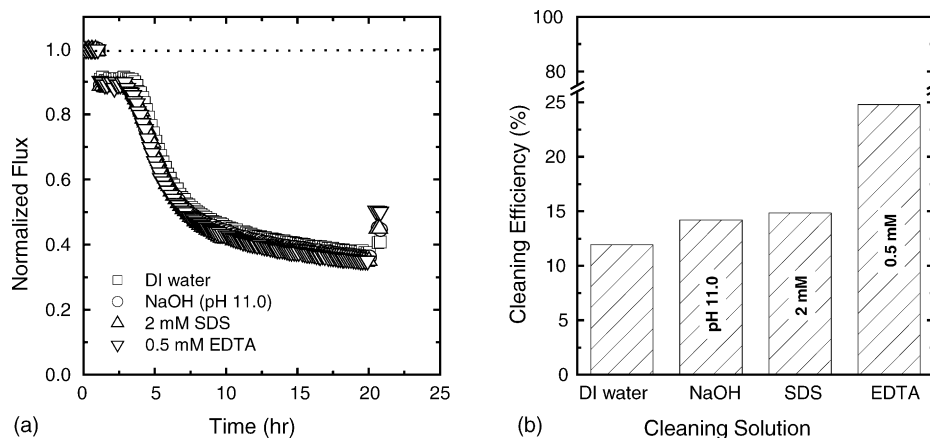


Fig. 2. Influence of cleaning solution type on cleaning of organic-fouled RO membranes: (a) flux behavior during the fouling/cleaning experiments and (b) variation in cleaning efficiency with respect to cleaning solution type. Conditions for fouling experiments: alginate concentration = 20 mg/l, calcium concentration = 0.5 mM, total ionic strength = 10 mM (i.e., 0.5 mM  $\text{Ca}^{2+}$  plus 8.5 mM NaCl), pH  $5.90 \pm 0.05$ , initial flux =  $20 \mu\text{m/s}$ , crossflow velocity = 8.56 cm/s, and temperature =  $20.0 \pm 0.2^\circ\text{C}$ . Conditions for cleaning experiments: time = 15 min, temperature =  $20.0 \pm 0.2^\circ\text{C}$ , crossflow velocity = 42.8 cm/s. Cleaning solutions were used without pH adjustment (ambient pH) except for the NaOH cleaning. Note that the last data points in Fig. 2a are for flux measured with DI water after the corresponding cleaning.

the flux profiles for subsequent fouling/cleaning experiments will not be shown, unless different concentrations and types of organic foulants were used, which would result in flux decline profiles different from those shown in Fig. 2.

Fig. 2a clearly shows that permeate flux during fouling runs decreased dramatically since alginate fouling of the RO membrane was accelerated in the presence of calcium ions (0.5 mM). As described earlier, calcium ions bind with carboxylic groups of alginate and bridge between adjacent alginate molecules, leading to the formation of a cross-linked alginate fouling layer on the membrane surface. This alginate fouling layer can also be explained by the gel formation of alginate in presence of calcium ions as commonly described by the ‘egg-box’ model [18,19]. Based on this model, divalent cations (such as calcium ions) induce gelation of alginate through binding with and bridging between alginate molecules in a highly cooperative manner, leading to the ‘egg-box’ shaped gel network. In fact, visual inspection of the membrane surface at the end of the fouling runs confirmed the presence of a thick alginate gel layer. Therefore, the efficiency of a cleaning agent depends on the ability of the cleaning agent to break down the alginate gel network in the fouling layer through chemical reaction of the cleaning agent with the fouling layer.

Fig. 2b presents the efficiency of each cleaning solution, determined by comparing the pure water fluxes before fouling and after cleaning (the initial and final water fluxes are shown in Fig. 2a). The cleaning efficiencies with NaOH (pH 11) and 2 mM SDS were 14 and 15%, respectively. This points out that NaOH and SDS cleaning performed at these experimental conditions was ineffective since the cleaning efficiency with DI water was already 12%. Cleaning with 0.5 mM EDTA was relatively more effective compared to NaOH and SDS, and the cleaning efficiency (25%) was two times higher than that of DI water. This is attributed to the preferential EDTA–calcium complexation compared to alginate–calcium complexation.

In the case of NaOH cleaning, it is inferred that chemical reaction between NaOH and alginate–calcium complexes in the alginate gel layer was limited and, thus, resulting in a poor cleaning efficiency. There are two possible ways to increase NaOH cleaning efficiency: an increase in NaOH concentration (i.e., higher pH) and/or use of more favorable physical conditions. The former, however, is not applicable in real world applications since most polymeric RO membranes tolerate a limited pH range (i.e., pH 3–12). Therefore, the latter possibility has been investigated, and the results will be shown later in this paper.

The ineffective SDS cleaning is attributed to the low SDS concentration applied during cleaning. The 2 mM concentration was much lower than the critical micelle concentration (CMC) of SDS, reported as 8.36 mM in DI water [29]. At this low SDS concentration, the interaction of the adsorbed SDS molecules with alginate–calcium complexes was not strong enough to break the intermolecular bridging formed with calcium ions. Li and Elimelech [25] demonstrated that a marked

increase in cleaning efficiency of an NOM-fouled NF membrane was observed when SDS concentration was higher than the CMC. The influence of SDS concentration on cleaning efficiency will be discussed later.

In the case of EDTA cleaning, cleaning efficiency is quite sensitive to solution pH. The chelating ability of EDTA to remove complexed calcium ions from alginate–calcium complexes through a ligand-exchange reaction increases at higher pH where more carboxylic groups of EDTA are deprotonated. This will be confirmed when the effect of cleaning solution pH on cleaning efficiency is reported.

