

# Natural organic matter fouling and chemical cleaning of nanofiltration membranes

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**Abstract** Fouling and subsequent chemical cleaning are two important issues for sustainable operation of nanofiltration (NF) membranes in water quality control applications. Because fouling strongly depends on the feed water quality, especially the ionic composition, chemical cleaning solutions should be chosen to target the solution chemistry that is most responsible for the formation of a compact, high resistance fouling layer. In this study, the effect of solution chemistry on natural organic matter (NOM) fouling of two NF membranes with different surface properties was investigated. Compared to monovalent cations, divalent cations were found to greatly enhance NOM fouling by complexation. Moreover, calcium ions caused a much greater fouling rate than magnesium ions, presumably due to the intermolecular bridging formed among NOM molecules through the calcium ions. Various chemical cleaning solutions were evaluated for water flux recovery efficiency. Although both deionized water and dilute NaOH solution were found effective in cleaning membranes fouled in the absence of calcium ions, efficient chemical cleaning in presence of calcium was achieved only when the calcium ion bridging was eliminated. The cleaning efficiency was shown to be highly dependent on solution pH and the concentration of the chemical cleaning agent.

**Keywords** Chemical cleaning; divalent cations; natural organic matter; membrane fouling; nanofiltration; solution chemistry

## Introduction

One of the greatest obstacles for efficient application of NF membrane technology is the deterioration of membrane performance caused by fouling. Natural organic matter (NOM), which is ubiquitous in natural waters, is a major and most recalcitrant membrane foulant. Despite the vast efforts to reduce membrane fouling, fouling is still inevitable. Consequently, chemical cleaning is necessary to ensure sustainable operation of membrane systems (Ebrahim, 1994; Sadhwani and Veza, 2001; Mohammadi *et al.*, 2003; Madaeni *et al.*, 2001; Liikanen *et al.*, 2002; Ren, 1987). The purpose of chemical cleaning is to disintegrate the compact structure of the fouling layer so that foulant materials can be removed by hydraulic rinsing. Therefore, it is necessary to understand the mechanisms of NOM fouling, especially the chemical aspects, as well as the chemical reactions between the foulant and the cleaning chemicals.

In this study, bench-scale fouling/chemical cleaning experiments were performed under various solution conditions – total ionic strength, divalent cation concentration, and pH – to determine the effect of solution chemistry on organic fouling and chemical cleaning of NF membranes. Two MF membranes with different surface properties were compared. Factors relevant to membrane chemical cleaning such as cleaning solution pH and concentration were also tested. The experimental results were used to delineate the mechanisms of NOM fouling and chemical cleaning of organic-fouled NF membranes.

## Methods

### NF membranes

Two thin-film composite NF membranes, NF-270 and NF-90 (FilmTec Corp., Minneapolis, MN), were tested. Membrane surface roughness determined by surface imaging using a Multimode atomic force microscope (AFM) (Digital Instruments, Santa Barbara, CA) showed that NF-90 has a much rougher surface (mean roughness  $R_a = 69.9$  nm) than NF-270 ( $R_a = 5.5$  nm). Zeta potential measurements with an electrokinetic analyzer (BI-EKA, Brookhaven Instruments Corp., Holtsville, NY) (Childress and Elimelech, 1996; Elimelech *et al.*, 1994) found both membranes to be negatively charged under all chemical conditions investigated. Membrane samples were stored in deionized water at 5°C, with water replaced regularly. All membrane samples were rinsed thoroughly with deionized water prior to use.

### Model foulant

The model organic foulant used was Suwannee River humic acid (SRHA) standard (International Humic Substances Society, St. Paul, MN). Stock solution (1 g/L) was prepared by dissolving the SRHA powder as received in deionized water and adjusting the pH to 8.2 with NaOH to ensure complete dissolution. The stock solution was then stored in a sterilized glass bottle at 5°C.

### Chemical cleaning solutions

Deionized water (used as a baseline condition), NaOH (pH 11), sodium ethylenediaminetetraacetate (EDTA), and sodium dodecyl sulfate (SDS) (Fisher Scientific, Pittsburgh, PA) were used as the model chemical cleaning agents. These chemical agents are common ingredients in commercial chemical cleaning solutions for organic-fouled membranes (Trägårdh, 1989). Solutions were freshly prepared with deionized water right before the experiment.

