



# Chemical cleaning of RO membranes fouled by wastewater effluent: Achieving higher efficiency with dual-step cleaning

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## ABSTRACT

The effect of different modes of cleaning of RO membranes fouled by wastewater treatment plant effluent has been investigated. Characterization of the wastewater effluent revealed the presence of foulants containing carboxylic and phenolic functional groups as well as calcium ions. The chemical cleaning agents, sodium hydroxide (NaOH), ethylenediaminetetraacetic acid (EDTA), sodium dodecyl sulfate (SDS), and sodium chloride (NaCl), were selected as models for alkaline solutions, metal chelating agents, surfactants, and salt cleaning, respectively. Specifically, we examined the impact of a sequence or a combination of two cleaning agents compared to the use of single cleaning agents. Increased cleaning efficiency was demonstrated when two cleaning agents were applied in a certain order and mixture. In particular, it was shown that addition of NaOH can enhance the overall cleaning performance when introduced with other chemical agents, due to its ability to loosen the fouling layer. Cleaning efficiency as high as 94% was obtained by simply increasing the pH of a NaCl cleaning solution, compared to 65% in the case of the individual salt solution with no pH adjustment. On the other hand, combining chemical cleaning agents was not advantageous in some cases, possibly because of the competing cleaning mechanisms of some of the agents. The most and the least effective cleaning modes were highlighted, suggesting a rationale for the design of chemical cleaning of RO membranes fouled by wastewater effluent. This study demonstrates that careful selection of cleaning agents and the steps through which those agents are applied allows the regeneration of high water productivity after fouling while minimizing both the cleaning time and the amount of chemicals.

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## 1. Introduction

The increase in global demand for potable water exerts considerable strain on the supply from conventional freshwater sources, such as rivers and lakes. Thus, alternative solutions that extract clean water from less conventional sources, such as the treatment of secondary wastewater effluent in advanced wastewater reclamation for indirect potable use [1,2], are gaining popularity. However, the use of membrane technology in advanced wastewater reclamation is impeded by the phenomenon of fouling. Secondary treated effluent from wastewater treatment plants contains dissolved organic matter, commonly known as effluent organic matter (EfOM), which contributes to organic fouling [1]. EfOM comprises polysaccharides, proteins, amino sugars, nucleic acids, humic and fulvic acids, organic acids, and cell components [1].

Since EfOM is generally smaller than the pore size of an ultrafiltration (UF) membrane, it can readily pass through the microfiltration (MF) or UF membrane typically employed in the pretreatment step of an advanced wastewater reclamation plant. The EfOM, which passes through the pretreatment process, causes fouling of the reverse osmosis (RO) membrane in the subsequent RO filtration step. Furthermore, the ubiquitous calcium cation ( $\text{Ca}^{2+}$ ) present in wastewater effluents contributes significantly to RO membrane fouling by forming complexes with the constituents of EfOM, such as polysaccharides [2] and natural organic matter [3]. Fouling of the membrane results in productivity decline, deteriorated permeate quality, increased energy consumption, increased treatment cost, and shortened membrane lifespan [4]. Periodic cleaning of the membrane is therefore required to restore this loss in membrane performance.

Chemical cleaning agents are commonly used to remove the foulant deposited on membrane surfaces [5–10]. Typical chemicals used for membrane cleaning include alkaline solutions, metal chelating agents, surfactants, and salt solutions [8,11,12]. Alkaline solutions clean organic-fouled membranes by hydrolysis and solubilization, and by generating electrostatic interactions between the

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negatively charged foulants and membranes when the solution pH is elevated [13]. Metal chelating agents break down the structural integrity of the fouling layer by removing divalent cations in the fouling layer, which serve as binding agents for organic molecules [3]. 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 [14], and help to clean the surface of the fouled membrane. Sodium chloride (NaCl) and other common inert salts can be used as an effective alternative for the cleaning of RO membranes fouled by gel-forming hydrophilic organic foulants [15]. The proposed cleaning mechanisms involve swelling of the fouling layer in the presence of a salt solution and ion-exchange reaction of Na<sup>+</sup> with the polysaccharide-calcium complex in the fouling layer.

Optimizing the use of cleaning agents is necessary to maximize cost-efficiency of the process and minimize the use of harmful chemicals. Underdosing of chemical agents will result in ineffective foulant removal and hence, achieve inadequate performance recovery. On the other hand, overdosing can have unintended detrimental effects on the membrane selective layer. For example, excess alkalinity in the cleaning agent can raise the solution pH beyond the membrane manufacturer's recommended exposure range, resulting in compromised selectivity [16]. The additional cost of superfluous chemicals as a result of overdosing can be significant. Furthermore, the discharge of chemicals into the environment can have deleterious effects. For instance, the discharge of ethylenediaminetetraacetic acid (EDTA), which is non-biodegradable, into receiving waters and the environment can remobilize toxic heavy metal ions from soil [17] and adversely affect contaminant transport.

