Journal of Membrane Science xxx (xxxx) xxx



Contents lists available at ScienceDirect

### Journal of Membrane Science



journal homepage: http://www.elsevier.com/locate/memsci

# Real-time detection of early-stage calcium sulfate and calcium carbonate scaling using Raman spectroscopy

Omkar D. Supekar<sup>a,b,d,\*</sup>, Danielle J. Park<sup>a,d</sup>, Alan R. Greenberg<sup>a,d</sup>, Juliet T. Gopinath<sup>b,c,d</sup>, Victor M. Bright<sup>a,d</sup>

<sup>a</sup> Department of Mechanical Engineering, University of Colorado, Boulder, CO, 80309, USA

<sup>b</sup> Department of Electrical, Computer, and Energy Engineering, University of Colorado, Boulder, CO, 80309, USA

<sup>c</sup> Department of Physics, University of Colorado, Boulder, CO, 80309, USA

<sup>d</sup> Membrane Science, Engineering and Technology Center, University of Colorado, Boulder, CO, 80309, USA

#### ABSTRACT

Early-stage scaling detection is a crucial component for optimizing proactive anti-fouling measures that enhance membrane lifetime and decrease operation costs. In this work, we utilize Raman spectroscopy to detect and chemically quantify multiple scalants during bench-scale reverse osmosis desalination. The experiments were conducted with a commercial brackish water thin-film composite membrane at a feed pressure of 1.2 MPa (175 psi) and a feed flow velocity of 4.2 cm/s. Raman measurements were performed in real-time at a laser excitation wavelength of 785 nm. Experimental results from single-feed solutions of CaSO<sub>4</sub> and CaCO<sub>3</sub> show consistent detection of the corresponding scalants with less than a 15% permeate flux decrease at detection inclusive of the permeate decline due to compaction. Experiments utilizing a mixed-feed solution containing CaSO<sub>4</sub> and CaCO<sub>3</sub> were also conducted. Results for the mixed-feed experiments showed detection of CaSO<sub>4</sub> scaling only. Subsequent analysis indicated that a modified sampling strategy was required for successful real-time detection of both CaSO<sub>4</sub> and CaCO<sub>3</sub> scaling.

#### 1. Introduction

The world's increasing potable water scarcity is caused by factors such as population growth, increased water usage due to rapid industrialization, poor environmental stewardship, and climate change [1]. As a result, there is much interest in expanding sea and brackish water desalination [2–5]. Factors that determine whether desalination technology is beneficial to and sustainable in a community include self-sufficiency and local resources and support [6]. Despite the maturity of desalination technology as a means of providing clean water, a serious remaining shortcoming is fouling, which results in a decrease in permeate quality, flux and membrane life [7]. Fouling hinders wider application of membrane-based desalination technology, especially in rural and inland communities that are sensitive to the maintenance requirements and operating costs [8].

Fouling is the formation of a barrier composed of feed solution components on the membrane surface and/or within the pores of the membranes. Scaling is a specific form of fouling that involves two main mechanisms: particulate fouling and surface crystallization. Particulate fouling, also known as cake formation or bulk crystallization, refers to bulk-phase crystals or secondary crystals that are convectively transported from the bulk solution to the membrane and block the membrane surface or pores. Surface crystallization is driven by concentration polarization, an inherent result of the separation process, where a boundary layer forms at the membrane surface with a higher salt concentration than that of the bulk layer. This increases the likelihood that the boundary layer will be supersaturated even if the bulk solution is unsaturated [9]. The higher salt-concentration boundary layer reaches a steady state when salt convection towards and diffusion away from the membrane are equal to each other. Crystallization occurs when scale-forming ions precipitate and adsorb onto the membrane and grow into crystals. Concentration polarization can be increased by convection towards the membrane as a result of increasing the permeation rate or filtration pressure, and can be decreased by increasing diffusion away from the membrane by increasing cross-flow velocity, temperature, or the solute diffusion coefficient [10].

Calcium sulfate and calcium carbonate are commonly studied scalants in reverse osmosis desalination and are major components in scaling [11]. Studies employing cross-flow configuration scaling experiments have demonstrated increased scaling from upstream to downstream along the flow direction [12,13]. While these studies are primarily conducted using controlled, single-component feed solutions, desalination of natural sea and brackish water involves complex scaling kinetics due to interaction between the components of the feed [11].

https://doi.org/10.1016/j.memsci.2019.117603

Received 14 August 2019; Received in revised form 22 October 2019; Accepted 23 October 2019 Available online 24 October 2019 0376-7388/© 2019 Elsevier B.V. All rights reserved.

<sup>\*</sup> Corresponding author. Department of Mechanical Engineering, University of Colorado, Boulder, CO, 80309, USA. *E-mail address:* omkar.supekar@colorado.edu (O.D. Supekar).



Fig. 1. Diagram of the cross-flow reverse osmosis system.

