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Fouling and cleaning of RO membranes fouled by mixtures of organic foulants simulating wastewater effluent

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ABSTRACT

The fouling and subsequent cleaning of RO membranes fouled by a mixture of organic foulants simulating wastewater effluent has been systematically investigated. The organic foulants investigated included alginate, bovine serum albumin (BSA), Suwannee River natural organic matter, and octanoic acid, representing, respectively, polysaccharides, proteins, humic substances, and fatty acids, which are ubiquitous in effluent organic matter. After establishing the fouling behavior and mechanisms with a mixture of organic foulants in the presence and absence of calcium ions, our study focused on the cleaning mechanisms of RO membranes fouled by the mixture of organic foulants. The chemical cleaning agents used included an alkaline solution (NaOH), a metal chelating agent (EDTA), an anionic surfactant (SDS), and a concentrated salt solution (NaCl). Specifically, we examined the impact of cleaning agent type, cleaning solution pH, cleaning time, and fouling layer composition on membrane cleaning efficiency. Foulant–foulant adhesion forces measured under conditions simulating chemical cleaning of a membrane fouled by a mixture of the investigated organic foulants provided insights into the chemical cleaning mechanisms. It was shown that while alkaline solution (NaOH) alone is not effective in disrupting the complexes formed by the organic foulants with calcium, a higher solution pH can lead to effective cleaning if sufficient hydrodynamic shear (provided by crossflow) prevails. Surfactant (SDS), a strong chelating agent (EDTA), and salt solution (NaCl) were effective in cleaning RO membranes fouled by a mixture of foulants, especially if applied at high pH and for longer cleaning times. The observed cleaning efficiencies with the various cleaning agents were consistent with the related measurements of foulant–foulant intermolecular forces. Furthermore, we have shown that an optimal cleaning agent concentration can be derived from a plot presenting the percent reduction in the foulant–foulant adhesion force versus cleaning agent concentration.

1. Introduction

As demand for potable water increases worldwide, the paradigm for selecting water sources to meet this demand is transitioning from conventional sources, such as reservoirs and lakes, to less conventional sources, such as treated secondary wastewater effluent. In order to produce water of superior quality, the use of membranes in desalination and wastewater reclamation has become more widespread. Membrane fouling is a major impediment to the use of membrane technology for such applications, because fouling is inevitable. Despite research efforts to develop better anti-fouling membranes [1] and improved fouling-control strategies [2,3], membrane fouling still occurs over time. Thus, a long-term solution would be to remove the foulant deposited on the membrane via chemical cleaning.

To select the appropriate cleaning agents and adopt an effective chemical cleaning protocol for fouled membranes in wastewater reclamation, the implications of wastewater effluent characteristics on membrane fouling have to be well-understood. Wastewater effluent contains dissolved organic matter, commonly known as effluent organic matter (EfOM), which comprises polysaccharides, proteins, aminosugars, nucleic acids, humic and fulvic acids, organic acids, and cell components [2–4]. Organic fouling of the RO membranes by the EfOM can be extensive since EfOM is generally small enough to pass through the pores of pretreatment (MF or UF) membranes [4]. In particular, recent findings suggest that while biofouling can prevail on the tail-element of the membrane module, fouling of the lead-element exposed to reclaimed water is dominated by EfOM adsorption [5]. In addition, higher potential of fouling was observed for the higher molecular weight hydrophobic/aromatic fraction of the EfOM [6,7]. The presence of Ca^{2+} in the feed source for the RO membranes has been reported to form complexes with the constituents of EfOM, such as polysaccharides

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[8] and natural organic matter [9], and to significantly enhance membrane fouling. While our previous studies have addressed the fouling of RO membranes by individual organic foulant types, such as polysaccharides [10], proteins [11], and fatty acids [12], only recently have investigations reported on the effects of a combination or mixture of foulants on the fouling of RO membranes [13,14].

A variety of chemical cleaning agents are commonly used to clean RO membranes fouled by organic matter [15]. Alkaline solutions remove organic foulants on membranes by hydrolysis and solubilization of the fouling layer. Alkaline solutions also increase the solution pH, and, therefore, increase the negative charges and solubility of the organic foulant. Metal chelating agents remove divalent cations from the complexed organic molecules and weaken the structural integrity of the fouling layer matrix [16]. Surfactants solubilize macromolecules by forming micelles around them [17], thereby facilitating removal of the foulants from the membrane surface. In our earlier study on salt cleaning of organic matter-fouled RO membranes [18], we demonstrated that 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. In the presence of a salt solution, the fouling layer swells and becomes more porous. As a result, this would facilitate the diffusion of Na^+ into the fouling layer and breakup of Ca^{2+}–alginate bonds by ion exchange. Understanding the fouling layer characteristics and the interaction of chemical agents with foulants is therefore critical for the effective cleaning of organic matter-fouled RO membranes.