Previous research on chemical cleaning of RO membranes has mostly focused on laboratory-prepared solutions containing mixtures of organic foulants to simulate wastewater effluent [11,18]. In this study, we investigate the chemical cleaning of RO membranes fouled by wastewater effluent collected at a municipal wastewater treatment plant. The chemical cleaning agents, sodium hydroxide (NaOH), EDTA, sodium dodecyl sulfate (SDS), and NaCl, were selected as models for alkaline solutions, metal chelating agents, surfactants, and salt cleaning, respectively. The fouled membranes were cleaned using: individual cleaning agents, various combinations of cleaning agents, and pairs of cleaning agents, administered in different sequences, to investigate the effects of different applications of cleaning agents on performance recovery. The results demonstrate enhanced cleaning effects when cleaning agents are used in a certain order during dual cleaning, as compared to cleaning with individual cleaning agents for the same duration of cleaning time.

## 2. Materials and methods

### 2.1. Wastewater effluent characterization

Wastewater effluent was collected at a municipal treatment plant located in Wallingford, Connecticut, USA. The effect of the presence of bacteria in the effluent was minimized by collecting the wastewater effluent after the UV disinfection stage at the treatment plant and by keeping the effluent in storage under refrigeration at 4 °C. Key properties of the secondary wastewater effluent are shown in Table 1. The parameters are analyzed based on 12–18 samples from 3 batches of wastewater effluent that were collected at the treatment plant every few weeks, with the exception of fatty acid analysis, which is based on 2 samples. The presented solution pH is the average of the solution pH taken at the start of the fouling experiment. The BOD data was obtained from the plant's laboratory. The cations and anions were analyzed using ion chromatography.

**Table 1**  
Wastewater effluent characteristic parameters.

Parameter	Value
pH	6.1–6.8
BOD	3–5 mg/L
TOC	6–10 mg/L
Ca <sup>2+</sup>	0.52 ± 0.03 mM
Na <sup>+</sup>	1.87 ± 0.12 mM
Mg <sup>2+</sup>	0.23 ± 0.03 mM
K <sup>+</sup>	0.21 ± 0.02 mM
Cl <sup>-</sup>	1.72 ± 0.33 mM
NO <sub>3</sub> <sup>-</sup>	0.37 ± 0.13 mM
PO <sub>4</sub> <sup>3-</sup>	0.08 ± 0.02 mM
SO <sub>4</sub> <sup>3-</sup>	0.04 ± 0.01 mM
Polysaccharides (as alginate)	32.9 ± 6.3 mg/L
Proteins (as BSA)	9.9 ± 2.5 mg/L
NOM (as SRNOM)	25.3 ± 1.5 mg/L
Fatty acids (C <sub>11</sub> –C <sub>24</sub> )	329.8 ± 1.6 µg/L

The polysaccharide, protein, NOM, and fatty acid concentrations were analyzed, respectively, by the Dubois colorimetric method [19], the modified Lowry method [20], ultraviolet–visible (UV–vis) spectroscopy [21], and electrospray ionization tandem mass spectrometry [22]. (Analysis was carried out by the Kansas Lipidomics Research Center, Kansas State University.)

The data suggest that the wastewater effluent was close to neutral pH range and had relatively low organic content. The average Ca<sup>2+</sup> concentration was similar to that of the feed solution (0.5 mM) in previous fouling experiments with organic foulants, and the approximate ionic strength was slightly less than half that of the feed solution (10 mM) [11,23,24]. Among the various foulant types, polysaccharides (using alginate as a reference polysaccharide) were the most abundant. The measurements of the various foulant types were not mutually exclusive; for example, some natural organic matter can contain protein-based substances.

### 2.2. Chemical cleaning agents

The chemical cleaning agents used were NaOH (pH 11.0) as an alkaline solution, certified grade disodium ethylenediaminetetraacetate (Na<sub>2</sub>-EDTA) as a metal chelating agent, certified grade sodium dodecyl sulfate (SDS) as an anionic surfactant, and NaCl as a salt cleaning solution. The agents were purchased from Fisher Scientific (Pittsburgh, PA) and used without further purification. The stock chemical solutions were freshly prepared by dissolving each chemical in deionized (DI) water. The pH of the EDTA, SDS, and NaCl cleaning solutions was adjusted with 1.0 M NaOH as necessary.

### 2.3. RO membrane and test unit

The relatively well-characterized thin-film composite LFC-1 membrane (Hydranautics, Oceanside, CA) was used as a model RO membrane. The average hydraulic permeability was determined to be  $3.92 \pm 0.47 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$  ( $1.09 \pm 0.13 \times 10^{-11} \text{ m s}^{-1} \text{ Pa}^{-1}$ ). The observed salt rejection was 98.7–99.3%, as determined using a 10 mM (584 mg/L) NaCl feed solution at an applied pressure of 20.68 bar (300 psi) and a crossflow velocity of 8.1 cm/s. Membrane samples were received as dry flat 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 of about pH 4 [25]. It has been suggested that the membrane is coated with a neutral polyalcohol layer rich in –COH functional groups, which make the surface less charged than the surfaces of other polyamide RO membranes without a coating layer [26].