Therefore, it is also crucial to study and understand the scaling kinetics of mixed feeds. Major inorganic components of brackish, ground, and waste waters likely to cause scaling are calcium, magnesium, carbonate, silica, and iron [14].

Current detection methods in industry use permeate flux decline as a scaling metric [15]. The limitation of this method is that detection significantly lags behind early scale formation [12]. In a laboratory setting, methods such as ultrasonic reflectometry [16–21] and electrical impedance spectroscopy [21–24] have demonstrated real-time scaling detection capability. These and other methods such as magnetic resonance imaging [25–27], on-line scaling monitors [28], and ex situ scale observation detector (EXSOD) [29–32], can provide relatively early fouling detection. Additionally, flow reversal informed by techniques such as ultrasonic reflectometry [19,20] and EXSOD [32], has been demonstrated in the literature as a strategy to delay the onset of significant performance decline due to scaling. However, these methods lack crucial information regarding the chemical composition of the fouling layer that can reveal important information about fouling mechanisms and water chemistry [21].

An attractive solution is spontaneous Raman spectroscopy, which provides both real-time detection and chemical identification using inelastic scattering from optical phonons. While Raman spectroscopy has been previously been proven capable of detecting organic foulants [33], the work in this paper extends the findings from our initial study [34] of Raman spectroscopy for inorganic scaling detection. In our methodology, a laser is focused onto the membrane surface. Inelastic or Raman scattering from optical phonons generates photons shifted in energy, which is measured by a spectrometer. The energy difference between the incident and scattered photons, termed as the Raman shift, is specific to the rotational and vibrational transitions of chemical bonds in a molecule. This methodology provides the capability for detecting the presence of scaling as well as organic fouling. Importantly, chemical identification of foulants can be made in real time based on their distinct Raman signature. While the literature reports successful detection of individual inorganic and organic foulants, additional work is needed to investigate simultaneous Raman detection of multiple foulants as a function of composition and concentration. If successful, such real-time detection of fouling from complex feeds such as seawater should enable more targeted and effective antifouling measures to be implemented.

#### 2. Materials and methods

#### 2.1. Bench-scale cross-flow reverse osmosis system

The bench-scale membrane flow-cell system is adapted from our previous work [34]. The flow cell is integrated with a Renishaw inVia Raman Microscope for in situ, real-time detection of membrane scaling (Fig. 1). The system is comprised of two 9-L feed tanks: one for a DI-H<sub>2</sub>O feed and the other for the salt feed. When the system is in operation, the feed tank is kept at a temperature of  $23.5 \pm 0.5$  °C using a heat exchanger and a chiller (T257P Precision Chiller, ThermoTek). An inline pressure head pump (Model 3-MD-SC, Little Giant Franklin Electric) was installed to avoid potential cavitation in the high-pressure rotary vane pump (Model TMFRSS051A, Fluid-o-Tech) that maintained the system at a pressure of 1.2 ( $\pm 7 \times 10^{-3}$ ) MPa (175  $\pm 1$  psi). A pressure gauge was installed at the inlet and another at the outlet of the flow cell to measure the pressure drop of the feed solution. A thermocouple measured the temperature of the retentate. A back-pressure regulator (Model 12-251B2-4AZ5-72, Neon) controlled the pressure of the system, and a flow meter (Model 74C-234G041-421330, King) and a bypass valve (Model SS-1RS4, Swagelok) were used to monitor and control the flow rate of the system, respectively. An inline filter (Model CCS-020-C1B, 0.2 µm, Advantec) downstream of the flow cell filtered any large particulates in the feed, and the permeate was collected in a glass beaker situated on a scale (Model PNX-2002, American Weigh Scales) for mass measurements at 1-min intervals.

The flow cell [34] shown in Fig. 2 consists of top and bottom components machined from stainless steel and sealed with a double O-ring





Fig. 2. (a) Cross-section of the flow cell showing the top and bottom components, and the optical clamp for the microscope objective; (b) The flow cell has a channel height of 2 mm, the channel height under the sensing region is 4 mm. (c) Image of the flow cell in operation. The Raman microscope is integrated with the flow cell using a Leica N-PLAN L50x/0.50 objective.

Table 1						
Summary of DI water experimental runs.						
Test	Total	Initial	Net permeate	CaSO <sub>4</sub>		

Test #	Total run time (min)	Initial permeate flux (l/m <sup>2</sup> h)	Net permeate flux reduction (%)	CaSO <sub>4</sub> detection	CaCO <sub>3</sub> detection
1	178	73.2	8.6	No	No
2	183	72.0	2.9	No	No
3	185	56.4	2.4	No	No

arrangement for high-pressure operation. Two ports on the top component serve as the feed inlet and outlet. The top component also contains a cavity that accommodates the optical window clamp to facilitate laser access to the membrane. The port on the bottom plate contains the permeate port. The membrane is supported by a stainless-steel mesh and sandwiched between the lower and upper plates.

