Effects of organic macromolecular conditioning on gypsum scaling of forward osmosis membranes

CrossMark

Yaolin Liu, Baoxia Mi *

Department of Civil and Environmental Engineering, University of Maryland, 1161 Glenn L. Martin Hall, College Park, MD 20742, USA

ARTICLE INFO

ABSTRACT

This study analyzed the membrane surface conditioning due to the adsorption of different organic macromolecules and investigated how such conditioning affected the gypsum scaling behavior in forward osmosis (FO) membrane processes. A commercially available cellulose acetate FO membrane was used as the base membrane. The membrane surface was conditioned respectively by representative organic macromolecules, namely bovine serum albumin (BSA), Aldrich humic acid (AHA), and sodium alginate, prior to gypsum scaling experiments. Results of direct observation and flux decline experiments showed that the chemistry of organic macromolecules greatly influenced the gypsum scaling of an FO membrane thus conditioned. Specifically, the AHA and alginate conditioning increased gypsum crystal sizes, shortened the crystal nucleation time, and accelerated the flux decline. In contrast, the BSA conditioning noticeably hindered the formation of gypsum crystals and thus slowed down the flux decline caused by gypsum scaling. Further investigation of the conditioning layer properties by quartz crystal microbalance with dissipation and the scaling layer morphologies by SEM suggested that the conditioning layers of AHA and alginate, each containing a high density of carboxylate functional groups along their long chain structures, exhibited strong adsorption of calcium ions as well as accelerated surface or heterogeneous crystallization; in comparison, the conditioning layer of BSA, which has a low carboxylate density and a three-dimensional structure, showed a low level of calcium ion adsorption and a slowdown in gypsum crystallization.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

As a promising alternative to reverse osmosis (RO) and nano-filtration membrane processes, the emerging forward osmosis (FO) is ideally poised at the water-energy nexus and thus has received a growing interest in a wide range of applications, such as seawater/brackish water desalination [1,2], landfill leachate treatment [3], and liquid food processing [4,5]. FO uses a natural osmotic pressure instead of conventional hydraulic pressure as the driving force for water permeation. The osmotic agent can then be reconcentrated by extracting pure water thereof. A salient advantage of the FO process is its high rejection (similar to that of RO) of a wide variety of water contaminants but with low hydraulic pressure requirement, thereby significantly decreasing energy consumption and reducing membrane fouling [3,6].

The FO technology to date, however, is still facing a number of outstanding challenges in improving membrane performance and advancing its application. One of such challenges is how to mitigate membrane fouling both effectively and efficiently. Membrane fouling is caused by the gradual accumulation of foreign substances (i.e., foulants) onto the surface and/or into the pores of a membrane, thereby degrading membrane performance (e.g., permeate flux and product water quality), shortening membrane life, and increasing system maintenance cost [7,8]. In terms of the specific type of foulants considered, membrane fouling can be generally categorized into biological fouling, colloidal/particulate fouling, inorganic scaling, and organic fouling.

Among the various types of foulants, organic macromolecules (e.g., natural organic matters or NOMs, proteins, polysaccharides) have raised the most concern not only because of their prevalence in all natural water sources (e.g., seawater, surface water, and groundwater) [9–12] but also due to their unique physicochemical characteristics (e.g., complex chemical formula, structure, functionality, and charge), which make the associated organic fouling mechanisms highly complex and thus very difficult to elucidate. Besides, it is generally believed that the adsorption of organic foulants onto the membrane surface produces the first conditioning layer, which greatly changes the membrane surface characteristics and hence further complicates the fouling behavior [13–15]. For example, it has been found that, when alginate and gypsum coexist, the flux decline in an FO membrane process becomes faster than that in the presence of individual foulants only; furthermore, the most severe flux decline occurs when alginate

* Corresponding author. Tel.: +1 301 405 1262; fax: +1 301 405 2585.
E-mail address: bmi@umd.edu (B. Mi).

is pre-coated on the membrane surface [16]. Although membrane cleaning can remove the adsorbed foulants and recover the membrane flux to various degrees [17,18], the conditioning of membrane surface by the accumulation of organic matter over time is almost unavoidable and may significantly change the membrane surface chemistry and subsequently affect the fouling behavior. Therefore, it is critical to investigate the membrane surface chemistry and understand the fouling behavior of the conditioned membranes in order to elucidate the underlying mechanisms and eventually develop useful strategies for fouling mitigation.

Although plenty of research has been devoted to assessing the effects of surface conditioning on the fouling of pressure-driven membrane processes, no study has been reported on this important topic for FO membrane processes [19–21]. The lack of cake layer compaction in the osmotically driven membrane processes may alter the effects of surface conditioning and hence the membrane fouling behavior. In particular, gypsum scaling is a very common problem in membrane processes for seawater/brackish water desalination due to the abundance of calcium and sulfate ions in natural waters [20–22]. Gypsum scaling usually leads to irreversible membrane flux decline because gypsum cannot be effectively removed by acid or chemical cleaning due to its insensitivity to pH. Research on gypsum scaling in the FO membrane process, however, is very limited [23] and has not addressed the effects of organic conditioning. Nevertheless, such effect was hinted in a recent study revealing that the presence of alginate could significantly worsen gypsum scaling due to the synergistic interaction between gypsum and organic foulants [16].