Atomic force microscopy (AFM) has been applied in membrane fouling/cleaning research to quantify intermolecular forces [10,19–21]. Our research has shown that foulant–foulant interactions could be determined by performing force measurements using a carboxylate-modified latex colloid probe in an AFM fluid cell [10,20]. The technique has been used to quantify the fouling behavior of a nanofiltration membrane fouled by humic acid and the cleaning efficiencies of EDTA and SDS [20], and has been extended to quantify RO membrane fouling by organic foulant in the form of alginate [10], BSA [11], and octanoic acid [12]. In this study, the AFM has also been employed as an alternative tool to indicate the optimal concentration of cleaning agent for cleaning fouled membranes. The original protocol [11,12] for using the AFM has been modified to investigate the intermolecular adhesion force between different foulants.

The objective of this study is to explore the mechanisms governing the fouling of RO membranes by mixtures of organic foulants simulating wastewater effluent, and the ensuing chemical cleaning of the fouled membranes by cleaning agents. To make this study relevant to wastewater reclamation, we systematically investigate the fouling of RO membranes by each individual organic foulant type (polysaccharides, proteins, humic acids, or fatty acids) and mixtures containing several types of organic foulants in the absence and presence of calcium ions. Cleaning experiments are performed with the fouled membranes using NaOH, EDTA, SDS, and NaCl as model alkaline solution, metal chelating agent, surfactant, and salt cleaning solution, respectively. The intermolecular adhesion forces between the different foulants and estimated aggregate sizes in foulant mixtures were used to explain the fouling mechanism of RO membranes and the cleaning behavior of a cleaning agent on the fouled membranes.

2. Materials and methods

2.1. Organic foulants

The model organic foulants chosen to represent the polysaccharides, proteins, humic acid, and fatty acids found in EfOM of wastewater effluent were sodium alginate (Sigma–Aldrich, St. Louis, MO), Suwannee River natural organic matter (SRNOM) (International Humic Substances Society, St. Paul, MN), bovine serum albumin (BSA) (Sigma–Aldrich, St. Louis, MO), and octanoic acid (OA) (Sigma–Aldrich, St. Louis, MO), respectively. According to 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 [22,23]. According to the manufacturer, the molecular weight of the BSA is about 66 kDa. BSA is reported to have an isoelectric point at pH 4.7 [24]. Octanoic acid (Sigma–Aldrich, St. Louis, MO) was selected to model fatty acids in EfOM because of its presence in food and solubility in water (saturation concentration of 4.7 mM at 20 °C) [12].

Sodium alginate, BSA, and SRNOM were received in powder form, and stock solutions (2 g/L) were prepared by dissolving each of the foulants in deionized (DI) water. DI water was supplied from a Milli-Q ultrapure water purification system (Millipore, Billerica, MA). 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-μm filter (Durapore, Millipore, Billerica, MA). The filtered stock solutions were stored in sterilized glass bottles at 4 °C. Octanoic acid was received in solution (≥98% concentration) and was stored at room temperature. To achieve the intended octanoic acid concentration during fouling, octanoic acid was dissolved separately for at least 8 h prior to fouling so that, at the initiation of fouling, octanoic acid could be introduced as a solution. A few hours before the initiation of fouling, the ionic strength of the stock solution was adjusted to the same concentration as that of the feed solution (10 mM) and the stock solution pH was elevated, as needed, from ambient pH of 3.9–9.0 by adding small amounts of 1 M NaOH.

2.2. Chemical cleaning agents

The chemical cleaning agents used were: NaOH (pH 11.0) as an alkaline solution, certified grade disodium ethylenediaminetetraacetate (Na_2–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 with no further purification. The stock chemical solutions were prepared fresh 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

The relatively well-characterized thin-film composite LFC-1 membrane (Hydranautics, Oceanside, CA) was used as a model RO membrane. The average hydraulic resistance was determined to be $9.16\ (\pm 0.11) \times 10^{13}\ \mathrm{m}^{-1}$ corresponding to a hydraulic permeability of $10.9\ (\pm 0.13) \times 10^{-11}\ \mathrm{m\,s^{-1}\,Pa^{-1}}$. 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 8.6 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 wastewater effluents, with an isoelectric point at about pH 4.6 [25]. The membrane has been reported to be coated with a neutral polyalcohol layer rich in –COH functional groups, which renders the surface less charged than the surfaces of other polyamide RO membranes without a coating layer [25,26].

2.4. Crossflow test unit

Fouling and the ensuing cleaning experiments were performed with a laboratory-scale crossflow test unit. The membrane test