For the above runs, visual inspection of the membranes after cleaning by all tested solutions revealed that there was still substantial alginate gel layer on the membrane surface. This observation is not surprising since the cleaning efficiency was less than 25% for all cases shown in Fig. 2b.

### 3.1.2. Effect of cleaning solution pH

The influence of solution pH on the cleaning efficiency of SDS and EDTA is illustrated in Fig. 3. It is shown that cleaning efficiency increased noticeably (i.e., from 25 to 44%) with increasing pH from 4.9 to 11.0 for EDTA, while there was only a slight increase for SDS at higher pH. At pH 11.0, all the carboxylic functional groups of EDTA are deprotonated ( $pK_a$  values are 1.99, 2.67, 6.16, and 10.26 [30,31]). The increase in the chelating ability of EDTA at pH 11.0 resulted in a more effective ligand-exchange reaction between EDTA and alginate–calcium complexes within the alginate gel layer. Consequently, the alginate gel layer was broken down relatively more easily compared to lower pH and, thus, resulted in a higher cleaning efficiency. On the other hand, solution pH showed very little effect on SDS cleaning, because the  $pK_a$  of the sulfate functional group of SDS is 2.12 [30,31], implying that SDS is in its ionic form at both pH values examined. The

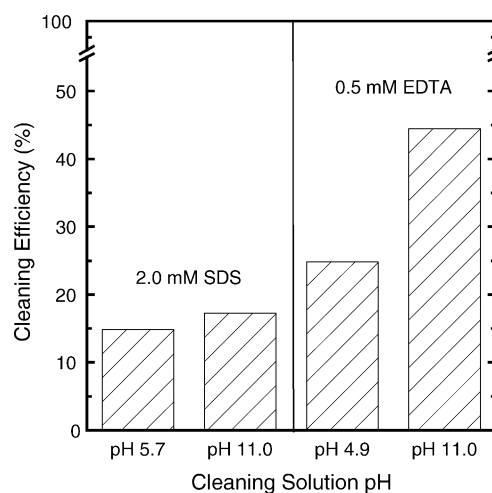


Fig. 3. Variation in SDS and EDTA cleaning efficiencies as a function of cleaning solution pH. Cleaning experiments were performed following fouling runs carried out at the same conditions as those in Fig. 2a. Conditions for cleaning experiments were identical to those in Fig. 2b except for the cleaning solution pH as indicated in this figure.

results imply that cleaning solution pH is a governing factor affecting chemical reaction between EDTA and deposited foulants, while chemical reaction between SDS and foulants is less influenced by cleaning solution pH.

It is noteworthy that the efficiency of the 0.5 mM EDTA cleaning solution at pH 11 was relatively low (less than 45%) compared to the results of other studies on EDTA cleaning of NOM-fouled NF membranes [20,25]. These studies showed that EDTA treatment was effective (almost 100% cleaning efficiency) in cleaning NOM-fouled NF membranes in the presence of calcium ions when the molar EDTA concentration (cleaning solution) was the same as the calcium concentration used during the fouling runs. Note that in our study, both EDTA and calcium concentrations during the cleaning and fouling experiments were 0.5 mM. The reason for this discrepancy is attributed to the structural difference in the fouling layers as well as the different extent of foulant accumulation on the membrane surface for these two cases. The fouling layer of the other studies comprised hydrophobic NOM with smaller molecular weight, whereas the fouling layer in this study comprised hydrophilic alginate with larger molecular weight. This argument will be discussed later in this paper (Section 3.1.4).

### 3.1.3. Effect of cleaning chemical dose

Cleaning experiments were also performed with cleaning solutions containing different doses of EDTA or SDS (both at the pH 11), as presented in Figs. 4 and 5, respectively. The results clearly show that cleaning efficiency with EDTA and SDS cleaning increased with increasing cleaning agent dose. For EDTA, cleaning efficiency increased proportionally with EDTA concentration and reached near 100% efficiency at 2.0 mM EDTA. Note that this molar EDTA concentration is four times higher than the calcium concentration employed during fouling. For SDS cleaning, there was a

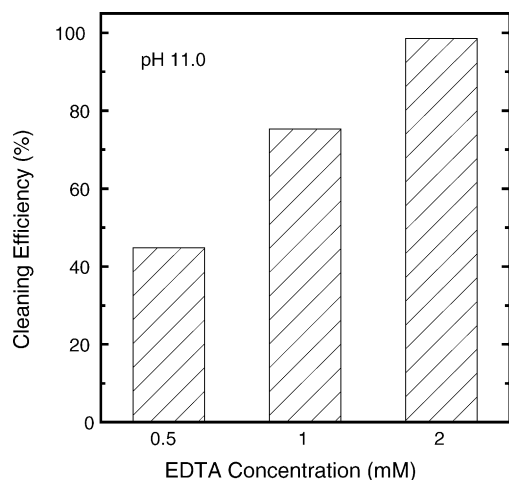


Fig. 4. Variation of EDTA cleaning efficiency with EDTA concentration. EDTA cleaning experiments were performed at pH 11.0 following fouling runs carried out at the same conditions as those in Fig. 2a. Other cleaning conditions were identical to those in Fig. 2b.