Fouling of the membranes and the ensuing cleaning experiments were performed with a laboratory-scale cross-flow test unit,

following the procedure described in our previous publication [11]. The membrane test unit comprised a membrane cell, pump, feed reservoir, temperature control system, and data acquisition system. The membrane cell is a rectangular plate-and-frame unit, containing a flat membrane sheet placed in a rectangular channel with dimensions measuring 7.7 cm long, 2.6 cm wide, and 0.3 cm high. Feed spacers were not employed, and the feed solution was circulated in crossflow along the length of the membrane channel. Both permeate and retentate were recirculated back to the feed reservoir. Permeate flux was registered continuously by a digital flow meter (Optiflow 1000, Humonics, Inc., Folsom, CA), interfaced with a computer. A floating disc rotameter (King Instrument Company, Garden Grove, 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 (U.S. Para Plate, Auburn, CA). Temperature was controlled by a recirculating chiller/heater (Model 633, Polysciences) with a stainless steel coil submerged in the feed water reservoir.

#### 2.4. Fouling and cleaning experiments

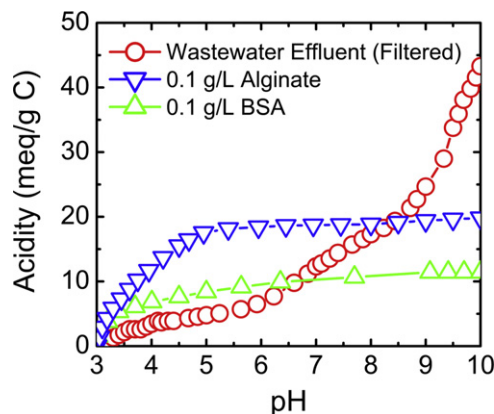
The membrane was first compacted with DI water until the permeate flux became constant, followed by the initial baseline performance for 1 h. The flux at which the baseline run was performed was pre-determined so that the initial flux at the onset of fouling dropped to a specified flux of  $83 \text{ L m}^{-2} \text{ h}^{-1}$  ( $2.3 \times 10^{-5} \text{ m/s}$ ) after decanting the DI water and adding the wastewater effluent to the feed reservoir. The pump was momentarily stopped to decant the DI water. It was restarted after adding the wastewater effluent and operated at the same applied hydraulic pressure used to obtain the baseline. To prepare the feed solution for fouling experiments, the wastewater effluent was carefully poured out of the storage containers to prevent settled particles from being stirred up. The wastewater effluent was then filtered with a  $38\text{-}\mu\text{m}$  sieve to remove particles in the feed, but was not pretreated with a filter possessing a pore size typical to that of an MF membrane, in order to maintain accelerated fouling conditions. Fouling runs were carried out for 17 h. At the end of fouling, the solution in the feed reservoir was discarded 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 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 to determine the pure water flux.

The crossflow velocity throughout the experiment, except during cleaning, was maintained at  $8.6 \text{ cm/s}$ . 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, defined as the ratio between the pure water fluxes determined after cleaning and before fouling. Throughout all of the fouling/cleaning stages, the wastewater effluent in the reservoir located on top of a magnetic stirrer was mixed vigorously to ensure complete mixing of the wastewater effluent.

### 3. Results and discussion

#### 3.1. Wastewater characteristics

Membrane fouling is influenced by the electrostatic interactions between the organic foulants and the membrane surface, (which affect foulant deposition during initial fouling), and among organic



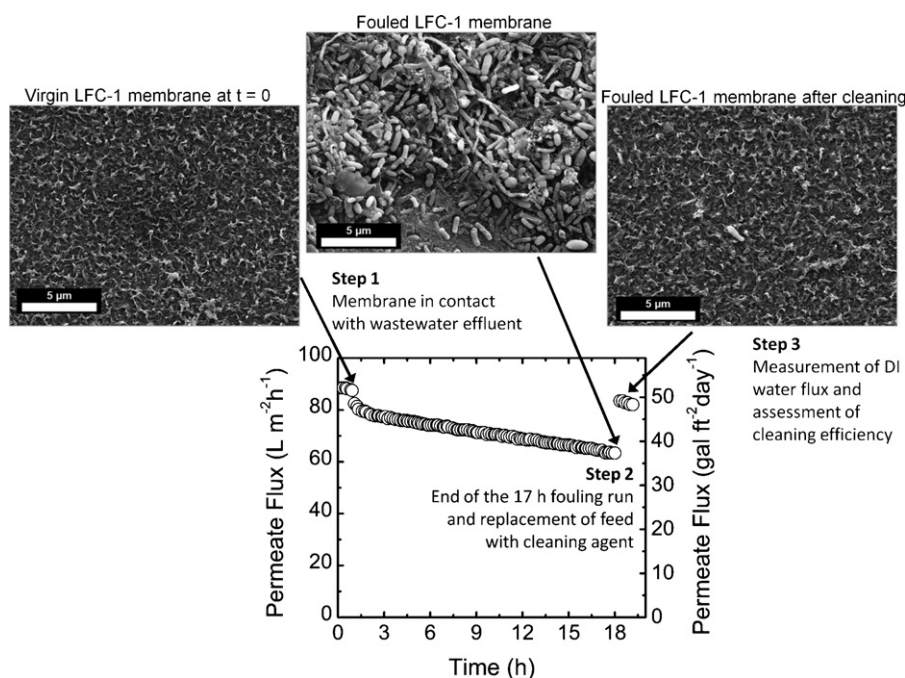
**Fig. 1.** Acidity of wastewater effluent as a function of pH, as compared to that of alginate and BSA. The wastewater effluent was filtered through a  $0.45\text{-}\mu\text{m}$  filter. The concentrations of alginate and BSA solutions are each  $0.1 \text{ g/L}$ , with a background electrolyte solution of  $10 \text{ mM NaCl}$ . Potentiometric titration was performed from pH 3.0 to 10.0 using  $0.10 \text{ M NaOH}$  in a carbonate-free  $\text{N}_2$  atmosphere at  $23 \pm 0.5^\circ \text{C}$ . Blank tests were performed with foulant-free electrolyte solution prior to each sample titration.