Prior to each experiment, the DI water and salt feed tanks were washed with RO water until a conductivity of  $0.5-1.0 \,\mu$ S/cm was achieved. The concentration prepared for the CaSO<sub>4</sub> feed was 1.8 g/L CaSO<sub>4</sub>·2H<sub>2</sub>O, and the concentration of CaCO<sub>3</sub> feed was prepared by combining 3.02 g NaHCO<sub>3</sub>, 2.66 g CaCl<sub>2</sub> and 8 L of DI-H<sub>2</sub>O. To prepare the CaSO<sub>4</sub> and CaCO<sub>3</sub> mixed feed, 3.02 g (4.5 mM) NaHCO<sub>3</sub> and 2.66 g (3 mM) CaCl<sub>2</sub> were added to an 8 L CaSO<sub>4</sub> (1.8 g/L concentration)



**Fig. 3.** Permeate flux and Raman signal intensity results from DI water test 2. Data indicate a 3% decrease in the permeate flux with no detection of scaling during the 183 min test.

#### O.D. Supekar et al.

Journal of Membrane Science xxx (xxxx) xxx

solution right before the start of the experiment to avoid premature precipitation. The commercial TFC RO membrane (UTC-73HA, Toray) was cut to size ( $115 \times 65$  mm) and soaked in a 50% isopropanol aqueous solution for 30 min, and the flow cell was cleaned with DI water and isopropanol. In order to obtain a steady-state flow rate and capture the compaction behavior of the membrane, the membrane was placed in the flow cell and subjected to DI water at 1.2 MPa for at least 15 h.

#### 2.2. Scaling detection using a Raman microscope

The Raman microscope (Model inVia Reflex, Renishaw) integrates with the optical window positioned in the center of the flow cell. The laser beam (Model I0785SR0090B-IS1, Innovative Photonic Solutions) has a wavelength of 785 nm and a power of  $\sim$ 20 mW, and is focused onto the surface of the membrane through a microscope objective (Model N-PLAN L50x/0.50, Leica Germany). After the multi-hour exposure to DI water, the scaling experiments are initiated by switching the feed to the desired salt solution, accompanied by real-time permeate mass measurement and Raman spectra acquisition.

#### 2.3. Post-mortem characterization

After each complete scaling experiment, the membrane is removed from the flow cell and dried for scanning electron microscopy (SEM) (Model JSM 6480-LV, JEOL) and energy-dispersive X-ray spectroscopy (EDS, Model Noran System SIX, ThermoFisher Scientific). Scaling morphology from SEM imaging and elemental analysis using EDS was used to confirm the presence of membrane scaling and the accuracy of Raman chemical identification. The analysis of scaling coverage on the post-mortem SEM images was performed using ImageJ software.

#### 3. Results and discussion

This comprehensive study consists of 13 independent experiments

#### Table 2

Results of the  $CaSO_4$  feed solution experiments showing detection sensitivity.  $CaSO_4$  peak detection time is defined as the time required to detect a  $CaSO_4$  peak with a relative intensity greater than 50%. The membranes used in test 4–6 were aged, while those in test 7–9 were new.

Test #	Membrane condition	Total run time (min)	Permeate flux at the end of compaction (l/m <sup>2</sup> h)	Initial permeate flux with $CaSO_4$ feed (l/m <sup>2</sup> h)	CaSO <sub>4</sub> peak detection time (min)	Permeate flux reduction at detection (%)
4	Aged	423	44.4	37.2	356	14.7
5	Aged	280	45.6	39.6	221	9.5
6	Aged	229	49.2	39.6	220	11.8
7	New	38	90.0	68.4	25	13.1
8	New	31	78.0	62.4	27	3.5
9	New	30	79.2	62.4	26	7.0



Fig. 4. Permeate flux and Raman CaSO<sub>4</sub> signal intensity results from (a) test 5 and (b) test 8. (c) CaSO<sub>4</sub> scaling morphology under Raman sensor (test 6), and (d) corresponding EDS spectrum.

#### O.D. Supekar et al.

with four different feed solutions. The first three experiments were replicate runs using DI water as the feed solution. These experiments served as proof that the scaling detection methodology did not yield false positives. In addition, these baseline experiments quantified the permeate flow-rate decrease due to membrane compaction over a period of 3 h. The second set of experiments consisted of six runs with a feed solution concentration of 1.8 g/L CaSO<sub>4</sub>·2H<sub>2</sub>O, with three replicate runs conducted using aged membranes (tests 4-6), and another three using new membranes (tests 7-9). The Raman spectroscopy scaling detection methodology captures the different scaling dynamics of the aged and new membranes, which are influenced by the permeate flow rate of each membrane. The third feed solution employed was a supersaturated CaCO<sub>3</sub> feed consisting of a mixture of 4.5 mM NaHCO<sub>3</sub> and 3 mM CaCl<sub>2</sub> solutions (tests 10-12). These experiments provided initial proof of concept regarding the CaCO<sub>3</sub> scaling detection capability of the methodology. Finally, a mixed-component feed solution consisting of 1.8 g/L CaSO<sub>4</sub>, 4.5 mM NaHCO<sub>3</sub> and 3 mM CaCl<sub>2</sub> was utilized, revealing the spatial dependence of the detection method. The chemical identification accuracy of the Raman detection method was confirmed by energydispersive X-ray spectroscopy (EDS). A detailed description of these scaling detection experiments is provided in the following sections.