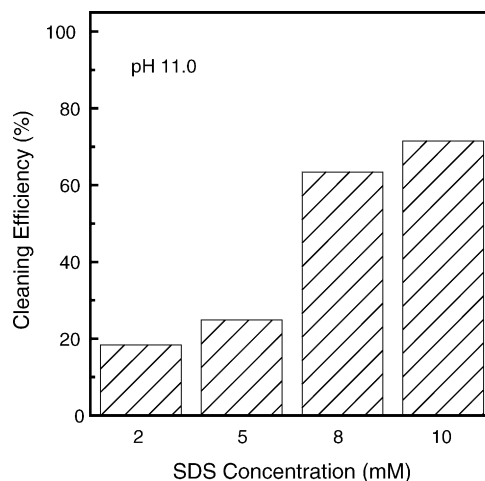


Fig. 5. Variation in SDS cleaning efficiency with SDS concentration. SDS cleaning experiments were performed at pH 11 following fouling runs carried out at the same conditions as those in Fig. 2a. Other cleaning conditions were identical to those in Fig. 2b.

notable increase in cleaning efficiency when SDS concentration increased from 5 to 8 mM. We note that an 8 mM SDS concentration is close to the CMC of SDS, reported as 8.36 mM in DI water [29]. Therefore, it is concluded that cleaning with SDS above the CMC is the critical factor for efficient SDS cleaning, allowing adequate chemical reaction between SDS and the foulants to break down the alginate gel network. A similar mechanism of SDS cleaning of fouled NF membranes by humic acid in presence of calcium ions, has been discussed in our recent work [25].

### 3.1.4. Effect of organic foulant composition

As discussed in previous sections, the fouling layer structure as well as the extent of foulant accumulation on the membrane surface is expected to affect cleaning efficiency for a given cleaning agent under the same cleaning conditions. To investigate the influence of structural difference of the organic fouling layer on cleaning efficiency, fouling runs were performed with feed waters containing different mass ratios of alginate to SRNOM. Several feed water foulant compositions were examined with the total foulant concentration maintained at 20 mg/l: (i) 20 mg/l alginate and no SRNOM, (ii) 14 mg/l alginate plus 6 mg/l SRNOM, (iii) 6 mg/l alginate plus 14 mg/l SRNOM, and (iv) 20 mg/l SRNOM and no alginate. It is expected that the difference in feed water organic composition will result in the formation of organic fouling layer, which is 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 0.5 mM EDTA (pH 11). The flux profiles of these fouling runs and the cleaning efficiencies determined from the subsequent cleaning experiments are presented in Fig. 6.

The flux behaviors depicted in Fig. 6a varied, indicating that the structure and/or amount of fouling layer were

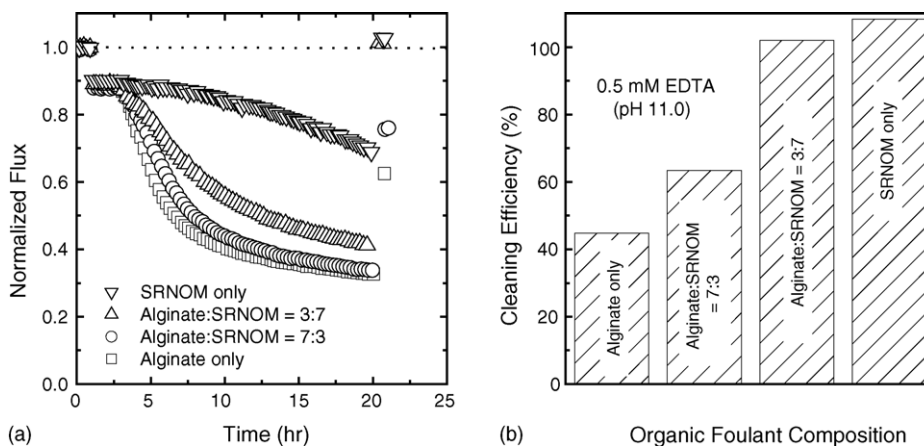


Fig. 6. Influence of feed water organic composition on cleaning of organic-fouled RO membranes: (a) flux behavior during the fouling/cleaning experiments and (b) variation in cleaning efficiency with respect to feed water organic composition. Fouling experiments were performed with feed waters containing: 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. 2a. Cleaning experiments were performed with 0.5 mM EDTA cleaning solutions at pH 11.0. Other cleaning conditions were identical to those in Fig. 2b. Note that the last data points in Fig. 6a are for flux measured with DI water after the corresponding cleaning.

different for each foulant composition. A more severe flux decline was observed with increasing alginate concentration, and there was a significant difference in the flux profiles for alginate (i.e., absence of SRNOM) and SRNOM (i.e., absence of alginate) fouling runs. This implies that the alginate fouling layer produced greater hydraulic resistance to permeate flow than the SRNOM fouling layer. This is attributed to the formation of gel-type alginate fouling layer as described earlier based on the 'egg-box' model. The gelation of charged macromolecules in the presence of calcium ions is predominant for hydrophilic organic macromolecules (such as acidic polysaccharides) compared to hydrophobic organic macromolecules (such as humic acids) [18,19]. However, it should be noted that NOM fouling in presence of calcium ions also results in severe flux decline during nanofiltration and tight-ultrafiltration [20,32,33]. The reason for the less pronounced flux decline with SRNOM observed in this study is that the additional hydraulic resistance of the SRNOM fouling layer to permeate flow is relatively much smaller than that of the RO membrane used in this study.