### Solution chemistry

Bench-scale membrane fouling/chemical cleaning experiments were conducted at a total ionic strength ranging from 10 to 100 mM and with various ionic compositions. Feed solution pH was kept at 8.1 in all experiments by adding 1 mM NaHCO<sub>3</sub> and a small amount of NaOH. In some experiments, CaCl<sub>2</sub> or MgCl<sub>2</sub> (Fisher Scientific, Pittsburgh, PA) was added at a concentration of 1 mM to study the effect of divalent cations. The desired total ionic strength was obtained by adjusting the concentration of NaCl (Fisher Scientific, Pittsburgh, PA). A constant SRHA concentration (20 mg/L) was used in all experiments. The SRHA concentration was confirmed by measuring total organic carbon (TOC) of the feed solution with a TOC analyzer (Shimadzu Corporation, Kyoto, Japan) and comparing the measured value with the organic carbon content provided by the International Humic Substances Society. Chemical cleaning experiments with EDTA or SDS were conducted at ambient (unadjusted) pH or at pH 11. The EDTA concentration used was 1 mM while SDS concentrations tested were 1, 5, 10, and 35 mM.

### Bench-scale fouling and chemical cleaning experiments

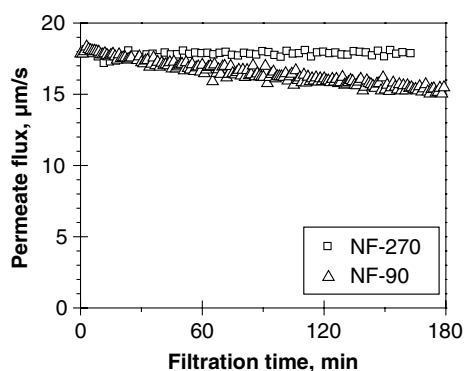
Fouling and chemical cleaning experiments were conducted in a bench-scale dead-end filtration system. The filtration unit comprises a 400 mL stainless steel stirred cell that houses a 76-mm diameter membrane sample. Through a 5-port valve, pressure can be applied directly to the stirred cell or to one of the two feed reservoirs holding the electrolyte solution and the feed foulant solution, respectively. Permeate flux was monitored by an analytical balance connected to a PC.

The fouling and chemical cleaning experimental protocol consists of 4 steps: compacting, conditioning, fouling, and chemical cleaning. First, the stirred cell was compacted with deionized water at 120 psi until the permeate flux stabilized. An electrolyte solution containing identical electrolyte concentrations to be used in the fouling run was then fed to the cell to condition the membrane and to establish a fouling-free baseline for 2 to 9 hours depending on the membrane tested. The applied pressure was adjusted to obtain the desired initial permeate flux for the fouling run. The initial permeate flux was kept constant in all experiments. After the membrane is equilibrated with the electrolyte solution, the organic foulant solution (SRHA) was filtered through the membrane at the same pressure to initiate fouling. Fouling continued until the permeate flux reached a predetermined final flux. During the conditioning and fouling stages, the mixing in the stirred cell was maintained at 225 rpm. Samples were taken from the permeate line at predetermined times and monitored for organic and electrolyte concentrations. Permeate TOC concentration was determined using a TOC analyzer (Shimadzu Corporation, Kyoto, Japan) and cation concentrations were measured by ICP-AES (Perkin Elmer, Boston, MA). The last step, chemical cleaning, involved the sequential addition of two batches of 250 mL cleaning solution and mixing at 470 rpm for 10 min for each batch. The filtration unit was rinsed thoroughly with deionized water after each cleaning procedure to remove the residual cleaning solution. Filtration was then resumed with the foulant-free electrolyte solution and the permeate flux was measured to assess the chemical cleaning efficiency. In cases where two cleaning solutions are likely to interfere with each other, separate fouling and chemical cleaning experiments were conducted.

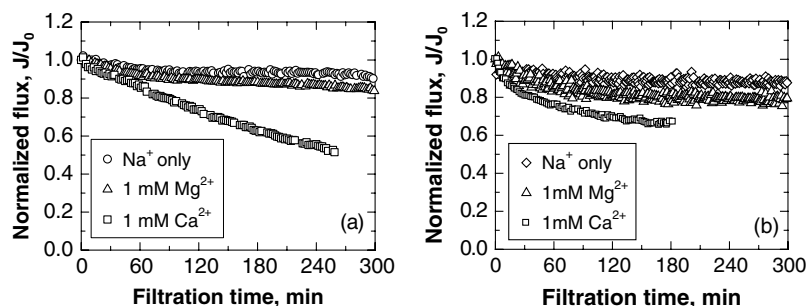
## Results and discussion

### Natural organic matter fouling of the NF membrane

During the filtration of the foulant solution, the observed flux decline is not caused solely by the SRHA. The increased salt concentration during dead-end filtration and the corresponding increase in osmotic pressure may also cause significant flux decline, which should be subtracted from the overall flux decline measured with the foulant solution. The permeate flux measured with the foulant-free electrolyte solution is shown in Figure 1 for both membranes. For the NF-270 membrane, the permeate flux with the electrolyte solution was very stable. Therefore, the flux decline observed during the fouling stage with the SRHA solution is attributable to accumulation of the organic foulant on the membrane surface. However, with the NF-90, the permeate flux with the foulant-free electrolyte solution