#### 3.1. DI water feed experiments

The mechanical behavior of polymeric thin-film composite reverse osmosis (TFC-RO) membranes can be described by viscoelastic models. The permeate flux decrease recorded in the DI water feed experiments can be expressed as an exponential decay function [35–38], indicating a time dependence of membrane performance attributed to deformation of the polymer matrix. To quantify this effect on the membranes used in this work, three independent 3 h experiments were conducted using a DI water feed with Raman detection. The results from these experiments are summarized in Table 1.

The results indicate as much as a 9% permeate flux decrease over a 3 h period (following the initial 15-h pressurized DI water exposure) that can be reasonably attributed to membrane compaction. The differences in the permeate flux reduction reflect the variability in membrane performance. This indicates for longer experiments, the flux decline at detection is due to mechanical compaction in addition to flux decline due to scaling and concentration polarization from salt feed solutions. Importantly, no indication of either CaSO<sub>4</sub> or CaCO<sub>3</sub> scaling was detected by Raman spectroscopy, establishing an absence of false positives from this methodology. Representative results for permeate flow rate and Raman signal intensity are shown in Fig. 3.

#### 3.2. Calcium sulfate scaling detection

To expand our initial work [34] regarding the detection sensitivity of the Raman spectroscopy-based methodology, two sets of three independent tests were conducted with a feed concentration of 1.8 g/L



Fig. 6.  $CaSO_4$  scaling detection time as a function of initial permeate flux. The data indicate an inverse relationship between detection time and initial permeate flux.

Table 3

Results of the CaCO<sub>3</sub> feed solution experiments showing detection sensitivity.

Test #	Total run time (min)	Permeate flux at the end of compaction (l/ m <sup>2</sup> h)	Initial permeate flux with CaCO <sub>3</sub> feed (l/m <sup>2</sup> h)	Time for CaCO <sub>3</sub> detection (min)	Permeate flux reduction at detection (%)
10 11	142 147	78.0 70.8	62.4 61.2	108 135	12.3 11.8
12	126	73.2	63.6	93	12.2

CaSO<sub>4</sub>. The first set used aged TFC-RO membranes while the second set employed new TFC-RO membranes. The experimental results are summarized in Table 2.

Aging can adversely affect membrane performance due to dehydration during storage that reduces wettability, which in turn decreases permeate flux [39]. Results from these experiments show successful scaling detection for both aged and new membranes. Fig. 4 provides representative data for permeate flow rate, Raman signal intensity and post-mortem SEM characterization.

Concentration polarization at the membrane surface is the driving force behind scaling initiation. A simplified film theory [40–42] predicts



Fig. 5. SEM images of the membrane from test 7 showing the extent of scaling upstream, midstream and downstream.



Fig. 7. (a) Permeate flux and Raman CaCO<sub>3</sub> signal intensity results from test 10. (b) CaCO<sub>3</sub> scaling morphology under Raman sensor, and (c) corresponding EDS spectrum.



Fig. 8. SEM images of the membrane from test 10 showing the extent of scaling upstream, midstream and downstream.

the relationship between concentration polarization and permeate flux assuming negligible axial solute convection near the membrane surface. This relationship is given by,

$$\frac{c_w - c_p}{c_b - c_p} = e^{\left(\frac{v_w\delta}{D}\right)} \tag{1}$$

where  $\delta$  is the layer thickness,  $v_w$  is the permeate velocity at the channel wall, D is the solute diffusion coefficient,  $c_w$ ,  $c_b$  and  $c_p$  are the solute concentrations at the membrane surface, in the feed, and the permeate, respectively. The solute concentration at the membrane surface is exponentially proportional to the permeate velocity or flux. However, for sparingly soluble salts, scaling initiates when the solute concentration at the membrane surface exceeds saturation. Due to concentration polarization, the feed concentration is higher downstream, which accounts for the usual observation of downstream scaling initiation with progression in the upstream direction. Analysis of the SEM images (2.5 mm  $\times$  1.7 mm) from Fig. 5 indicate 0%, 33% and 26% scalant coverage at upstream, midstream and downstream locations, respectively. The channel height at the center of the flow cell is 4 mm (2 mm everywhere else) to accommodate the optical window clamp. This results in a lower cross-flow velocity, hence increasing the concentration polarization and scaling extent relative to the downstream region.