It is also noteworthy that, in the case of alginate fouling, the flux declined rapidly in the initial stage and, then, declined gradually. On the other hand, for SRNOM fouling, the fouling rate increased as fouling progressed (i.e., flux declined more rapidly with filtration time). This implies that the alginate gel layer was denser and more compact than the SRNOM fouling layer, leading to a substantial hydraulic resistance upon gel formation. However, this alginate fouling layer was likely less compressible than the SRNOM fouling layer that became more compact during filtration, resulting in a higher fouling rate as fouling progressed. In addition, the flux decline behavior with the higher SRNOM proportion (i.e., alginate:SRNOM = 3:7) was more similar to that for alginate fouling (i.e., 20 mg/l alginate and absence of SRNOM) than

that for SRNOM fouling (i.e., 20 mg/l SRNOM and absence of alginate). This suggests that a small amount of alginate (6 mg/l alginate and 14 mg/l SRNOM) was enough to form alginate gel layer on the membrane surface, and the alginate molecules more easily accumulated on the membrane surface compared to SRNOM molecules.

Fig. 6b clearly shows that the cleaning efficiency with 0.5 mM EDTA (pH 11) increased when the fouling runs were performed with feed waters containing a higher proportion SRNOM to alginate. The SRNOM-fouled membrane (i.e., absence of alginate) achieved the highest cleaning efficiency (108%), while the alginate-fouled membrane (i.e., absence of SRNOM) had the lowest efficiency (44%). The combined organic fouling with alginate to SRNOM ratios of 3:7 and 7:3 had cleaning efficiencies of 102 and 64%, respectively. These values were expected as they were within the range of the cleaning efficiencies for the alginate- and SRNOM-fouled membranes. The high cleaning efficiency of SRNOM-fouled membrane was in agreement with our recent study on EDTA cleaning of NOM-fouled NF membrane [20]. A cleaning efficiency of over 100% suggests that the recovered flux after EDTA cleaning was higher than the flux of the original clean membrane, probably due to the presence of a small amount of EDTA and/or NOM on the membrane surface, making the membrane more hydrophilic, and thus, enhancing the partitioning and passage of water molecules [20].

The difference in the EDTA cleaning efficiency for the alginate- and SRNOM-fouled membranes can be attributed to one or more of the following: (i) the stronger binding and bridging of calcium to alginate than SRNOM, (ii) the gel-forming nature of alginate which yields a denser and more compact fouling layer compared to SRNOM, and (iii) the larger mass of alginate accumulating on the

membrane surface compared to SRNOM. The first explanation is not likely since a strong chelating agent, such as EDTA, can easily remove the complexed calcium from both alginate–calcium and SRNOM–calcium complexes via a ligand-exchange reaction. The second explanation is based on the observation that, in the presence of divalent cations, the alginate gel layer produced more resistance to permeate flow than the SRNOM fouling layer. This behavior suggests that the alginate fouling layer is much denser and more compact than the SRNOM fouling layer due to its gel-like structure. Consequently, during EDTA cleaning, EDTA molecules diffused more easily into the looser SRNOM fouling layer. Thus, a more rigorous ligand-exchange reaction is likely to occur within the SRNOM fouling layer than within the alginate fouling layer and, consequently, this has more impact on breaking up the intermolecular bridging of SRNOM induced by calcium ions than that of alginate. A third possible explanation for the difference in cleaning of the alginate- and SRNOM-fouled membranes is the variation in the amount of accumulated foulant on the membrane surface. At the given hydrodynamic conditions (i.e., initial flux and crossflow velocity), the larger alginate macromolecules may accumulate more effectively on the RO membrane surface compared to the smaller SRNOM molecules because of the lower back-diffusion experienced by larger macromolecules. In the previous results (Fig. 3), an almost 100% cleaning efficiency was demonstrated for the alginate-fouled RO membrane when 2.0 mM EDTA was used. This suggests that 0.5 mM EDTA was not enough to react with all the alginate–calcium complexes in the gel layer (within the 15 min cleaning time), while this dose was sufficient to react with all the SRNOM–calcium complexes in the fouling layer (over 100% cleaning efficiency). Thus, to better understand the cleaning mechanisms, the “stoichiometry” between the cleaning agent dose and amount of foulant on the membrane surface must be considered.

### 3.2. Physical aspects of cleaning

In this section, we investigate the physical aspects of cleaning – crossflow velocity, cleaning time, and temperature – to determine the favorable conditions for effective mass transfer. During cleaning, mass transfer of foulants from the fouling layer to the bulk solution takes place after the chemical reaction between the cleaning agent and deposited foulants has weakened the structural integrity of the fouling layer. Crossflow velocity in the membrane cell mainly controls the mass transfer, and cleaning time and temperature affect the overall mass transfer as the rate and extent of solute transport are functions of time and temperature. Cleaning experiments – following fouling runs carried out under identical conditions (Section 2.5) – were performed at fixed chemical conditions, thus focusing on the physical aspects of cleaning. However, it is important to note that cleaning time and temperature also affect chemical reaction between cleaning agent and foulants since contact time (between cleaning agent and fouling layer) and solution temperature influence the extent and rate of reaction. While investigating the influence of a certain physical factor on the efficiency of a cleaning agent, all other physical factors are kept constant.

#### 3.2.1. Effect of cleaning time

The influence of cleaning time on the efficiency of each cleaning agent was investigated. The flux behaviors during the fouling/cleaning runs and the resulting cleaning efficiencies with NaOH (pH 11) and 0.5 mM EDTA (pH 11) are shown in Fig. 7. The influence of cleaning time on cleaning efficiency is also compared for two different SDS concentrations (2 and 10 mM; both at pH 11) as shown in Fig. 8. In all cases, the results are compared for cleaning performed for 15 and 60 min.