foulants, (which affect intermolecular adhesion and subsequent foulant deposition on the fouled membrane). To gain insight into the charge characteristics of the wastewater effluent, the acidity of wastewater effluent was determined by potentiometric titration from pH 3.0 to pH 10.0 (Fig. 1). The acidity profiles of alginate and BSA are also included for comparison purposes.

The increase in acidity of the wastewater effluent from pH 3.0 to 8.0 is attributed to the deprotonation of the carboxylic functional groups [27]. The increase in acidity from pH 8.0 to 10.0 was relatively more significant, and is attributed to the presence of phenolic functional groups [27]. Thus, unlike specific organic foulants, such as alginate or BSA, the wastewater effluent is made up of a complex mixture of organic foulants with varying charge characteristics. Nonetheless, the charged functional groups of the wastewater effluent in the pH range indicated in Table 1 are predominantly the carboxylic moieties.

#### 3.2. Fouling behavior with wastewater effluent

A typical profile of the permeate flux with time is shown in Fig. 2, together with representative SEM images of the virgin membranes (before fouling run), membranes that had been fouled by wastewater effluent (at the end the fouling run), and fouled membranes subsequently cleaned with  $2 \text{ mM EDTA}$  (after chemical cleaning). The SEM image of the virgin membrane indicates a pristine polyamide active layer that is free of foulants. The initial flux data (0–1 h) represent the permeate flux of the virgin membrane with DI water. After an hour of baseline run, the pump was stopped and DI water was decanted. After adding wastewater effluent to the feed reservoir (Step 1), the pump was restarted. The permeate flux dropped immediately due to the immediate impact of the feed osmotic pressure. During the fouling stage, the flux decreased almost constantly with time until the fouling run ended after 17 h. The SEM image of the fouled membrane shows a complete coverage of the active layer by deposited foulants. Cleaning of the fouled membrane was performed by adding the cleaning agent solution to the feed reservoir (Step 2). At the end of the cleaning time (15 min), the cleaning agent solution in the feed reservoir was emptied. To determine the efficiency of the cleaning agent, the RO membrane was subjected to a second baseline run by filling the reservoir with DI water and running it at the same operating pressure as that in the earlier baseline run (Step 3). Cleaning efficiency is defined as the ratio of the DI water flux after Step 3 to the initial DI water



**Fig. 2.** Representative permeate flux profile and SEM micrographs of the surface of the RO membrane during the fouling and cleaning experiments. The initial constant permeate flux (Step 1) is the first baseline performance with DI water, and the permeate flux at the end of the run (Step 3) is the second baseline performance with DI water after cleaning of the fouled membrane was performed. The cleaning efficiency is determined from the two baseline performances, by taking the ratio of permeate water fluxes in Step 3 to Step 1 (multiplied by 100). Here, the cleaning agent solution is 2 mM EDTA (pH 11) and the cleaning efficiency is determined as 79%. Initial permeate flux during fouling =  $83 \text{ L m}^{-2} \text{ h}^{-1}$  ( $23 \mu\text{m s}$  or  $49 \text{ gal ft}^{-2} \text{ day}$ ), crossflow velocity =  $8.6 \text{ cm/s}$ , operating pressure =  $20.68\text{--}24.13 \text{ bar}$  ( $300\text{--}350 \text{ psi}$ ), and temperature =  $21.0 \pm 0.5 \text{ }^\circ\text{C}$ .

flux at the beginning of the experiment. The SEM image of the cleaned membrane indicates a significant reduction in the amount of foulant deposited on the membrane surface, compared to the fouled membrane.

### 3.3. Membrane cleaning efficiency

To look into the optimization of cleaning by cleaning agents, the effects of single, dual, and combined chemical cleaning on membranes fouled with wastewater effluent were investigated. The cleaning agents used were NaOH (pH 11), 500 mM NaCl, 2 mM EDTA, and 10 mM SDS. NaCl has been proven to be effective in cleaning RO membranes fouled with hydrophilic organic matter such as alginate [15], while EDTA and SDS have been used more extensively in our research and proven to be effective in cleaning alginate-fouled membranes [24] and membranes fouled by mixtures of various organic foulants [11].

