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## Gypsum scaling in forward osmosis: Role of membrane surface chemistry

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## ABSTRACT

Forward osmosis (FO) membranes with varying surface chemical functionalities respond differently to gypsum scaling. Using a real-time monitoring system, gypsum scaling was quantified between an asymmetric cellulose triacetate (CTA) and a thin-film composite (TFC) polyamide membrane in terms of water flux decline, gypsum surface coverage and gypsum crystal morphology. At the same initial water flux, the TFC membrane was subjected to more severe gypsum scaling than the CTA membrane in terms of water flux decline and gypsum crystal surface coverage. The gypsum crystal morphology on the CTA membrane featured with slender platelets; in contrast, that on the TFC membrane demonstrated the formation of rosette arrangements. Fourier transform infrared spectra and X-ray photoelectron spectroscopy proved that the gypsum scaling on CTA membrane was dominated by bulk crystallisation with subsequent deposition; while that on the TFC membrane was driven by surface crystallisation via specific interaction between carboxylic functional groups and calcium ions. No interaction between gypsum and CTA membrane surface was demonstrated by the largely unchanged ratio of wavenumbers  $1740\text{ cm}^{-1}$  (C=O stretching) to  $1366\text{ cm}^{-1}$  (C–O stretching), as well as binding energy of C1s on the CTA membrane. In contrast, specific interaction between carboxylic functional groups with calcium ions during gypsum scaling was revealed by a gradual increase in the ratio of absorbance wavenumber  $3400\text{ cm}^{-1}$  (O–H stretching) to  $2970\text{ cm}^{-1}$  (C–H stretching), and the occurrence of the carboxylate functional group at binding energy of 288.1 eV on the TFC membrane during the formation of gypsum scaling.

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## 1. Introduction

Forward osmosis (FO), an osmosis-driven membrane process, could potentially advance desalination and wastewater reuse. FO utilises the osmotic pressure of a highly concentrated draw solution as the driving force to transfer water from the feed solution to the draw solution through a dense polymeric membrane. FO has demonstrated a much lower fouling propensity and higher fouling reversibility than RO, which was attributed to the lack of applied hydraulic pressure [1–4]. Consequently, FO is widely used to treat low quality feedwater, including landfill leachate [5], anaerobic digester concentrate [6], activated sludge solution [7,8], and municipal wastewater [9–11].

The core of FO membrane has advanced from asymmetric cellulose triacetate (CTA) membrane to polyamide thin-film composite (TFC) membranes because of the excellent mass transfer properties of polyamide [12–14]. Indeed, the TFC membrane not only produces higher water permeability but also exhibits better

contaminant rejections in comparison with the CTA membrane. For example, the TFC membrane achieved rejections of four pharmaceuticals above 95%; in contrast, the CTA membrane exhibited varying rejections of these compounds from 65% to 95% [15]. This better performance of the TFC membrane was further demonstrated by substantially higher rejections of neutral contaminants than the CTA membrane [16].

Membrane surface chemistry of CTA and TFC membranes are markedly different. Unlike the CTA membrane abundant with hydroxyl functional groups, the TFC membrane is characterised by a high density of carboxylic acid functional groups, which results in potentially high fouling propensity. Previous knowledge from RO membrane fouling demonstrated that carboxylic functional groups enabled the formation of calcium bridging between the membrane surface and a wide range of organic foulants, and consequently increased organic fouling. Wu et al. [17] found that the carboxylic functional groups on RO membrane exhibited the highest initial alginate adsorption rate in seawater desalination. This higher adsorption was further revealed by measuring the alginate – membrane surface intermolecular force [18], which increased with higher density of carboxylic functional groups.

Role of membrane surface chemistry in FO membrane fouling is

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conflicting and not well understood. Limited investigations were conducted to compare FO membrane fouling behaviour between CTA and TFC membranes with different surface chemical functionalities. For instance, more severe gypsum scaling of the TFC membrane was observed in comparison with the CTA membrane [19,20], which was attributed to stronger adhesion force measured by atomic force measurement (AFM). In contrast, negligible difference in water flux decline was observed between the TFC and CTA membranes during silica scaling. In addition, the adhesion force measurement by AFM also showed stronger hydrogen bonding between silica and the CTA membrane abundant with hydroxyl functional groups [20]. As a result, the role of membrane surface chemistry on FO fouling is not straightforward and necessitates systematic investigation.