For NaOH (pH 11) cleaning, an increase in cleaning time from 15 to 60 min resulted in negligible difference in cleaning

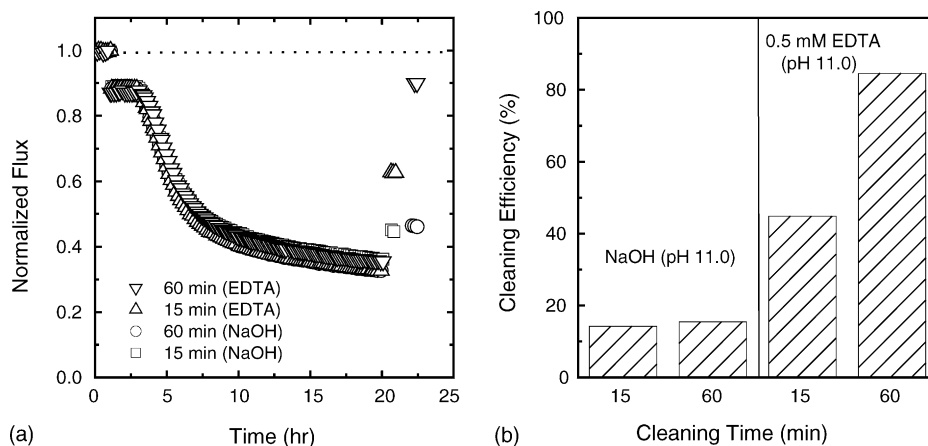


Fig. 7. Variation in NaOH and EDTA cleaning efficiencies with respect to cleaning time: (a) flux behavior during fouling/cleaning experiments and (b) cleaning efficiency. Cleaning experiments were performed at pH 11.0 following fouling runs carried out at the same conditions as those in Fig. 2a. Other cleaning conditions were identical to those in Fig. 2b except the cleaning time as indicated in the figure. Note that the last data points in Fig. 7a are for flux measured with DI water after the corresponding cleaning.

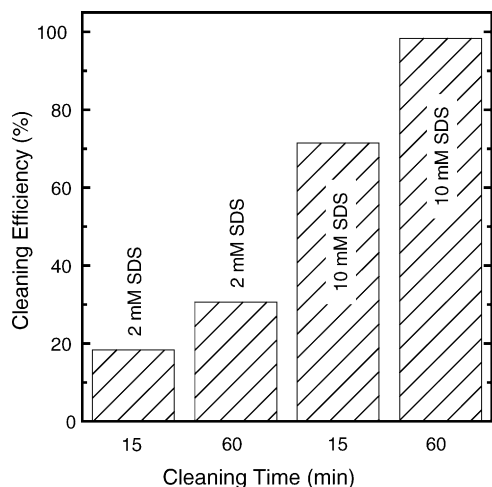


Fig. 8. Variation in SDS cleaning efficiency with respect to cleaning time at different SDS concentrations. Cleaning experiments were performed at pH 11 following fouling runs carried out at the same conditions as those in Fig. 2a. Other cleaning conditions were identical to those in Fig. 2b except the cleaning time as indicated in the figure.

efficiency (Fig. 7). This is attributed to the limited chemical reaction between NaOH and foulants in the alginate gel layer. In other words, a longer contact time did not contribute to enhancing cleaning efficiency, unless there was a favorable chemical reaction between the cleaning agent and foulants in the fouling layer to lessen foulant–foulant interactions. Therefore, we conclude that NaOH is not a suitable cleaning agent for membranes fouled by organic matter in presence of calcium ions. Besides, as mentioned earlier, increasing the NaOH concentration and, hence, resulting in a pH higher than 12, is not applicable for most polymeric RO membranes. In the case of EDTA cleaning, there was a twofold increase in cleaning efficiency when the cleaning time was increased from 15 to 60 min. Contrary to NaOH, EDTA is a favorable cleaning agent since EDTA reacts specifically within the fouling layer through a ligand-exchange reaction.

Previous results (Fig. 5) demonstrated that the efficiency of SDS cleaning is significantly influenced by SDS concentration with respect to its CMC. As shown in Fig. 8, increasing cleaning time from 15 to 60 min resulted in nearly 100% cleaning efficiency when 10 mM SDS was used. However, cleaning with 2 mM SDS for 60 min was still ineffective (less than 30% cleaning efficiency). This observation is closely related to the previous results for NaOH and EDTA cleaning performed for different cleaning times. Similar to NaOH, cleaning with 2 mM SDS was, to some extent, limited in terms of chemical reaction and, thus, increasing cleaning time did not significantly enhance the cleaning efficiency. However, increasing cleaning time for the 10 mM SDS solution led to an almost complete cleaning of the fouled membrane since cleaning with 10 mM SDS was favorable in terms of chemical reaction between SDS and the foulants within the fouling layer. Therefore, while considering the chemical aspects of cleaning (e.g. deciding the cleaning agent dose), optimization

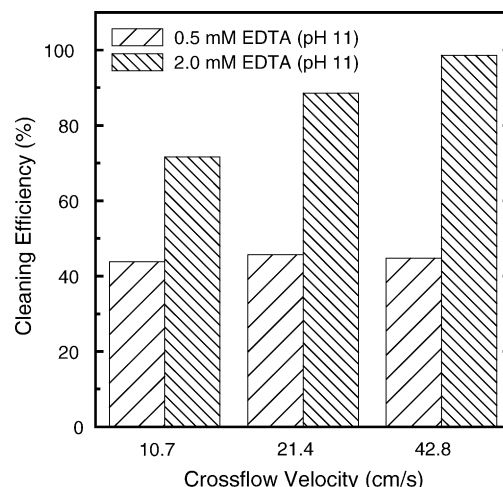


Fig. 9. Variation in EDTA cleaning efficiency with the crossflow velocity during cleaning with different EDTA concentrations. Cleaning experiments were performed at pH 11 following fouling runs carried out at the same conditions as those in Fig. 2a. Other cleaning conditions were identical to those in Fig. 2b except the crossflow velocity as indicated in the figure.

of cleaning time should be taken into account since increasing cleaning time does not always result in a corresponding increase in cleaning efficiency.