Fig. 3 presents a summary of the cleaning efficiencies measured in this study for all the agent combinations. Similar results, within experimental variation, were found for duplicate experiments carried out for selected fouling and cleaning runs (data not shown), indicating reproducibility of the data. Columns and rows refer to the first and second cleaning agent, respectively, used in dual-stage cleaning experiments of 7.5 min each. The shaded cells refer to one cleaning agent used for both steps, i.e., a single-stage cleaning experiment lasting 15 min. The cleaning efficiency of combined cleaning agents is reported in brackets. The last row represents the cleaning efficiency of single-stage cleanings carried out for 7.5 min.

Membrane fouling was largely irreversible, as cleaning the fouled membrane with DI water resulted in 32% cleaning efficiency. The cleaning efficiencies of NaOH (pH 11), 500 mM NaCl (unadjusted pH 6.4), 10 mM SDS (pH 7), and 2.0 mM EDTA (pH 7), were, respectively, 59, 65, 77, and 82% (shaded cells). In all cases, the cleaning efficiency of single agents was higher when cleaning time was increased from 7.5 (last row) to 15 min (shaded cells).

By comparing the cleaning efficiency of DI water on the membranes fouled by wastewater effluent (32%) with that of the membranes fouled by combined model organic foulants in previous studies (19%) [11], we can conclude that fouling by wastewater effluent has a larger potential for reversible fouling. On the other hand, the various cleaning agents had lower cleaning efficiencies on membranes fouled by wastewater effluent. This observation suggests that the foulants within the irreversible fouling layer on membrane surfaces fouled by wastewater effluent have higher intermolecular adhesion force among themselves, as compared to the foulants on membrane surfaces fouled by synthetic organic foulants [11].

		1 <sup>st</sup> -Stage Cleaning Agent			
		NaOH	NaCl	SDS	EDTA
2 <sup>nd</sup> -Stage Cleaning Agent	NaOH	59.2	91.2 (94.0)	78.2 (82.0)	92.8 (79.5)
	NaCl	78.9 (94.0)	65.2	70.1 (80.2)	67.8 (81.6)
	SDS	91.1 (82.0)	65.6 (80.2)	77.4	54.4 (74.0)
	EDTA	78.9 (79.5)	91.6 (81.6)	65.5 (74.0)	82.1
	7.5 min	44.2	58.0	57.0	73.6

**Fig. 3.** Efficiencies of chemical cleaning. The columns denote the cleaning agent employed in the first-stage, while the rows represent the cleaning agent used in the second-stage. The efficiencies of single-stage cleaning (i.e., the same chemical throughout the cleaning) are indicated by the shaded cells. The efficiencies of a single-stage cleaning using a mixture of two chemical agents are shown in parenthesis below the cleaning efficiency. All cleaning strategies, except for the last row, were performed for 15 min (7.5 min each for the 1st-stage and 2nd-stage). The last row represents the cleaning efficiency of a single-stage cleaning for 7.5 min.

In the following sections, results obtained using single agents will be compared to dual-stage cleaning experiments and significant trends will be highlighted. Practical insight can be gained by identifying the most functional combinations of cleaning agents, and drawing a connection to the cleaning mechanism of each respective agent. We note that in industrial spiral wound modules the use of spacers can enhance the mixing at the membrane-feed boundary layer, and thus increase the magnitude of the chemical cleaning efficiency of fouled membranes compared to our experiments [28,29]. Nonetheless, the general trends of cleaning efficiency discussed in this study are expected to be applicable to such spiral wound modules and other similar membrane systems. This knowledge can help to instruct efforts to maximize cleaning efficiency and, in turn, restore higher membrane water productivity.

### 3.4. Influence of alkaline solution on efficiency of dual-step cleaning

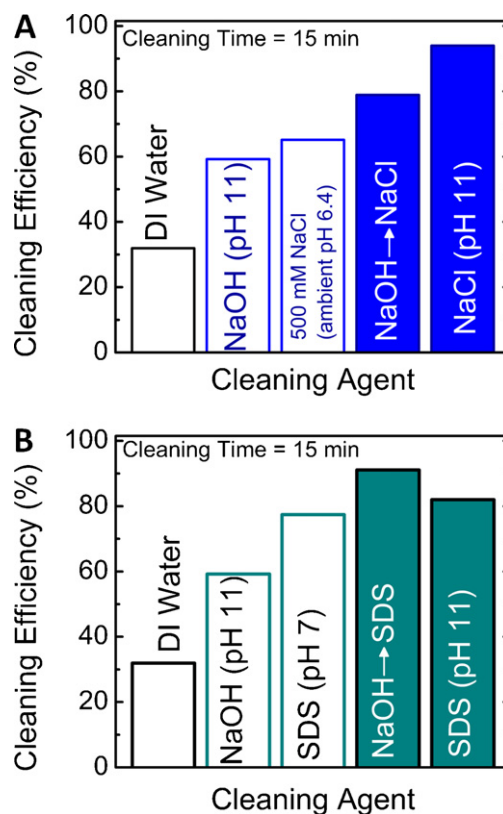
In our study, cleaning efficiencies were usually enhanced when the solution pH was increased during the first stage of a dual-stage cleaning experiment, or when NaOH was used in combination with other cleaning agents, compared to the respective single-stage cleaning protocols (Fig. 3). This observation is consistent with the findings reported in other studies [30–32]. At pH 11, most of the functional groups present in the wastewater effluent are deprotonated (Fig. 1) and, therefore, the foulants are negatively charged. Under these conditions, the repulsive interactions among the constituents of the fouling layer were previously observed to facilitate the release of the layer and the transport of foulants from the membrane surface to the bulk solution [11,24]. As NaOH removes foulant on the membrane surface by hydrolysis and solubilization, the fouling layer matrix becomes more porous and facilitates the transfer of other cleaning agents into the fouling layer matrix [11].