The data in Table 2 summarize the inverse relationship between initial permeate flow-rate and  $CaSO_4$  Raman peak-detection time. Fig. 6 shows the detection time as a function of initial permeate flux for

experiments 4–9 as well as results from our previous work [34]. Overall, the data indicate that in addition to sensitive detection of scaling with chemical identification, the Raman-based sensing methodology can also provide important insight regarding scaling dynamics. Clearly, such information can be expanded with the use of more sophisticated sensor sampling strategies.

#### 3.3. Calcium carbonate scaling detection

To determine the applicability of the Raman methodology to a wider range of scalants, we evaluated CaCO<sub>3</sub> scaling detection. Three independent experiments were each conducted using a feed solution consisting of 4.5 mM NaHCO<sub>3</sub> and 3 mM CaCl<sub>2</sub>. A summary of the results from these experiments is presented in Table 3. The data shows that the Raman-based sensing technique can first detect CaCO<sub>3</sub> scaling at a time scale corresponding to a permeate flux decrease of <13%. Fig. 7 provides representative data for permeate flux, Raman signal intensity and post-mortem SEM characterization from test 10.

The scaling morphology from these experiments appears to be predominately comprised of aragonite structures in the form of circular flakes with some evidence of rhombic calcite crystals [43]. The scalant size-scale is of the same order ( $\sim$ 10 µm) as the laser spot diameter (3 µm full width, half maximum) on the membrane surface. The increase in Raman signal intensity corresponds to the growth of the scalant. The results indicate a more gradual increase in the Raman signal intensity as compared to the CaSO<sub>4</sub> scaling experiments.



**Fig. 9.** (a) Permeate flux progression and Raman signal intensity for CaSO<sub>4</sub> and CaCO<sub>3</sub> from test 13. (b) SEM image from test 13 showing CaSO<sub>4</sub> and CaCO<sub>3</sub> scaling morphology in a location near, but not under the sensor. (c) and (d) corresponding EDS spectra for CaCO<sub>3</sub> and CaSO<sub>4</sub>, respectively.

The effect of concentration polarization on the membrane surface along the flow direction is less pronounced than with  $CaSO_4$  because of the supersaturated  $CaCO_3$  feed concentration. This is confirmed by postmortem SEM imaging at locations upstream, midstream and downstream (Fig. 8) at which scalant coverage is 33%, 45% and 41%, respectively.

#### 3.4. Mixed-feed scaling detection

For maximum utility the Raman methodology must be capable of detecting multiple scalants in sea water and brackish water. A scaling experiment with a mixed-feed solution containing both  $CaSO_4$  and  $CaCO_3$  was thus conducted to assess the wider applicability of the methodology. The feed solution had a concentration of 1.8 g/L CaSO<sub>4</sub>, 4.5 mM NaHCO<sub>3</sub> and 3 mM CaCl<sub>2</sub>. After 228 min, CaSO<sub>4</sub> scaling was detected corresponding to a permeate flux reduction of 22.8%. Fig. 9 shows the permeate flux variation, Raman signal progression and post mortem SEM and EDS characterization results from test 13.

The co-precipitation of CaCO<sub>3</sub> and CaSO<sub>4</sub> is governed by the scaling dynamics of CaCO<sub>3</sub> [44] whereby the CaCO<sub>3</sub> would nucleate first in a supersaturated mixed feed. However, given the difference in crystal size between CaSO<sub>4</sub> (100's of  $\mu$ m) and CaCO<sub>3</sub> (10's of  $\mu$ m) (Fig. 9(b)), there is a much higher probability that CaSO<sub>4</sub> crystals will grow under the small area interrogated by the fixed-coordinate Raman laser beam. It is important to note that detection will also occur if CaCO<sub>3</sub> nucleates under the sensor instead of CaSO<sub>4</sub>. In addition, detection of both CaSO<sub>4</sub> and CaCO<sub>3</sub> in this fixed laser-beam arrangement can occur if CaSO<sub>4</sub> nucleates on top of the CaCO<sub>3</sub> or vice versa (Fig. 10(a)). This is clearly a limitation of the single-point sensing arrangement currently employed. This shortcoming can be addressed by utilizing a more sophisticated sampling strategy.

Initial results for scalant detection over a larger area were obtained from a post-mortem scan on the test 13 membrane using the inVia stage. The scans (Fig. 10 (b) & (c)) were conducted over a  $150 \times 100 \,\mu m^2$  area comprising a representative portion of the region shown in Fig. 10(a). Results show that both scalants with chemical identification can be detected using Raman spectroscopy. These larger-area scans will be incorporated into the Raman methodology in our future work on scaling detection.