### 3.2.2. Effect of crossflow velocity

The influence of crossflow velocity (during cleaning) on cleaning efficiency was investigated with solutions containing different doses of EDTA (0.5 and 2.0 mM; both at pH 11), as shown in Fig. 9. It is shown that cleaning efficiency with 0.5 mM EDTA did not improve significantly with increasing crossflow velocity, while there was a discernible increase in cleaning efficiency with 2.0 mM EDTA as crossflow velocity increased. We have shown earlier that, for a cleaning agent to be effective, the chemical reaction with the foulants has to be favorable before physical interaction (due to crossflow velocity) takes place. With 0.5 mM EDTA, the concentration of cleaning agent was not enough to produce a favorable chemical reaction with the foulants in the fouling layer within the 15 min cleaning time. An increase in crossflow velocity which resulted in an increase in the shear rate did not enhance the mass transfer of foulants in the fouling layer to the bulk solution because the EDTA molecules did not react strongly with the foulants, and the structural integrity was still very much intact. However, with 2.0 mM EDTA, an increase in shear rate enhanced the mass transfer of the foulants from the fouling layer to the bulk solution, as 2.0 mM EDTA is favorable for a rigorous chemical reaction. This led to an increase in cleaning efficiency with increasing crossflow velocity. We conclude that the chemical reaction of the cleaning agent with deposited foulants and the associated mass transfer phenomena are quite important in membrane cleaning.

### 3.2.3. Effect of temperature

The results for EDTA cleaning performed at different temperatures are presented in Fig. 10. We note that, in both

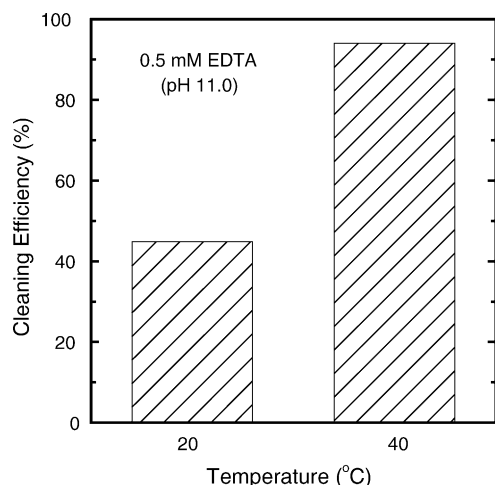


Fig. 10. Variation in EDTA cleaning efficiency with respect to cleaning solution temperature. Cleaning experiments were performed with 0.5 mM EDTA solution at pH 11 following fouling runs carried out at the same conditions as those in Fig. 2a. Other cleaning conditions were identical to those in Fig. 2b except the temperature as indicated in the figure.

cases, the pure water flux after cleaning was determined at 20 °C. The cleaning efficiency with 0.5 mM EDTA (pH 11) increased dramatically with increasing cleaning temperature from 20 to 40 °C. Both the rate of chemical reaction of EDTA with the deposited foulants and the diffusive transport of foulants from the fouling layer to the bulk solution increased as temperature was increased. At a higher temperature, the swelling of the alginate gel layer might have also contributed to weakening its structural stability [34,35].

### 3.3. Relating cleaning efficiency to measured adhesion forces

Based on the preceding results, it has been shown that chemical reaction of the cleaning agent with the foulants in

the fouling layer plays a critical role in determining the overall cleaning efficiency. Determining the intermolecular adhesion forces between foulants in the fouling layer in the presence, or absence, of cleaning solution enables us to predict the capability of chemical reaction between cleaning agent and the foulants. A more favorable (or reactive) cleaning agent will result in less intermolecular adhesion force between foulants in the fouling layer.

The intermolecular adhesion force was first determined in the absence of cleaning solution to serve as a baseline and, then, in the presence of the cleaning agent. In the absence of cleaning solution, the interfacial adhesion force was determined with the same solution used as feed water for the fouling runs (i.e., 20 mg/l alginate, 0.5 mM  $\text{Ca}^{2+}$ , 10 mM total ionic strength, and pH 6.0). The interfacial adhesion forces determined in the presence of cleaning solutions (same solution chemistries as those used in the cleaning experiments) were compared with the cleaning efficiency determined from fouling/cleaning experiments, as shown in Fig. 11.

Fig. 11a shows the intermolecular adhesion forces determined in the presence of different cleaning solutions (i.e., NaOH, 0.5 mM EDTA, and 10 mM SDS, all at pH 11) as well as in the absence of cleaning solution. The maximum adhesion force (corresponds to the minimum in the adhesion force curve) in the absence of cleaning solution was about 1.5 mN/m. The addition of SDS to the test solution was the most effective, almost eliminating the adhesion force. The addition of EDTA to the test solution decreased substantially the adhesion force, reducing the maximum adhesion force to 0.4 mN/m. In the presence of NaOH (pH 11), however, a significant adhesion force (1.3 mN/m) was still present. It is also noted that, with the reduction in adhesion force in presence of the cleaning solution, the distance from the fouling layer on the membrane surface to the point where no adhesion force was observed was reduced correspondingly. The reduction in intermolecular adhesion force with each

