Silica scaling and scaling control in pressure retarded osmosis processes

Yi-Ning Wang[a], Xuesong Li[a], Rong Wang[a,b,*]

[a] Singapore Membrane Technology Centre, Nanyang Environmental and Water Research Institute, 637141 Singapore
[b] School of Civil and Environmental Engineering, Nanyang Technological University, 639798 Singapore

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ABSTRACT

The performance of pressure retarded osmosis (PRO) processes is significantly limited by membrane fouling. This study systematically investigated PRO scaling by silica, which is one of the most common salts causing membrane scaling. In particular, the effect of silica concentration, the initial water flux, the chemistry of feed solution (FS) /draw solution (DS), and the type of membrane were studied in the PRO mode of operation. It has been observed that a low silica concentration (e.g., 10 mg/L SiO_2) could even cause membrane scaling during a PRO process. The rate and extent of the scaling was mainly governed by the internal concentration of silica in the membrane support layer and the solution chemistry of the FS/DS. The results suggested that the scaling could be mitigated by decreasing the internal concentration through the reduction of bulk silica concentration, the optimization of operating water flux, and the decrease in membrane structural parameter. The structural parameter seems to play a dominant role in PRO scaling by silica than the membrane materials and other physico-chemical properties. In addition, silica scaling can be controlled by lowering the pH of the FS and/or DS. For the first time, it has been demonstrated that utilizing an acidic DS was highly effective in controlling PRO scaling, which can be attributed to the low local pH in the membrane support layer as a result of the internal concentration polarization (ICP) of the reversely diffused H^+. This method opens a new dimension for PRO scaling/fouling control.

1. Introduction

The energy released from the mixing of freshwater with saltwater is a potential source of renewable and sustainable energy, which can be harvested by pressure retarded osmosis (PRO) process [1–5]. In a PRO operation, the active layer of a semi-permeable membrane is preferentially oriented towards the concentrated draw solution (DS)/saltwater and the support layer is facing the feed solution (FS)/freshwater, in order to withstand the high pressure from the DS side and as well as to gain higher osmotic power (as a result of less internal concentration polarization (ICP)) [6–9]. However, membrane in this orientation generally suffers from more severe fouling [7,9–18], particularly inorganic scaling that is mainly dependent on salt solubility [10,18,19]. To date, most of the PRO scaling investigations focused on gypsum scaling/phosphate scaling [13,20–22] or a combined fouling by organic and inorganic foulants [13,23]. There is limited number of studies on PRO scaling by silica [23], although silica scaling is commonly occurred in membrane filtration processes.

Silica (SiO_2) is ubiquitous and abundant in natural waters and its concentration is normally in the range of 20–60 mg/L [24]. The solubility of silica is about 120–150 mg/L at pH below 8 and temperature of 25 °C [24,25]. The dissolved silica normally exists as monosilicic acid

(H_4SiO_4) at near neutral pH [24,26]. Extensive research shows that silica scaling in reverse osmosis (RO) typically occurs through the deposition on membrane surface, polymerization and the accumulation of colloidal particles [27], which subsequently results in the partial block of water passage through the membrane. Nevertheless, the mechanisms and chemistry involved in silica scaling are complex and the prediction of silica scale depends on a number of factors, including silica concentration, background matrix and many other physical and chemical variables [27,28]. Similar to RO, the presence of silica in feed water also causes scaling problems in forward osmosis (FO) where the membrane active layer is facing the feed solution (AL-FS) [24,29]. One prior study reported almost identical flux decline rates by comparing silica scaling in FO and RO modes [24].

Different from RO and FO (generally in AL-FS orientation) where membrane scaling typically occurs on the active surface, the majority of scale formation in PRO process/mode (in AL-DS orientation) occurs in the porous support layer [10,11,13,20]. In a PRO process, the concentrative ICP of foulant/scale precursors could result in a significantly higher concentration in the support layer as compared with that in the bulk FS, implying that PRO scaling can occur in spite of low feed concentration (i.e., AL-DS operation is more vulnerable to scaling). Prior study showed that silica was one of the scalants that contributed

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to PRO fouling when a RO retentate received from a wastewater treatment plant was used as the feed stream [23]. Nevertheless, systematic investigation on the factors influencing PRO scaling by silica is lacking in the existing literature. Among the questions to be answered, it is of particular interest that whether a cellulose triacetate (CTA) FO/PRO membrane is more prone to silica scaling by comparing with its counterpart thin film composite (TFC) polyamide FO/PRO membrane, although previous research speculated that the hydroxyl group owned by the CTA membrane may lead to a rapid silica polymerization [23,29]. On the other hand, the unique concentrative ICP in PRO may offer new silica scaling control strategies. The solutes in the DS could reversely diffuse to the FS as a result of concentration gradient, which could alter the environment inside the porous support layer [20,30,31], in addition to the FS solution chemistry [32,33]. Hence, it is worth understanding if a DS with tailored solution chemistry (containing favorable ions/solutes) has potential to mitigate PRO scaling by silica. The discussion on the positive effect of reverse solute diffusion is rarely found in the existing literature [34].

The objective of this study is to systematically investigate the factors affecting silica scaling during PRO processes and to provide relevant scaling control methods. In specific, the effect of silica concentration, initial water flux (driving force), membrane type, and the chemistry of FS and DS will be studied.