To answer the question of how the adsorbed organic layer on membrane surface affects the gypsum scaling, we investigated in the present study the role of surface conditioning by representative organic macromolecules in changing the membrane surface chemistry and hence affecting the gypsum scaling behavior in FO processes. The gypsum scaling and subsequent cleaning of the virgin and organically conditioned membranes were investigated and compared. We then employed a direct observation method to study the gypsum scaling kinetics. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) analyses of the scaling layers were conducted to identify how the characteristics of organic macromolecules may influence the gypsum scaling. A quartz crystal microbalance with dissipation (QCM-D) study was further performed to investigate the adsorption of calcium ions on each organically conditioned membrane surface.

2. Materials and methods

2.1. FO membranes

The FO membranes tested in the present study were provided by Hydration Technology Innovations (Albany, OR). The membrane is made of cellulose acetate (CA) and supported by an embedded polyester mesh to enhance its mechanical strength [3] (Fig. 1). The CA membrane has an asymmetric structure with a total thickness of approximately 50 μm based on the examining of SEM images [18]. The pure water permeability of the CA membrane tested in an RO mode was 9.7×10^{-13} m/(s Pa). More information on the CA membrane can be found in a previous study [16].

2.2. Organic and inorganic foulants

All the chemicals needed to prepare the fouling solutions were obtained from Sigma-Aldrich (St. Louis, MO) and used as received. Three organic macromolecules – bovine serum albumin (BSA), Aldrich humic acid (AHA), and sodium alginate – were selected as model organic foulants to represent protein, NOM, and extracellular polysaccharides, respectively, which are three common types
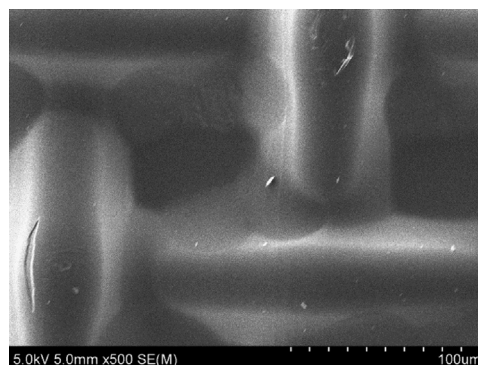

Fig. 1. An SEM image of the cellulose acetate membrane surface.

Table 1
Properties of three representative organic macromolecules.

	Molecular weight (kDa)	Surface functional groups	Carboxylic acidity (meq./g)
BSA	66.4	C=O, NH	1–1.5 [37]
AHA	20–50	COOH, C=O, NH, OH	3.3 [43]
Alginate	75–100	COOH	3–3.5 [37]

of organic macromolecules in natural waters. Properties of the three representative organic foulants are provided in Table 1.

The stock solutions of organic macromolecules (10 g/L) were prepared by dissolving solids in deionized (DI) water with continuous stirring at room temperature for over 24 h. Then, the stock solutions of alginate and BSA were each transferred to sterilized glass bottles and stored at 4 °C, while the AHA stock solution was further purified to decrease the ash content in solution following a purification procedure [17,24]. The stock solutions of $CaCl_2$ (3.5 M) and Na_2SO_4 (1 M) were prepared for the gypsum ($CaSO_4 \cdot 2H_2O$) scaling experiments.

Prior to each scaling experiment, the stock solutions were diluted to desired concentrations for use as the feed solutions in the baseline, organic conditioning, and gypsum scaling experiments, respectively. Chemical composition of the feed solutions is listed in Table 2. Note that the product of Ca^{2+} and SO_4^{2-} concentrations in the feed solution was made slightly higher (with a saturation index of 1.3) than the solubility product of gypsum so that scaling can take place at a reasonable speed [23].

2.3. Experimental setup

The scaling and cleaning experiments were conducted in parallel using two bench-scale membrane cross-flow systems (an FO system and an FO direct observation system), which were previously used for an FO fouling study [25]. Basically, the FO system comprises a custom-built cross-flow membrane cell with identically dimensioned rectangular channels (77 mm long, 26 mm wide, and 3 mm deep) on both sides of the membrane. Two variable speed gear pumps were used to generate cross flows that formed separate closed loops for feed and draw solutions, respectively. The draw solution tank was placed on a digital scale (Denver Instruments, Denver, CO) so that weight change could be monitored by a computer to record the permeate flux. The feed solution tank was placed on a stir plate so that the feed solution could be continuously stirred to avoid foulant precipitation. A constant temperature of 20 ± 1 °C was maintained for both feed and draw solutions using a water bath (Neslab, Newington, NH). The FO direct observation system has a similar setup as the FO system, except that a built-in glass window was created in the membrane cell to allow the