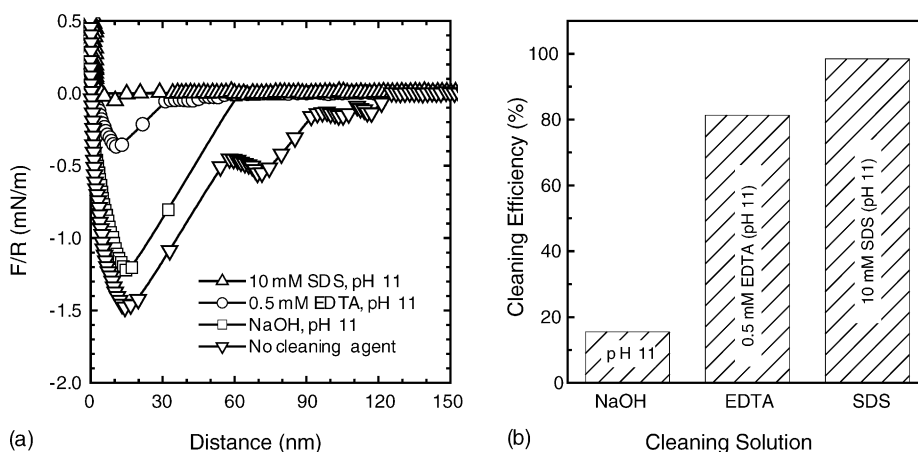


Fig. 11. Relationship between intermolecular adhesion forces and cleaning efficiency: (a) variation in foulant–foulant adhesion forces as a function of cleaning solution type (the curve indicated as ‘no cleaning agent’ was determined in the absence of cleaning solution) and (b) variation in cleaning efficiency as a function of cleaning solution type. The test solutions used in the interfacial force measurements were the same as those used during fouling runs and also contained cleaning solutions as indicated in the figure. Cleaning experiments were carried out for 60 min following fouling runs performed at the same conditions as those in Fig. 2a. Other cleaning conditions were identical to those in Fig. 2b.

cleaning solution was directly related to the cleaning efficiency as shown in Fig. 11b. These cleaning efficiencies were determined from experiments with each cleaning solution at fixed physical cleaning conditions (60 min cleaning time, crossflow velocity of 42.8 cm/s, and 20 °C).

The results in Fig. 11 demonstrate a strong relationship between the efficiency of a cleaning solution and the residual intermolecular adhesion force in the presence of the same cleaning solution. This is because the efficiency of a cleaning solution at fixed physical conditions was mainly

governed by the chemical reaction of the cleaning agent with the foulants in the fouling layer. A more favorable chemical reaction would lead to a lower foulant–foulant adhesion force and hence higher cleaning efficiency. This general relationship between intermolecular adhesion force and cleaning efficiency has also been demonstrated in our recent study with humic acid-fouled NF membranes [25]. Therefore, the selection of a favorable cleaning solution in terms of chemical reaction between the cleaning agent and the foulants in the fouling layer can be predicted by measuring the