This synergy was apparent for the cleaning experiments using NaOH in conjunction with NaCl. Fig. 4A presents the cleaning efficiencies of NaOH and NaCl for different cleaning orders and combinations on membranes fouled by wastewater effluent. By cleaning with NaOH followed by NaCl (NaOH → NaCl) and, especially, by using a combination of the two agents (NaOH + NaCl, i.e., NaCl at pH 11), the transfer of NaCl from the bulk solution to the fouling layer was facilitated. The resultant cleaning efficiencies were significantly higher than cleaning efficiencies of NaOH or NaCl used as single cleaning agents for the same duration of 15 min.

The same synergistic effect was observed when NaOH was used in combination with SDS (Fig. 4B). The cleaning mechanism of SDS involves the formation of SDS micelles around the foulant and subsequent transport of the foulant from the membrane surface to the bulk solution [24,30]. SDS molecules do not interact specifically with Ca<sup>2+</sup> in the polysaccharide–calcium complex. Thus, SDS molecules are expected to have more difficulty in breaking down the structural integrity of the fouling layer matrix and removing the foulant when the SDS is added first as opposed to when it is added as a succeeding cleaning agent after NaOH. Our experiments confirmed that addition of NaOH as a preceding or combined cleaning agent helped to achieve higher cleaning efficiencies than those obtained by using SDS alone. NaOH facilitated SDS in breaking up the fouling layer matrix, forming micelles around the foulant, and transporting the foulants from the membrane surface to the bulk solution.

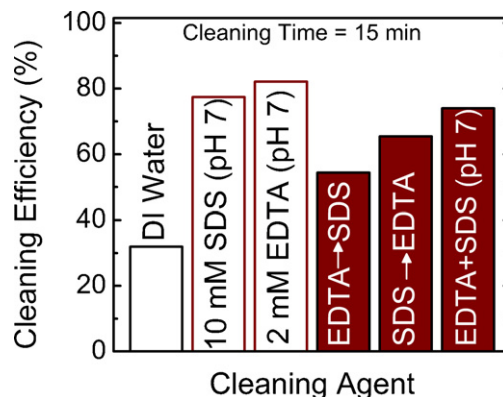
### 3.5. Comparing single- and dual-step cleaning at ambient pH

Combining two different cleaning agents was not necessarily advantageous, in particular when the cleaning mechanisms of the two agents were such that the agents could not intensify each other.

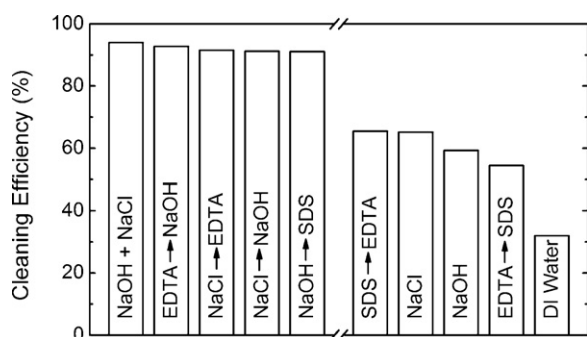


**Fig. 4.** Cleaning efficiencies of (A) NaOH and NaCl and (B) NaOH and SDS on membranes fouled by wastewater effluent, as single-step cleaning, dual-step cleaning, and combination of usage. Cleaning efficiency of DI water is also reported. Cleaning was performed at 0 psi (no permeation) and at a cross-flow velocity of 42.8 cm/s (5 times the velocity employed during fouling experiments). The temperature during cleaning was maintained at  $21.0 \pm 0.5$  °C.

Fig. 5 shows the efficiencies of EDTA and SDS for different cleaning orders and combinations on membranes fouled by wastewater effluent. No combination of the two agents resulted in cleaning efficiencies as high as using single-stage, 15-min cleaning protocols. It is hypothesized that having one of the two agents adsorbed onto the fouling layer after the first cleaning stage hinders the cleaning process of the agent used in the second stage. Also, the simultaneous presence of both SDS and EDTA in the cleaning mixture negatively impacted the efficiency of each respective agent.