#### 4. Conclusion

This study demonstrates real-time scaling detection and chemical identification via Raman spectroscopy in a bench-scale cross-flow RO system. Consistent scaling detection using single-solute CaSO<sub>4</sub> and CaCO<sub>3</sub> feeds is shown with a significant increase in the Raman peak intensity of the corresponding scalant. The real-time data is confirmed by post-mortem analysis. Detection times for these scaling experiments show an inverse correlation to the initial permeate flux from the membrane, which is consistent with the scaling dynamics. Modification of the methodology to incorporate larger-area interrogation by the Raman sensor resulted in successful detection of both scalants from a CaSO<sub>4</sub> and CaCO<sub>3</sub> mixed-feed solution. The real-time chemical identification provided by the Raman methodology could provide important information that can help inform proactive antifouling measures.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### O.D. Supekar et al.



**Fig. 10.** (a) SEM image of the mixed-feed test 13 membrane showing CaCO<sub>3</sub> (red outline), CaSO<sub>4</sub> (black outline) scaling and CaCO<sub>3</sub> crystals over CaSO<sub>4</sub> crystals (white outline). Post-mortem Raman spectroscopy results from the  $150 \times 100 \,\mu\text{m}^2$  scans showing (b) CaCO<sub>3</sub> (1086 cm<sup>-1</sup>) and (c) CaSO<sub>4</sub> (1008 cm<sup>-1</sup>) relative peak intensity. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

#### Acknowledgements

The authors gratefully acknowledge support of this work by the Membrane Science, Engineering and Technology Center (MAST IUCRC Award IIP 1624602) at the University of Colorado Boulder (UCB), United States and the technical insights provided by Dr. Joseph Swisher and Dr. Abhoyjit Bhown from the Electrical Power Research Institute (EPRI). The authors appreciate the invaluable machining assistance provided by Dragan Mejic and technical assistance by Masoud Aghajani and Dr. Joseph Brown. The authors are grateful to Prof. Virginia Ferguson in the Department of Mechanical Engineering at UCB for access to the Raman microscope system.

#### References

- R. Baten, K. Stummeyer, How sustainable can desalination be? Desalin. Water Treat. 51 (2013) 44–52, https://doi.org/10.1080/19443994.2012.705061.
- [2] M. Qasim, M. Badrelzaman, N.N. Darwish, N.A. Darwish, N. Hilal, Reverse osmosis desalination: a state-of-the-art review, Desalination 459 (2019) 59–104, https:// doi.org/10.1016/j.desal.2019.02.008.
- [3] M. Elimelech, W.A. Phillip, The future of seawater desalination: energy, technology, and the environment, Science 333 (2011) 712–717, https://doi.org/ 10.1126/science.1200488 (80-.).
- [4] K.P. Lee, T.C. Arnot, D. Mattia, A review of reverse osmosis membrane materials for desalination — development to date and future potential, J. Membr. Sci. 370 (2011) 1–22, https://doi.org/10.1016/j.memsci.2010.12.036.
- [5] R.F. Service, Desalination freshens up, Science 313 (2006) 1088–1090, https://doi. org/10.1126/science.313.5790.1088 (80-.
- [6] E. Mathioulakis, V. Belessiotis, E. Delyannis, Desalination by using alternative energy: review and state-of-the-art, Desalination 203 (2007) 346–365, https://doi. org/10.1016/j.desal.2006.03.531.

- [7] S. Lee, Effect of operating conditions on CaSO4 scale formation mechanism in nanofiltration for water softening, Water Res. 34 (2002) 3854–3866, https://doi. org/10.1016/s0043-1354(00)00142-1.
- [8] L.F. Greenlee, D.F. Lawler, B.D. Freeman, B. Marrot, P. Moulin, Reverse osmosis desalination: water sources, technology, and today's challenges, Water Res. 43 (2009) 2317–2348, https://doi.org/10.1016/j.watres.2009.03.010.
- [9] S. Lee, J. Kim, C.H. Lee, Analysis of CaSO4 scale formation mechanism in various nanofiltration modules, J. Membr. Sci. 163 (1999) 63–74, https://doi.org/ 10.1016/S0376-7388(99)00156-8.
- [10] S. Shirazi, C.J. Lin, D. Chen, Inorganic fouling of pressure-driven membrane processes - a critical review, Desalination 250 (2010) 236–248, https://doi.org/ 10.1016/j.desal.2009.02.056.
- [11] W. Guo, H.H. Ngo, J. Li, A mini-review on membrane fouling, Bioresour. Technol. 122 (2012) 27–34, https://doi.org/10.1016/j.biortech.2012.04.089.
- [12] C. Tzotzi, T. Pahiadaki, S.G. Yiantsios, A.J. Karabelas, N. Andritsos, A study of CaCO3 scale formation and inhibition in RO and NF membrane processes, J. Membr. Sci. 296 (2007) 171–184, https://doi.org/10.1016/j. memsci.2007.03.031.
- [13] W.-Y. Shih, A. Rahardianto, R.-W. Lee, Y. Cohen, Morphometric characterization of calcium sulfate dihydrate (gypsum) scale on reverse osmosis membranes, J. Membr. Sci. 252 (2005) 253–263, https://doi.org/10.1016/j. memsci.2004.12.023.
- [14] D.E. Potts, R.C. Ahlert, S.S. Wang, A critical review of fouling of reverse osmosis membranes, Desalination 36 (1981) 235–264, https://doi.org/10.1016/S0011-9164(00)88642-7.
- [15] M.A. Saad, Early discovery of RO membrane fouling and real-time monitoring of plant performance for optimizing cost of water, Desalination 165 (2004) 183–191, https://doi.org/10.1016/j.desal.2004.06.021.
- [16] A.P. Mairal, A.R. Greenberg, W.B. Krantz, L.J. Bond, Real-time measurement of inorganic fouling of RO desalination membranes using ultrasonic time-domain reflectometry, J. Membr. Sci. 159 (1999) 185–196, https://doi.org/10.1016/ S0376-7388(99)00058-7.
- [17] R.D. Sanderson, J. Li, D.K. Hallbauer, S.K. Sikder, Fourier wavelets from ultrasonic spectra: a new approach for detecting the onset of fouling during microfiltration of paper mill effluent, Environ. Sci. Technol. 39 (2005) 7299–7305, https://doi.org/ 10.1021/es050414y.

