Desalination 392 (2016) 85–90

Contents lists available at ScienceDirect

Desalination

journal homepage: www.elsevier.com/locate/desal

Spacer-induced forward osmosis membrane integrity loss during gypsum scaling

Ming Xie [a,*], Chuyang Y. Tang [b], Stephen R. Gray [a]

[a] Institute for Sustainability and Innovation, College of Engineering and Science, Victoria University, PO Box 14428, Melbourne, Victoria 8001, Australia
[b] Department of Civil Engineering, The University of Hong Kong, Hong Kong

HIGHLIGHTS

- FO membrane integrity was compromised during gypsum scaling with spacer.
- Gypsum preferentially accumulated adjacent to the spacer.
- Measuring membrane transport parameters cannot detect FO membrane integrity loss.
- Fluorescent Rhodamine challenge test revealed decrease of log removal value to 3.5.
- Latex nanoparticle challenge test show wider and larger particle size in the draw.

ARTICLE INFO

Article history:
Received 17 December 2015
Received in revised form 7 April 2016
Accepted 15 April 2016
Available online 30 April 2016

Keywords:
Forward osmosis
Gypsum scaling
Membrane integrity
Fluorescent Rhodamine WT tracer
Amine-modified latex nanoparticle

ABSTRACT

We demonstrated forward osmosis (FO) membrane integrity loss during gypsum scaling with the presence of membrane spacer. The gypsum scalant had preferential accumulation adjacent to membrane spacer where the needle-shape gypsum potentially compromised polyamide thin-film composite FO membrane integrity. However, the loss of FO membrane integrity cannot be sensitively detected by *in situ* measurements of membrane water and salt (NaCl) permeability coefficients. We, for the first time, employed membrane integrity challenge tests to reveal the impaired FO membrane integrity by fluorescent Rhodamine WT tracer and amine-modified latex nanoparticles, respectively. Challenge tests using Rhodamine WT tracer showed that membrane log removal value decreased to 3.5 after three scaling–cleaning cycles, which corresponded to a pinhole size of 0.06 μm^2 on the FO membrane. This result was further corroborated by challenge test using latex nanoparticle where the particle size distribution in the permeate became wider and the average particle size increased over the three scaling–cleaning cycles. Both challenge tests were sensitive enough to identify impaired FO membrane integrity. Results reported here have significant implications for achieving better membrane spacer and module design, as well as demanding periodical monitoring of FO membrane integrity in water reuse.

1. Introduction

Membrane technologies respond to the global challenge for adequate and safe water [1,2]. Forward osmosis (FO), an emerging osmosis-driven membrane process, has the potential to advance seawater desalination and wastewater reuse [3]. Because of the low fouling propensity and high fouling reversibility with simple membrane flushing, FO has potential applications in treatment of a variety of high fouling potential source waters [4–7], including desalination of high salinity brines from shale gas produced water [8–11], municipal wastewater reclamation [12–16], and valuable resource recovery [17–19].

These challenging waste streams with complex foulants stress membrane mechanical properties and subsequent membrane performance. For instance, recent studies reported minor changes in FO membrane properties and performance after exposure to oil and gas wastewaters [20]. More importantly, damage to FO membrane active layer was visualized after gypsum scaling with the presence of membrane spacers [21]. These prior findings warrant a close examination of FO membrane integrity during processing of wastewaters with high fouling propensity.

Varying techniques were proposed to examine reverse osmosis (RO) membrane integrity, such as fluorescent spectroscopy [22–24], Rutherford backscattering spectrometry [25,26], and flow cytometry [27]. For instance, fluorescence signatures, such as peak C as $\lambda_{ex/em}$ = 300/400 nm, were proposed to monitor RO membrane integrity due to relatively low noise and variability of these fluorescent organic molecules [22]. For biological contaminants, such as virus, flow cytometry demonstrated good sensitivity and reproducibility for quantifying virus reduction rate along the treatment processes, which provide direct evidence for RO membrane integrity monitoring [27].

* Corresponding author.
E-mail address: ming.xie@vu.edu.au (M. Xie).

http://dx.doi.org/10.1016/j.desal.2016.04.017
0011-9164/

These techniques aim to ensure that RO membrane achieves high log removal value (LRV) for virus removal so as to address public health protection concerns, as well as regulatory requirements. However, to date, there is no existing study that examines membrane integrity of FO process, particularly in treatment of high fouling wastewaters. Such fundamental understanding can lead to the development of monitoring techniques for FO membrane integrity, which will significantly increase the efficiency and robustness of FO process.

In this study, we demonstrate that FO membrane integrity was compromised during gypsum scaling. Membrane gypsum scaling was visualized by a real-time observation system. Membrane integrity of three scaling–cleaning cycles was examined using challenge tests comprising sensitive fluorescent Rhodamine WT tracer and amine-modified latex nanoparticles.

2. Materials and methods

2.1. Real-time FO observation system

A transparent, acrylic FO membrane cell coupled with microscopic observation enabled real-time observation of gypsum scaling (Fig. S1, Supplementary data). Specifically, a membrane coupon with an effective area of 20.2 cm^2 was placed in a transparent FO membrane cell. A crossflow rate of 1 L/min (corresponding to crossflow velocity of 9 cm/s) was maintained for both the feed and draw solutions using micro gear pumps. The FO water flux was determined by measuring the weight changes of the feed solution at specific time intervals with a precision balance connected to a computer and a data logging system.

