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Gypsum scaling and membrane integrity of osmotically driven membranes: The effect of membrane materials and operating conditions

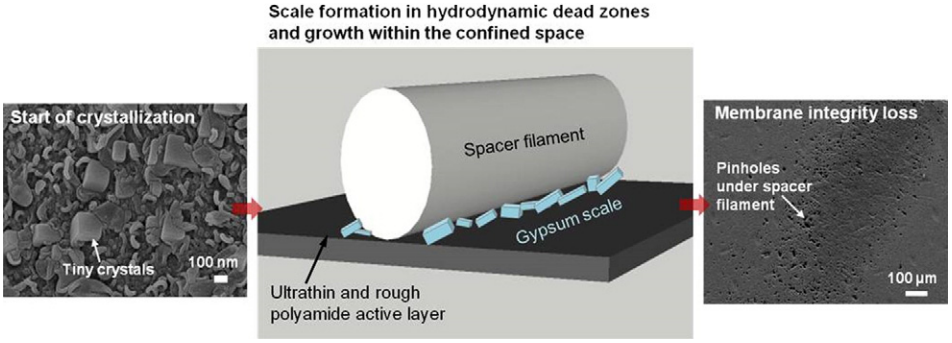
Yi-Ning Wang [a,b], Eliisa Järvelä [b], Jing Wei [a], Minmin Zhang [a,c], Hanna Kyllönen [b], Rong Wang [a,c], Chuyang Y. Tang [d,*]

[a] Singapore Membrane Technology Centre, Nanyang Technological University, Singapore 637141, Singapore
[b] VTT Technical Research Centre of Finland, Jyväskylä 40400, Finland
[c] School of Civil and Environmental Engineering, Nanyang Technological University, Singapore 639798, Singapore
[d] Department of Civil Engineering, The University of Hong Kong, Hong Kong

HIGHLIGHTS

- TFC FO membrane is more vulnerable to scaling than CTA FO membrane
- Spacer promotes crystal formation between its filament and membrane surface
- Crystal growth in AL-FS between membrane and spacer may damage rejection layer
- Severe internal scaling in AL-DS results in remarkable flux drop
- Antiscalant can effectively prevent scaling in AL-FS, but had little effect in AL-DS

GRAPHICAL ABSTRACT



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ABSTRACT

The emerging thin film composite (TFC) forward osmosis (FO) and pressure retarded osmosis (PRO) membranes generally have better separation properties compared with their cellulose triacetate (CTA) counterparts. Nevertheless, their scaling performance has been rarely reported. In the current study, the phenomenon of membrane integrity loss as a result of scaling is reported for the first time for osmotically driven membrane processes (ODMPs). The results show that the TFC membrane suffered marked flux reduction during the scaling in the active-layer-facing-feed-solution (AL-FS) orientation, accompanied with the severe damage of the membrane active layer. The membrane integrity loss is attributed to the scale formation and growth in the confined space between the membrane and the feed spacer. Compared with the CTA membrane, the TFC was more prone to scaling and membrane damage due to its unfavorable physiochemical properties (presence of Ca^{2+} binding sites and ridge-and-valley roughness). Although antiscalant addition was shown to be effective for scaling control in AL-FS, it was ineffective in the active-layer-facing-draw-solution orientation. The current study reveals the critical need for scaling control in ODMP processes with respect to the membrane integrity and flux stability. The results also have far-reaching implications for FO and PRO membrane design and process operation.

* Corresponding author at: HW 6-19b, Haking Wong Building, Pokfulam Road, Department of Civil Engineering, The University of Hong Kong, Hong Kong.
E-mail address: tangc@hku.hk (C.Y. Tang).

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1. Introduction

Osmotically driven membrane processes (ODMPs) utilize the osmotic pressure difference between a concentrate draw solution (DS) and a dilute feed solution (FS) separated by a semi-permeable membrane to drive the permeation of water from the FS to the DS. Depending on the applied pressure in the DS, ODMPs can be classified into forward osmosis (FO, pressure = 0) and pressure retarded osmosis (PRO, pressure > 0). ODMPs have recently gained more and more research interests due to its potential applications in low-energy separation processes and power generation [1–7].

Membrane scaling is a critical challenge for ODMPs, particularly for applications involving scaling precursors at high concentrations (e.g., high [Ca^{2+}] and/or [SO_4^{2-}]) [8–11]. From the experiences of pressure-driven reverse osmosis (RO), it is understood that inorganic scale starts to grow when the concentration of sparingly soluble salts in bulk or near membrane surface exceeds their solubility [12]. Their deposition on a membrane results in the reduction of membrane permeability. Scaling can be influenced by various operating conditions, such as solution pH, temperature, crossflow velocity and permeation rate [12]. Although these experiences are applicable to ODMPs, the additional transport phenomena in ODMPs including internal concentration polarization (ICP) and reverse solute diffusion (RSD) may lead to more difficult scaling control. Despite that membrane water flux appears to be more easily restored in ODMPs compared with RO after cleaning [8,10], a few FO/PRO scaling studies reported severe internal scaling when membrane support layer was facing the FS [9]. Furthermore, the RSD of scaling precursors from the DS plays an important role in promoting scaling. In some cases, complete cease of water flux occurred within merely a few hours of scaling test [9,10].