2. Materials and methods

2.1. Chemicals and FO membranes

Analytical grade chemicals were used as received without further purification. Ultrapure water with a resistivity of 18.2 MΩ cm (Millipore Integral 10 water purification system) was used to prepare all working solutions. Soluble salt sodium silicate (10.6% Na_2O and 26.5% SiO_2, 338443-1L, Sigma-Aldrich) was spiked in the feed solutions (FSs) to yield a silica concentration of 10.7, 42.9, or 85.7 mg/L (corresponding to 5, 20, 40 mg/L of silicon). Sodium chloride (NaCl) was used to prepare draw solutions (DSs) and as well as to adjust the ionic strength of the FSs. Magnesium chloride ($MgCl_2$) or calcium chloride ($CaCl_2$) were added to certain FSs to achieve a divalent ion concentration of 1 mM. The solution pH was adjusted by the addition of hydrochloric acid (HCl)/sodium hydroxide (NaOH).

A commercial cellulose triactetate (CTA) FO membrane was received from Hydration Technology Innovations LLC (HTI, Albany, OR) and was employed for most of the experiments in this study. An in-house fabricated polyamide-based thin film composite (TFC) FO membrane was used for comparison to understand the effect of membrane type on silica scaling. The fabrication of this TFC membrane can be found in our previous study (named "TFC1" in ref. [35]). In brief, it had a polysulfone substrate prepared via phase inversion and a rejection layer formed via interfacial polymerization between m-phenylenediamine (MPD) and trimesoyl chloride (TMC). Both the CTA and TFC membranes are flat-sheet membranes. Upon being received or synthesized, they were cut into small coupons, soaked in ultrapure water and stored in 4 °C fridge prior to experiments.

2.2. A, B and S value determination

The membrane water permeability and NaCl rejection were measured using a lab-scale cross-flow filtration RO setup [10]. Pure water flux (J) was measured under an applied pressure (ΔP) of 1–5 bar with ultrapure water. NaCl rejection (R) was obtained by filtering a 10 mM NaCl feed solution (10 L) at a cross-flow velocity of 20 cm/s. The water permeability (A) and NaCl permeability (B) were determined from the following equations.

$$A = \frac{J}{\Delta P} \tag{1}$$

$$B = J\left(\frac{1}{R} - 1\right) \tag{2}$$

The FO water flux was measured using an FO bench-scale crossflow filtration system [10] and its schematic is shown in Appendix A. In brief, a membrane coupon with an active area of 42 cm^2 was housed in an FO membrane cell (CF042, Sterlitech). Diamond-patterned spacers (65 mil (1.651 mm) spacer, GE Osmonics) were placed in both the FS and DS fluid channels. The water flux (J_v) was measured using 10 mM NaCl FS and 0.5–3 M NaCl DS in both the FO mode (active-layer-facing-FS (AL-FS)) and PRO mode (active-layer-facing-DS (AL-DS)). The structural parameter (S) of the membrane support layer was calculated by plugging A and B values to the following equations which describe the FO water flux (J_v) being affected by internal concentration polarization (ICP) [10,36].

$$\text{AL−DS: } J_v = \left(\frac{1}{k_F} + \frac{1}{k_m} + \frac{1}{k_D}\right)^{-1} \ln \frac{A\pi_D + B - J_v \exp(J_v/k_D)}{A\pi_F + B} \tag{3}$$

$$\text{AL−FS: } J_v = \left(\frac{1}{k_F} + \frac{1}{k_m} + \frac{1}{k_D}\right)^{-1} \ln \frac{A\pi_D + B}{A\pi_F + B + J_v \exp(-J_v/k_F)} \tag{4}$$

where π_D and π_F are the osmotic pressures of the DS and FS, respectively; k_F, k_D and $k_m \equiv D/S$ are the mass transfer coefficient of the draw solution stream, feed solution stream and in the membrane support layer. D is the solute diffusion coefficient (NaCl diffusion coefficient of 1.6×10^{-9} m^2/s was used for the calculation [10]). The calculation of mass transfer coefficient (k_F and k_D) can be found elsewhere [37] and the equations are provided in Appendix B.

2.3. Scaling experiment in PRO mode

To exclude the influences due to membrane damage/deformation under high hydraulic pressure, all the PRO scaling tests were performed at zero hydraulic pressure. This condition also corresponds to the highest water flux for a fixed DS concentration, and generally represents the case of the greatest fouling potential [20,38]. Membrane scaling experiments were conducted using the same bench-scale crossflow filtration system as the one used for S value determination. Three liters of FS and two liters of DS were circulated at the two sides of the membrane using two variable speed peristaltic pumps (Cole-Parmer, Vernon Hills, IL) to generate cross-flows at ~9 cm/s in both fluid channels. The FS containing silica was prepared prior to each run in order to provide enough time for pH adjustment. The weight change of the FS was recorded using a digital balance (Mettler Toledo, Switzerland) interfaced with a data logging system for water flux acquisition. The water in the FS tank was replenished and the NaCl was dosed to the DS at a time interval of 20–30 min, to ensure that the weight variation of the FS and the concentration variation of the DS were within 3%. Meanwhile, the solution pH was well maintained by the addition of NaOH/HCl during each run. The solution pH and conductivity were monitored using a pH meter (Mettler Toledo, Switzerland) and a conductivity meter (Thermo Scientific, USA), respectively. All experiments were conducted at room temperature (23 ± 1 °C). A new membrane coupon was used for each scaling experiment. The key experiments were repeated for two times to ensure the repeatability of the results.

2.4. FESEM characterization

Both the clean membrane and the membrane after scaling tests were characterized using a field emission scanning electron microscopy (FESEM, JSM-7600F, JEOL, Japan). All membrane samples were gently rinsed with ultrapure water and dried in vacuum at room temperature for 24 h. For the cross section preparation, the CTA membrane was cut with a razor blade (due to the embedded woven mesh that cannot be fractured by hand) while the TFC membrane was fractured using hand after being frozen in liquid nitrogen. The dried samples were sputter