Real-time membrane surface images of 2048 × 1536 pixel resolution were recorded using a high resolution digital camera and an optical microscope (20× magnification). To minimize the interference from air bubbles, the feed and draw solutions were degassed prior to circulation in the FO setup. Through the combination of optical magnification along with a unique combination of bright and low angle dark field illumination, provided by ultra-bright fiber optic illuminator, digital image capture and analysis, occurrence and subtle changes of gypsum crystal could be effectively monitored.

2.2. Membrane and spacer

A polyamide thin-film composite (TFC) forward osmosis (FO) membrane was employed in this study. The TFC membrane was made of a thin selective polyamide active layer on top of a porous polysulfone support layer [28].

Spacers are essential to an FO membrane module to maintain flow channel and provide hydrodynamic conditions. Diamond-patterned, polypropylene spacers (65 mil (1.651 mm) spacer, GE Osmonics), which were also the current standard RO membrane spacer, were placed in both the feed and draw channels during the experiments.

2.3. Experimental protocol for gypsum scaling and cleaning

A total of three gypsum scaling–cleaning cycles were conducted. The protocol for gypsum scaling experiments comprised the following steps. First, a new membrane coupon, with the active layer facing the feed solution, was placed in the membrane cell before each experiment and stabilized to obtain a constant flux. The membrane in the FO mode (i.e., membrane active layer faces feed solution) was stabilized with deionized water feed and 2 M NaCl draw. Next, the gypsum scaling experiment was performed for about 24 h to obtain approximately 1400 mL cumulative permeate volume at the conclusion of each experiment. The gypsum scaling solution was comprised of 35 mM $CaCl_2$, 20 mM Na_2SO_4, and 19 mM NaCl, with a gypsum ($CaSO_4 \cdot 2H_2O$) saturation index (SI) of 1.3. Other experimental conditions were: crossflow velocity of 9 cm/s, ambient pH (pH 6.8), and temperature of 25.0 ± 0.1 °C. Water flux was continuously monitored throughout the fouling experiments by a data logger. A baseline experiment (i.e., feed without $CaCl_2$ and Na_2SO_4) was also carried out to correct the flux decline due to the continuous concentration of the feed solution and dilution of the draw solution, as described in our previous publication [7]. The real-time monitoring system captured images of the FO membrane surface every 30 min during the scaling experiment to identify the occurrence and development of gypsum crystals on FO membrane surface during scaling experiment.

Membrane cleaning was performed immediately after the FO scaling experiments. Deionized water flushing was carried out in both feed and draw flow channels at 18 cm/s for 30 min. The membrane water flux after cleaning was measured using deionized water feed and 2 M NaCl draw.

Key membrane transport parameters (water permeability coefficient, A and salt (NaCl) permeability coefficient, B) of pristine membrane and membrane after each cycle were determined according to a method previously described [29]. Briefly, the determination of key membrane transport parameters comprises a single FO experiment divided into four stages, each using a different concentration of draw solution. The experimental water and reverse salt fluxes measured in each stage are fitted to the corresponding FO transport equations by performing a least-squares non-linear regression. Four different NaCl draw concentrations (approximately 0.2, 0.4, 0.7, and 1.2 M NaCl) were employed. These parameters were adjusted to fit the experimental data of water and reverse salt fluxes to the corresponding governing equations. This method allowed an *in situ* measurement of membrane characteristics *without* taking the FO membrane out of the membrane cell and transferring into a pressurized RO filtration setup, which could potentially impair membrane integrity.

2.4. FO membrane integrity examination

Apart from measuring key membrane transport parameters, FO membrane integrity at the conclusion of each gypsum scaling–cleaning cycle was examined by challenge tests using two tracers: fluorescent Rhodamine WT (Tuner Designs, CA, USA) and amine-modified polystyrene latex nanoparticle (Sigma-Aldrich, MO, USA), respectively. Details regarding these two tracers were provided in the Supplementary data (Table S1). Specifically, the challenge tests were conducted in single-pass mode where neither feed nor draw solution were returned to their reservoirs. A pulse of either fluorescent Rhodamine WT solution of 50 mg/L or amine-modified polystyrene latex nanoparticle solution of 20 mg/L was injected into the FO feeding tube for 60 s at a crossflow rate of 1 L/min (corresponding to crossflow velocity of 9 cm/s). At the same time, the draw solution at a crossflow rate of 1 L/min (corresponding to crossflow velocity of 9 cm/s) was sampled every 10 s for a total of 540 s to generate either a time-concentration profile of fluorescent Rhodamine WT or the nanoparticle size distribution in the draw solution. A detailed description of challenge tests is provided in the Supplementary materials and methods, Supplementary data. Concentration of fluorescent Rhodamine WT was quantified by a fluorometer (AquaFluor, Tuner Design, CA, USA) at excitation wavelength of 530 nm and emission wavelength of 555 nm. Nanoparticle size distribution was determined by dynamic light scattering (Zetasizer Nano ZSP, Malvern Instruments, Worcestershire, UK).

The log removal value (LRV) of fluorescent Rhodamine WT was calibrated as a function of pinhole size in order to quantify the degree of FO membrane integrity loss. The FO membrane integrity loss was artificially induced by lightly tapping the membrane samples using a tip of a hypodermic needle (GL Sciences, Tokyo, Japan). Pinholes of various sizes (0.02–0.08 μm^2) were created on the FO membrane sample that was subjected to the aforementioned fluorescent Rhodamine WT challenge test. The LRV value was calculated by:

$$LRV = \log\left(\frac{C_{draw} DF}{C_{feed}}\right) \quad (1)$$