Most existing ODMP scaling studies used the commercially available cellulose triacetate (CTA) membranes (Hydration Technology Innovations [HTI], Albany, OR) [8,9,13,14]. On the other hand, the more recently developed thin film composite (TFC) polyamide (PA) FO/PRO membranes are believed to be promising replacement to CTA membranes, thanks to their better chemical and biological stability and improved separation properties (higher water permeability and salt rejection) [15–18]. To date, very few papers have investigated the scaling of TFC FO/PRO membranes [8]. Although the PA layer has high selectivity, the carboxylic surface functional groups of the PA layer are presumably the effective binding sites for divalent cations such as Ca^{2+} [19], which may promote subsequent crystal growth on the TFC membranes. In addition, the thickness of a typical TFC PA rejection layer is on the order of 100 nm, which is much thinner compared with that of CTA membranes (a few μm) [15]. One potential concern is the mechanical stability of the PA layer. The deposition and growth of scalant crystals may introduce local mechanical stress, leading to potential loss of membrane integrity. To the best knowledge of the authors, such phenomenon has not yet been systematically reported in the literature.

The objectives of the current study are 1) to systematically compare scaling behavior between TFC and CTA membranes and 2) to investigate the factors that affect the mechanical integrity of FO/PRO membranes under the influence of scaling.

2. Materials and methods

2.1. Chemicals and solution chemistry

Analytical grade chemicals (purity > 99%) were used as received without further purification. $CaCl_2$ and Na_2SO_4 were used as scaling precursors to study gypsum scaling. NaCl was used for conductivity adjustment and draw solution (DS) preparation. A typical feed solution (FS) contained 26.1 mM $CaCl_2$, 72 mM Na_2SO_4 and 10 mM NaCl. It had an osmotic pressure of 7.5 bar and a gypsum saturation index (SI) of 2.0, as calculated using OLI Stream Analyzer 3.1 software (OLI systems, Inc., Morris Plains, NJ) [9]. Another FS prepared with 163 mM NaCl was used as control for baseline tests (SI = 0, osmotic pressure = 7.5 bar). No pH adjustment was performed (pH = ~6.0).

Polyacrylic acid (sodium salt) (PAA, KemGuard 5804, Kemira, Finland) was used as the antiscalant (AS), and it had an average molecular weight of 2200 Da. Where the effect of AS was studied, 2 ppm PAA was dosed into the FS.

2.2. FO membranes

A polyamide (PA) based thin film composite (TFC) FO membrane and a cellulose triacetate (CTA) asymmetric FO membrane were employed in this study. Both were received from HTI (Albany, OR) as dry flat sheet coupons and stored in 4 °C fridge in dark. Prior to FO experiment, membrane coupons were cut into smaller size and soaked in ultrapure water for 1 day.

2.3. FO filtration experiments

FO tests were performed with a bench-scale crossflow filtration system (Appendix A) and the experimental procedures were adapted from prior studies [20,21]. Briefly, the FO membrane cell (CF042-FO, Sterlitech) had an effective membrane area of 42 cm^2. Diamond-patterned spacers (65 mil (1.651 mm) spacer, GE Osmonics) were placed in both the FS and DS channels unless otherwise specified (e.g., where the effect of FS spacer was evaluated, the feed channel was not filled with any spacer). An FS of 3.5 L and a DS of 3 L were circulated with two variable speed peristaltic pumps (Watson-Marlow, Cornwall, UK) to generate a crossflow of ~10 cm/s in both channels. The DS tank was placed on a digital balance (Sartorius U4100 S, Germany) that was connected to a computer for water flux acquisition. The FS was well mixed by a magnetic stirrer and its conductivity was monitored by using a conductivity meter (SevenGo™ portable conductivity, Mettler Toledo). FO scaling experiments were performed in both active layer-facing-feed solution (AL-FS) and active layer-facing-draw solution (AL-DS) orientations. Unless specified otherwise, both FS and DS were freshly prepared prior to each test. The DS concentration was adjusted to achieve an identical initial FO water flux of 9 ± 1.5 L/m^2·h.

Membrane cleaning and flux reversibility tests were performed immediately after the FO scaling experiments. The ultrapure water flushing was carried out in both FS and DS flow channels at 15 cm/s for 30 min. The recovered flux after cleaning was measured with 2 M NaCl DS and ultrapure water FS, and was compared with the clean membrane flux obtained under the same testing condition (i.e., 2 M NaCl (DS), ultrapure water (FS) and same orientation). All the FO experiments and membrane cleaning were performed at room temperature (22 ± 1 °C).

2.4. Reverse osmosis (RO) tests for A, B, and S values

The membrane water permeability and NaCl rejection were evaluated in RO experiments using a laboratory-scale crossflow filtration setup [22,23]. Pure water flux (J) was measured under an applied pressure (ΔP) of 7 bar (101 psi) with ultrapure water as the feed. NaCl rejection (R) was obtained by filtering 10 mM NaCl feed solution (10 L) at 7 bar and a crossflow velocity of 20 cm/s. The water permeability (A) and NaCl permeability (B) were determined from the following equations:

$$A = \frac{J}{\Delta P} \quad (1)$$