**Fig. 5.** Cleaning efficiencies of SDS and EDTA on membranes fouled by wastewater effluent as single-step cleaning, dual-step cleaning, and combination of usage. Cleaning efficiency of DI water is also reported. Cleaning was performed at 0 psi (no permeation), and the cross-flow velocity was 42.8 cm/s (5 times the velocity employed during fouling experiments). The temperature during cleaning was maintained at  $21.0 \pm 0.5$  °C.



**Fig. 6.** Cleaning efficiencies of the top and bottom five performing strategies. All cleaning runs were performed for 15 min at 0 psi (no permeation) and at a cross-flow velocity of 42.8 cm/s (5 times the velocity employed during fouling experiments). The temperature during cleaning was maintained at  $21.0 \pm 0.5$  °C.

Another example showing higher efficacy of individual agents compared to their use in dual-stage cleaning protocols occurred with NaCl and SDS. Cleaning with NaCl followed by SDS yielded only a small increase in cleaning efficiency (65.6%) compared to single, 7.5-min (58.0%) and 15-min (65.2%) cleaning experiments with NaCl. When the cleaning agents were added in the opposite order (SDS → NaCl), a higher cleaning efficiency was observed (70.1%), although it was still lower than that observed when using only SDS for 15 min (77.4%). These experiments suggest that combining cleaning agents is only beneficial if their cleaning mechanisms are mutually compatible. On the other hand, cleaning hindrance can occur between different agents if the respective cleaning mechanisms interfere with each other.

### 3.6. Combined chemical agents yield high cleaning efficiency

The cleaning efficiencies of all strategies investigated in this study are summarized in Fig. 3. To compare the most and least effective methods, the five highest and five lowest cleaning efficiencies among the 15-min cleaning experiments were identified and presented in Fig. 6 in decreasing order of cleaning efficiency. The highest cleaning efficiency (94.0%) for the RO membrane fouled by wastewater effluent was achieved using a 500 mM NaCl solution adjusted to pH 11.0. On their own, NaOH and NaCl had the third and fourth lowest cleaning efficiency, respectively. Furthermore, when we look at the top five strategies, all of them involved dual or combined cleaning agents. Both of these findings indicate that, by strategically pairing two cleaning chemicals in dual or combined application, higher cleaning performance can be achieved when compared to the use of individual cleaning agents.

The emphasis here is on the appropriate pairing of chemicals such that their cleaning mechanisms complement each other. For example, the occurrence of NaOH in four of the five most effective strategies is a testament to the synergistic effect of elevated alkalinity on improving cleaning efficiency, as discussed earlier in Section 3.4. On the other hand, the mismatching of chemical agents, such as the pairing of EDTA with SDS (as discussed in Section 3.5 and illustrated in Fig. 5), would yield the opposite effect, resulting in a drastic decrease in cleaning performance.

## 4. Conclusion

This study presents the findings on the efficiency of various chemical cleaning strategies for an RO membrane fouled by a wastewater effluent. The use of single and paired chemicals and chemical combinations from four categories of cleaning agents that included alkaline solutions, metal chelating agents, surfactants, and salt solutions was investigated. The results indicate that

by strategically pairing chemical agents that have complementary cleaning mechanisms, a higher cleaning efficiency can be attained. In particular, NaOH demonstrates exceptional capacity to enhance overall cleaning performance when introduced with other chemical agents, possibly due to its ability to loosen the fouling layer. These conclusions have significant implications for mitigating fouling of RO membranes in wastewater reuse applications. Pairing of cleaning agents not covered in this study, such as acid rinsing [18], could potentially produce similar synergistic effects and yield even higher cleaning efficiencies. Prudent cleaning strategies, where two or more chemical agents are employed in sequence or in combination, can be formulated to achieve optimal performance recovery while minimizing overall chemical consumption.

