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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).

Keywords: Membrane cleaning; Chemical cleaning; Organic fouling; RO membrane; Intermolecular adhesion force; Foulant–foulant interaction

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 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 μm 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 (Na_2-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 $(\pm 0.11) \times 10^{13}\,m^{-1}$. 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].