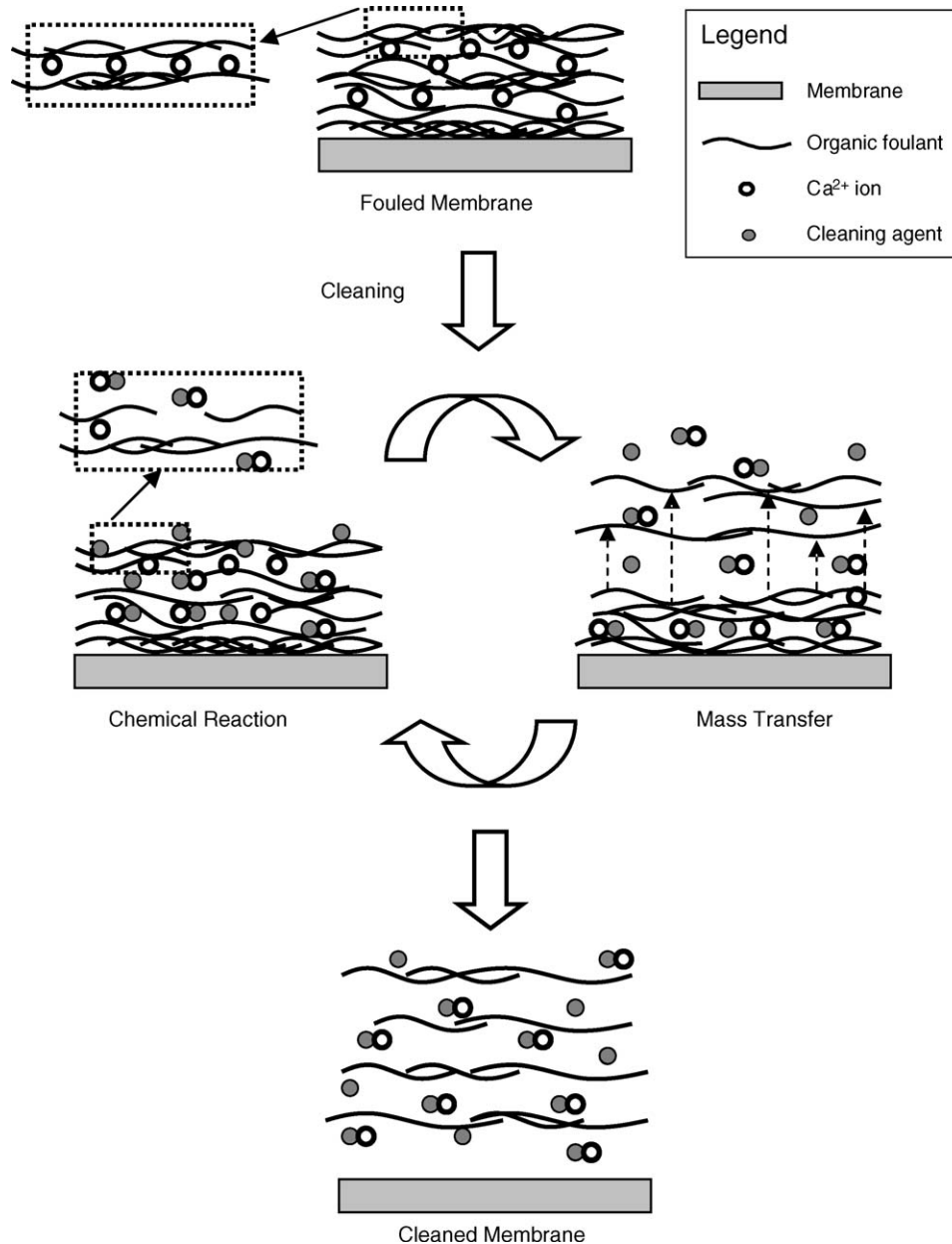


Fig. 12. Schematic representation for effective cleaning of organic-fouled RO membranes. A cross-linked fouling layer is formed on the membrane surface in presence of calcium ions, which bind to organic foulants and form bridges between adjacent foulant molecules. During cleaning, the cleaning agent reacts with the foulants in the fouling layer yielding loosened foulants. These reaction products are removed from the fouling layer to the bulk solution through the hydrodynamics/mass transfer. Thus, efficient cleaning can be achieved through the coupling between the chemical reaction and mass transfer along with the optimization of cleaning conditions responsible for the favorable chemical reaction and mass transfer.

intermolecular adhesion force prior to the fouling/cleaning experiments. Following this prediction, the selected favorable cleaning solution can be used for cleaning experiments to determine the optimal physical cleaning conditions in terms of both cleaning efficiency and operating cost.

#### 3.4. Effective cleaning requires favorable chemical and physical interactions

Membrane cleaning involves both chemical and physical interactions. These interactions include (i) chemical reaction between the cleaning agent and the foulants in the fouling layer and (ii) mass transfer of cleaning agent from the bulk solution to the fouling layer and the foulants from the fouling layer back to the bulk solution. A schematic representation of the roles of chemical and physical interactions for effective cleaning of organic-fouled RO membranes is shown in Fig. 12. Effective cleaning can be achieved only when both the chemical and physical interactions are favorable as discussed below.

In the presence of a cleaning solution, chemical reaction will occur between the cleaning agent and the foulants in the fouling layer. In this study, we have seen that the effectiveness of cleaning in terms of chemical reactivity depends on the type of cleaning solution, cleaning solution pH, cleaning chemical dose, and the foulant chemical composition. When a cleaning agent has a favorable chemical reactivity, the cleaning agent, upon contact with the foulants, will be able to react with the foulants and weaken the structural integrity of the fouling layer. The physical (hydrodynamic) conditions, which are mainly responsible for the mass transfer of the reaction products, then play an important role in removing the foulants from the fouling layer.

As we have shown earlier, some physical conditions (i.e., cleaning time and temperature) affect the mass transfer and chemical reaction concurrently, unless the cleaning agent is limited in terms of chemical reactivity. When a cleaning agent has a favorable chemical reaction with the foulants in the fouling layer, an optimization of the physical conditions improves its cleaning efficiency significantly, as illustrated for 0.5 mM EDTA and 10 mM SDS solutions when the cleaning time was increased from 15 to 60 min. However, optimizing the physical conditions will not enhance the cleaning efficiency of a cleaning agent which does not have a favorable chemical reaction with the foulants, as shown for NaOH solution when the cleaning time was increased from 15 to 60 min. As we emphasized earlier, effective cleaning of organic-fouled RO membranes requires both the physical and chemical interactions to be favorable.

## 4. Conclusion

The cleaning of organic-fouled RO membranes is accomplished by the chemical reaction between cleaning agents and foulants in the fouling layer, followed by the mass transfer

of loosened foulants from the fouling layer to the bulk solution. The chemical reaction is greatly influenced by the type and dose of cleaning agent as well as cleaning solution pH. In addition, the fouling layer composition also influences the reactivity of a cleaning agent with foulants in the fouling layer.

EDTA and SDS were quite effective in reacting with organic foulants in the fouling layer formed in the presence of calcium ions, while NaOH cleaning resulted in poor cleaning efficiency due to its limited reactivity with deposited foulants. Cleaning efficiency with EDTA and SDS was improved by optimizing cleaning agent dose and solution pH. However, these chemical factors hardly contributed to improving the efficiency of NaOH cleaning. For favorably reactive cleaning agents, cleaning efficiency can be further improved by enhancing the mass transfer of the reaction products from the fouling layer to the bulk solution. Mass transfer of the foulants from the fouling layer to the bulk solution was mainly controlled by the crossflow velocity, whereas cleaning time and temperature affected both the mass transfer and chemical reaction.

The AFM force measurements show that the chemical reaction between cleaning agents and deposited foulants plays an important role in reducing the intermolecular adhesion force between foulants in the fouling layer. A remarkable correlation is noted between the cleaning efficiencies and the magnitudes of the adhesion force measured in the presence of the corresponding cleaning solutions. The cleaning efficiency was inversely related to the residual foulant–foulant adhesion force, implying that favorable cleaning agents are those effective in reducing the intermolecular adhesion force. It is therefore suggested that AFM force measurements can be used as a tool to predict the effectiveness of the chemical reactivity of a cleaning agent. The selection of reactive cleaning agents is of paramount importance in determining the overall cleaning efficiency since the optimization of physical conditions could improve the cleaning efficiency only when the chemical reaction of the cleaning agent with deposited foulants is favorable.

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