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## References

- [1] D. Barker, S. Salvi, A. Langenhoff, D. Stuckey, Soluble microbial products in ABR treating low-strength wastewater, *Journal of Environmental Engineering-ASCE* 126 (2000) 239–249.
- [2] S. Lee, W.S. Ang, M. Elimelech, Fouling of reverse osmosis membranes by hydrophilic organic matter: implications for water reuse, *Desalination* 187 (2006) 313–321.
- [3] S. Hong, M. Elimelech, Chemical and physical aspects of natural organic matter (NOM) fouling of nanofiltration membranes, *Journal of Membrane Science* 132 (1997) 159–181.
- [4] C.R. Bartels, M. Wilf, K. Andes, J. Long, Design considerations for wastewater treatment by reverse osmosis, *Water Science and Technology* 51 (2005) 473–482.
- [5] S. Ebrahim, Cleaning and regeneration of membranes in desalination and waste-water applications—state-of-the-art, *Desalination* 96 (1994) 225–238.
- [6] R. Liikanen, J. Yli-Kuivila, R. Laukkanen, Efficiency of various chemical cleanings for nanofiltration membrane fouled by conventionally-treated surface water, *Journal of Membrane Science* 195 (2002) 265–276.
- [7] S.S. Madaeni, T. Mohamamdi, M.K. Moghadam, Chemical cleaning of reverse osmosis membranes, *Desalination* 134 (2001) 77–82.
- [8] T. Mohamamdi, S.S. Madaeni, M.K. Moghadam, Investigation of membrane fouling, *Desalination* 153 (2003) 155–160.
- [9] D.Q. Ren, Cleaning and regeneration of membranes, *Desalination* 62 (1987) 363–371.
- [10] J.J. Sathwani, J.M. Veza, Cleaning tests for seawater reverse osmosis membranes, *Desalination* 139 (2001) 177–182.
- [11] W.S. Ang, A. Tiraferri, K.L. Chen, M. Elimelech, Fouling and cleaning of RO membranes fouled by mixtures of organic foulants simulating wastewater effluent, *Journal of Membrane Science* 376 (2011) 196–206.
- [12] G. Tragardh, Membrane cleaning, *Desalination* 71 (1989) 325–335.
- [13] N.M. D'Souza, A.J. Mawson, Membrane cleaning in the dairy industry: a review, *Critical Reviews in Food Science and Nutrition* 45 (2005) 125–134.
- [14] M. Rosen, *Surfactant and Interfacial Phenomena*, 2nd ed., Wiley, New York, 1989.
- [15] S. Lee, M. Elimelech, Salt cleaning of organic-fouled reverse osmosis membranes, *Water Research* 41 (2007) 1134–1142.
- [16] A.M. Klupfel, F.H. Frimmel, Nanofiltration of river water—fouling, cleaning and micropollutant rejection, *Desalination* 250 (2010) 1005–1007.
- [17] P. Pihko, T. Rissa, R. Aksela, Enantiospecific synthesis of isomers of AES, a new environmentally friendly chelating agent, *Tetrahedron* 60 (2004) 10949–10954.
- [18] S.S. Madaeni, S. Samieirad, Chemical cleaning of reverse osmosis membrane fouled by wastewater, *Desalination* 257 (2010) 80–86.
- [19] M. Dubois, K. Gilles, J. Hamilton, P. Rebers, F. Smith, Colorimetric method for determination of sugars and related substances, *Analytical Chemistry* 28 (1956) 350–356.
- [20] P.C.C.T. Bulletin, Instructions for Modified Lowry Protein Assay Kit in, Pierce Biotechnology Inc., 2005.
- [21] G. Wang, S. Hsieh, Monitoring natural organic matter in water with scanning spectrophotometer, *Environment International* 26 (2001) 205–212.

- [22] B. Brugger, G. Erben, R. Sandhoff, F.T. Wieland, W.D. Lehmann, Quantitative analysis of biological membrane lipids at the low picomole level by nano-electrospray ionization tandem mass spectrometry, *Proceedings of the National Academy of Sciences of the United States of America* 94 (1997) 2339–2344.
- [23] W.S. Ang, M. Elimelech, Fatty acid fouling of reverse osmosis membranes: implications for wastewater reclamation, *Water Research* 42 (2008) 4393–4403.
- [24] W.S. Ang, S.Y. Lee, M. Elimelech, Chemical and physical aspects of cleaning of organic-fouled reverse osmosis membranes, *Journal of Membrane Science* 272 (2006) 198–210.
- [25] E. Vrijenhoek, S. Hong, M. Elimelech, Influence of membrane surface properties on initial rate of colloidal fouling of reverse osmosis and nanofiltration membranes, *Journal of Membrane Science* 188 (2001) 115–128.
- [26] C. Tang, Y. Kwon, J. Leckie, Probing the nano- and micro-scales of reverse osmosis membranes—a comprehensive characterization of physiochemical properties of uncoated and coated membranes by XPS, TEM, ATR-FTIR, and streaming potential measurements, *Journal of Membrane Science* 287 (2007) 146–156.
- [27] M. Collins, G. Amy, C. Steelink, Molecular weight distribution, carboxylic acidity, and humic substances content of aquatic organic matter: implications for removal during water treatment, *Environmental Science & Technology* 20 (1986) 1028–1032.
- [28] M.L. Johns, S.A. Creber, J.S. Vrouwenvelder, M.C.M. van Loosdrecht, Chemical cleaning of biofouling in reverse osmosis membranes evaluated using magnetic resonance imaging, *Journal of Membrane Science* 362 (2010) 202–210.
- [29] J.S. Vrouwenvelder, D.A.G. von der Schulenburg, J.C. Kruihof, M.L. Johns, M.C.M. van Loosdrecht, Biofouling of spiral-wound nanofiltration and reverse osmosis membranes: a feed spacer problem, *Water Research* 43 (2009) 583–594.
- [30] Q.L. Li, M. Elimelech, Organic fouling and chemical cleaning of nanofiltration membranes: measurements and mechanisms, *Environmental Science & Technology* 38 (2004) 4683–4693.
- [31] M. Beyer, B. Lohrengel, L.D. Nghiem, Membrane fouling and chemical cleaning in water recycling applications, *Desalination* 250 (2010) 977–981.
- [32] Y.H. Mo, J.H. Chen, W.C. Xue, X. Huang, Chemical cleaning of nanofiltration membrane filtrating the effluent from a membrane bioreactor, *Separation and Purification Technology* 75 (2010) 407–414.