**Figure 1** Permeate water fluxes for the two studied membranes with foulant-free electrolyte solutions. Feed solution: 1 mM  $\text{NaHCO}_3$  and 9 mM  $\text{NaCl}$



**Figure 2** Effect of divalent cations on permeate flux decline of (a) NF-270 membrane and (b) NF-90 membrane. Feed solution: 20 mg/L SRHA, 1 mM  $\text{NaHCO}_3$ , divalent cations as indicated, and NaCl to adjust the total ionic strength to 10 mM. Initial permeate flux =  $18.5 \pm 0.3 \mu\text{m/s}$  and  $\text{pH} = 8.1$

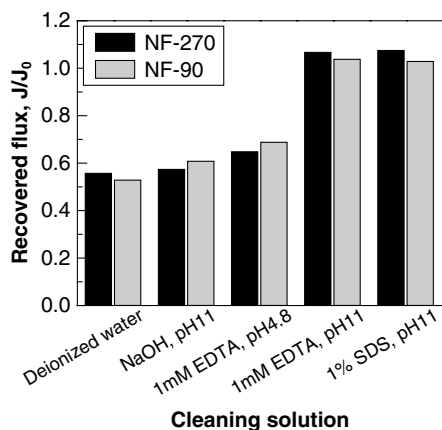
decreased by 17% in 3 hours and 31% in 9 hours. This osmotic-pressure related flux decline was subtracted from the total flux decline measured with the SRHA solution to obtain the flux reduction caused by SRHA fouling. The different behavior of the two membranes is attributed to the marked difference in their salt rejection characteristics. The NF-270 membrane has low rejection of  $\text{Na}^+$  and  $\text{Ca}^{2+}$  (44 and 53%, respectively), while the  $\text{Na}^+$  and  $\text{Ca}^{2+}$  rejections of NF-90 are 88% and 99%, respectively.

$\text{Na}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  were chosen as model cations because they are the major cations in surface waters. All fouling experiments were conducted with 20 mg/L SRHA at a total ionic strength of 10 mM, with zero to 1 mM  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$  in the feed solution to determine the effect of divalent cations on fouling. Figure 2a, b shows the normalized membrane flux as a function of time in the presence of different cations for the NF-270 and NF-90 membranes, respectively. As shown, with divalent cations present in solution, SRHA did not cause much flux decline: the membrane permeate flux decreased by approximately 10% over a period of 300 min. Compared to  $\text{Na}^+$ ,  $\text{Mg}^{2+}$  caused an increase in the membrane flux decline rate. The most dramatic fouling, however, was observed with solutions containing  $\text{Ca}^{2+}$ , particularly for the NF-270 membrane.

The increased flux decline rate in the presence of divalent cations is in agreement with previous findings (Hong and Elimelech, 1997; Seidel and Elimelech, 2002), which attributed the enhanced fouling by divalent cations to metal-humic complexation and therefore a more compact conformation of humic acid molecules. However, the substantial difference between the effects of  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  indicates that intramolecular metal-humic complexation is not the only mechanism since carboxylate- $\text{Ca}^{2+}$  and carboxylate- $\text{Mg}^{2+}$  complexation have been found to have comparable stability constants (Paney *et al.*, 2000). It is proposed that  $\text{Ca}^{2+}$  forms intermolecular bridging among humic acid molecules, which arranges humic acid molecules into a “cross-linked” structure in the fouling layer. As a result, the fouling layer formed in the presence of  $\text{Ca}^{2+}$  is very compact and highly resistant to mechanical and hydrodynamic forces. It was also observed that the initial flux decline rate of the NF-90 membrane was much higher than that of the NF-270. This may be attributed to the much higher surface roughness of NF-90 and the higher cation concentration near the membrane surface caused by its much higher salt rejection.

#### Chemical cleaning and flux recovery

Chemical cleaning of the fouled membranes was conducted using deionized water, NaOH, EDTA, and SDS following the procedure described in Materials and Methods. As shown in the previous section, membrane flux decline was fairly small in the absence of divalent