#### O.D. Supekar et al.

- [18] K.D. Cobry, Z. Yuan, J. Gilron, V.M. Bright, W.B. Krantz, A.R. Greenberg, Comprehensive experimental studies of early-stage membrane scaling during nanofiltration, Desalination 283 (2011) 40–51, https://doi.org/10.1016/j. desal.2011.04.053.
- [19] X. Lu, E. Kujundzic, G. Mizrahi, J. Wang, K. Cobry, M. Peterson, J. Gilron, A. R. Greenberg, Ultrasonic sensor control of flow reversal in RO desalination-Part 1: mitigation of calcium sulfate scaling, J. Membr. Sci. 419–420 (2012) 20–32, https://doi.org/10.1016/j.memsci.2012.05.027.
- [20] G. Mizrahi, K. Wong, X. Lu, E. Kujundzic, A.R. Greenberg, J. Gilron, Ultrasonic sensor control of flow reversal in RO desalination. Part 2: mitigation of calcium carbonate scaling, J. Membr. Sci. 419–420 (2012) 9–19, https://doi.org/10.1016/ j.memsci.2012.05.026.
- [21] A. Antony, J.H. Low, S. Gray, A.E. Childress, P. Le-Clech, G. Leslie, Scale formation and control in high pressure membrane water treatment systems: a review, J. Membr. Sci. 383 (2011) 1–16, https://doi.org/10.1016/j.memsci.2011.08.054.
- [22] A. Antony, T. Chilcott, H. Coster, G. Leslie, In situ structural and functional characterization of reverse osmosis membranes using electrical impedance spectroscopy, J. Membr. Sci. 425–426 (2013) 89–97, https://doi.org/10.1016/j. memsci.2012.09.028.
- [23] Z. Hu, A. Antony, G. Leslie, P. Le-Clech, Real-time monitoring of scale formation in reverse osmosis using electrical impedance spectroscopy, J. Membr. Sci. 453 (2014) 320–327, https://doi.org/10.1016/j.memsci.2013.11.014.
- [24] J. Cen, M. Vukas, G. Barton, J. Kavanagh, H.G.L. Coster, Real time fouling monitoring with electrical impedance spectroscopy, J. Membr. Sci. 484 (2015) 133–139, https://doi.org/10.1016/j.memsci.2015.03.014.
- [25] S.A. Creber, J.S. Vrouwenvelder, M.C.M. van Loosdrecht, M.L. Johns, Chemical cleaning of biofouling in reverse osmosis membranes evaluated using magnetic resonance imaging, J. Membr. Sci. 362 (2010) 202–210, https://doi.org/10.1016/ j.memsci.2010.06.052.
- [26] S. Buetehorn, L. Utiu, M. Küppers, B. Blümich, T. Wintgens, M. Wessling, T. Melin, NMR imaging of local cumulative permeate flux and local cake growth in submerged microfiltration processes, J. Membr. Sci. 371 (2011) 52–64, https:// doi.org/10.1016/j.memsci.2011.01.018.
- [27] X. Li, Y. Mo, J. Li, W. Guo, H.H. Ngo, In-situ monitoring techniques for membrane fouling and local filtration characteristics in hollow fiber membrane processes: a critical review, J. Membr. Sci. 528 (2017) 187–200, https://doi.org/10.1016/j. memsci.2017.01.030.
- [28] C.A.C. van de Lisdonk, J.A.M. van Paassen, J.C. Schippers, Monitoring scaling in nanofiltration and reverse osmosis membrane systems, Desalination 132 (2000) 101–108, https://doi.org/10.1016/S0011-9164(00)00139-9.
- [29] M. Uchymiak, A. Rahardianto, E. Lyster, J. Glater, Y. Cohen, A novel RO ex situ scale observation detector (EXSOD) for mineral scale characterization and early detection, J. Membr. Sci. 291 (2007) 86–95, https://doi.org/10.1016/j. memsci.2006.12.038.
- [30] P. Le-Clech, Y. Marselina, Y. Ye, R.M. Stuetz, V. Chen, Visualisation of polysaccharide fouling on microporous membrane using different characterisation techniques, J. Membr. Sci. 290 (2007) 36–45, https://doi.org/10.1016/j. memsci.2006.12.012.