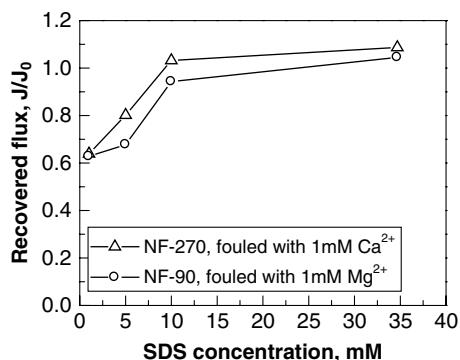


**Figure 3** Recovered membrane flux after cleaning with different cleaning chemicals. The feed solution contains 1 mM  $\text{NaHCO}_3$ , 1 mM  $\text{CaCl}_2$ , and NaCl with a total ionic strength of 10 mM. The pH is fixed at 8.1 and the applied pressures (or initial permeate fluxes) are the same as those used in the preceding fouling runs

cations. For the NF-270 membrane, even  $\text{Mg}^{2+}$  did not cause serious fouling. Fouling experiments under these conditions were stopped after filtering 1.6 L feed solution through the membrane, which took more than 300 min. For experiments where severe fouling occurred (i.e., NF-270 in the presence of  $\text{Ca}^{2+}$  and NF-90 with  $\text{Mg}^{2+}$  or  $\text{Ca}^{2+}$ ), the fouling runs were stopped when the permeate flux decreased to approximately 50% of the initial flux. After the membrane was cleaned, a foulant-free electrolyte solution, with identical ionic composition to the feed foulant solution, was filtered through the membrane to measure the recovered water flux. It was found that membrane samples fouled with SRHA in the absence of divalent cations (i.e., with  $\text{Na}^+$  only) could be easily cleaned by all the chemical cleaning solutions tested, and the flux was completely recovered after deionized water cleaning alone. For the NF-270 membrane fouled in the presence of  $\text{Mg}^{2+}$ , complete flux recovery was also obtained after deionized water cleaning. Therefore, cleaning results discussed below are for membranes fouled with feed solutions containing  $\text{Ca}^{2+}$ , and for the NF-90 membrane fouled in the presence of  $\text{Mg}^{2+}$ .

Figure 3 shows the membrane flux measured with electrolyte solution after the membrane is fouled in the presence of  $\text{Ca}^{2+}$  and then cleaned with various cleaning solutions. Deionized water and NaOH solution at pH 11 were both not effective in recovering the permeate water flux. In this case, the recovered flux was only 5 to 7% higher than the final flux after fouling. In contrast, 1 mM EDTA and 1% SDS at pH 11 were able to completely recover the initial clean membrane water flux.

Although the cleaning efficiency with SDS was found to be independent of cleaning solution pH (data not shown), the efficiency of EDTA cleaning is highly sensitive to pH. As shown in Figure 3, complete flux recovery was obtained after 1 mM EDTA cleaning at pH 11. However, the membrane flux after EDTA cleaning at unadjusted pH (pH 4.8) was only 66% and 70% of the clean membrane flux for the NF-270 and NF-90 membranes, respectively. The effect of pH on EDTA cleaning can be explained by the formation of Ca-EDTA or Mg-EDTA complexes. The membrane is cleaned by EDTA because EDTA is a strong chelating agent for  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . It can replace the humic acid molecules that were associated with  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$  in the fouling layer. Consequently, humic acid molecules lose the compact conformation resulting from intra-molecular complexation with  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$  as well as the “cross-link” structure of the fouling layer due to inter-molecular bridging



**Figure 4** Effect of SDS concentration on membrane flux recovery. Cleaning solution pH was fixed at 11

through  $\text{Ca}^{2+}$ . The number of deprotonated carboxylic groups of EDTA, the functional groups that associate with  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$ , is a function of pH. The  $\text{pK}_a$  values of EDTA are 2.72, 3.24, 6.68, and 11.12. At pH 4.8, only two of the four carboxylic groups are deprotonated, while at pH 11, almost all the carboxylic groups are deprotonated and available for  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$  complexation. Therefore, chemical cleaning is much more efficient at higher pH.

The cleaning efficiency of SDS was found to be a function of SDS concentration. Figure 4 shows that the recovered flux increases with increasing the SDS concentration used in cleaning for both membranes. This can be explained by the formation of local micelles of SDS at higher concentrations. SDS cleaning results with the NF-90 membrane fouled in the presence of  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$  are similar; therefore, only the results with  $\text{Mg}^{2+}$  are shown in Figure 4. The cleaning efficiencies of SDS are higher for the NF-270 membrane than for the NF-90 membrane, which can be explained by the higher roughness and salt rejection of the NF-90 membrane.

## Conclusions

The ionic composition of the membrane feed water plays an important role in natural organic matter fouling of nanofiltration membranes. Divalent cations, especially calcium ions, can significantly enhance natural organic matter fouling rate. Therefore, pretreatment preventing interactions between divalent cations and natural organic matter that lead to a compact organic fouling layer should be able to reduce the organic fouling rate and hence achieve higher membrane flux. Chemical cleaning methods should be chosen based on the solution chemistry that controls the membrane fouling mechanism. The pH of the cleaning solution and the concentration of the chemical cleaning agent should be carefully considered to obtain efficient flux recovery.

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