- [31] A.R. Bartman, E. Lyster, R. Rallo, P.D. Christofides, Y. Cohen, Mineral scale monitoring for reverse osmosis desalination via real-time membrane surface image analysis, Desalination 273 (2011) 64–71, https://doi.org/10.1016/j. desal.2010.10.021.
- [32] M. Uchymiak, A.R. Bartman, N. Daltrophe, M. Weissman, J. Gilron, P. D. Christofides, W.J. Kaiser, Y. Cohen, Brackish water reverse osmosis (BWRO) operation in feed flow reversal mode using an ex situ scale observation detector (EXSOD), J. Membr. Sci. 341 (2009) 60–66, https://doi.org/10.1016/j. memsci.2009.05.039.
- [33] T. Virtanen, S.P. Reinikainen, M. Kögler, M. Mänttäri, T. Viitala, M. Kallioinen, Real-time fouling monitoring with Raman spectroscopy, J. Membr. Sci. 525 (2017) 312–319, https://doi.org/10.1016/j.memsci.2016.12.005.
- [34] O.D. Supekar, J.J. Brown, A.R. Greenberg, J.T. Gopinath, V.M. Bright, Real-time detection of reverse-osmosis membrane scaling via Raman spectroscopy, Ind. Eng. Chem. Res. 57 (2018) 16021–16026, https://doi.org/10.1021/acs.iecr.8b01272.
- [35] H. Ohya, An expression method of compaction effects on reverse osmosis membranes at high pressure operation, Desalination 26 (1978) 163–174, https:// doi.org/10.1016/S0011-9164(00)82198-0.
- [36] M. Aghajani, S.H. Maruf, M. Wang, J. Yoshimura, G. Pichorim, A. Greenberg, Y. Ding, Relationship between permeation and deformation for porous membranes, J. Membr. Sci. 526 (2017) 293–300, https://doi.org/10.1016/j. memsci.2016.12.048.
- [37] Y.A. Hussain, M.H. Al-Saleh, A viscoelastic-based model for TFC membranes flux reduction during compaction, Desalination 344 (2014) 362–370, https://doi.org/ 10.1016/j.desal.2014.04.010.
- [38] M. Aghajani, M. Wang, L.M. Cox, J.P. Killgore, A.R. Greenberg, Y. Ding, Influence of support-layer deformation on the intrinsic resistance of thin film composite membranes, J. Membr. Sci. 567 (2018) 49–57, https://doi.org/10.1016/j. memsci.2018.09.031.
- [39] M.A. Kuehne, R.Q. Song, N.N. Li, R.J. Petersen, Flux enhancement in TFC RO membranes, Environ. Prog. 20 (2001) 23–26, https://doi.org/10.1002/ ep.670200112.
- [40] S. Sablani, M. Goosen, R. Al-Belushi, M. Wilf, Concentration polarization in ultrafiltration and reverse osmosis: a critical review, Desalination 141 (2001) 269–289, https://doi.org/10.1016/S0011-9164(01)85005-0.
- [41] S. Kim, E.M.V. Hoek, Modeling concentration polarization in reverse osmosis processes, Desalination 186 (2005) 111–128, https://doi.org/10.1016/j. desal.2005.05.017.
- [42] M.J. Clifton, N. Abidine, P. Aptel, V. Sanchez, Growth of the polarization layer in ultrafiltration with hollow-fibre membranes, J. Membr. Sci. 21 (1984) 233–245, https://doi.org/10.1016/S0376-7388(00)80216-1.
- [43] M. Ni, B.D. Ratner, Differentiating calcium carbonate polymorphs by surface analysis techniques-an XPS and TOF-SIMS study, Surf. Interface Anal. 40 (2008) 1356–1361, https://doi.org/10.1002/sia.2904.
- [44] M. Sudmalis, R. Sheikholeslami, Coprecipitation of CaCO 3 and CaSO 4, can, J. Chem. Eng. 78 (2000) 21–31, https://doi.org/10.1002/cjce.5450780106.

#### Journal of Membrane Science xxx (xxxx) xxx