In this study, we investigated the role of FO membrane surface chemistry on gypsum scaling using CTA and TFC membranes. Membrane surface chemistry – surface charge and surface functional groups – were characterised. Gypsum scaling of the CTA and TFC membranes was conducted in a real-time observation setup and was quantified in terms of water flux decline, gypsum surface coverage and gypsum crystal morphology. Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy were used to capture changes of membrane surface chemistry on the CTA and TFC membranes during gypsum scaling, thereby elucidating the role of membrane surface chemistry on gypsum scaling in FO process. We provided, for the first time, a time-resolved gypsum scaling profile of CTA and TFC membranes in FO process. The real-time observation, microscopic imaging as well as comprehensive membrane surface chemistry characterization constituted compelling experimental evidence to elucidate the scaling mechanism.

## 2. Materials and methods

### 2.1. FO membranes

An asymmetric cellulose triacetate (CTA) and a polyamide thin-film composite (TFC) forward osmosis (FO) membrane were employed in this study. The CTA membrane was composed of a cellulose triacetate layer with an embedded woven support mesh [21,22]. The TFC membrane was made of a thin selective polyamide active layer on top of a porous polysulfone support layer [23,24].

### 2.2. Real-time observation FO setup

A transparent acrylic FO membrane cell coupled with microscopic observation enabled real-time observation of gypsum scaling on membrane surface (Fig. S1, Supplementary Data). Specifically, a membrane coupon with an effective area of 20.2 cm<sup>2</sup> was placed in a transparent FO membrane cell. 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 pixels 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 fibre optic illuminator, digital image capture and analysis

processing, occurrence and subtle changes of gypsum crystal could be effectively monitored. Recorded images of the scaled membrane surface were processed with image analysis softwares – Image J and Adobe Photoshop – to quantify the time evolution of gypsum surface coverage.

### 2.3. Experimental procedure of membrane scaling

Both CTA and TFC FO membranes were employed in the gypsum scaling experiments. Varying initial water fluxes of the CTA and TFC membranes were achieved by using different concentrations of NaCl. The evolution of gypsum scaling of the CTA and TFC membranes were continuously monitored by the real-time observation FO setup.

The protocol for all 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 stabilised to obtain a constant flux. The stabilization process took about one hour for FO. The membrane in the FO mode was stabilised with deionised water as the feed and varying concentration of NaCl as the draw solution to induce different initial water flux. 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<sub>2</sub>, 20 mM Na<sub>2</sub>SO<sub>4</sub>, and 19 mM NaCl, with a gypsum (CaSO<sub>4</sub> · 2H<sub>2</sub>O) saturation index (SI) of 1.3. Other experimental conditions were: cross-flow rate of 1 L/min (corresponding to the cross-flow velocity of 8.5 cm/s), ambient pH (pH 6.8), and temperature of 25.0 ± 0.1 °C. Scaling experiment was operated for around 25 h, attaining cumulative permeate volume of 1.4 L. Water flux was continuously monitored throughout the fouling experiments by a data logger. A baseline experiment (i.e., feed without CaCl<sub>2</sub> and Na<sub>2</sub>SO<sub>4</sub>) 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 [25]. The real-time monitoring system captured images of the FO membrane surface every hour to identify the occurrence of and development of gypsum crystals on FO membrane surface during scaling experiment.

### 2.4. Relating gypsum scaling to membrane surface chemistry

A suite of techniques were employed to elucidate the mechanisms of gypsum scaling on CTA and TFC membranes whose membrane surface chemistry was markedly different. Specifically, for pristine membranes, surface charge and major functional groups of CTA and TFC membranes were characterised by streaming potential and x-ray photoelectron spectroscopy (XPS). For gypsum-scaled membranes, the morphology of gypsum scaling layer on CTA and TFC membranes was examined by scanning electron microscopy (SEM); changes in bonding chemistry of the CTA and TFC membranes after gypsum scaling was quantified by a high resolution C1s scan using XPS. In addition, the evolution of gypsum scaling on CTA and TFC membrane surface was observed by Fourier transform infrared spectroscopy (FTIR).

#### 2.4.1. Streaming potential measurement

Membrane surface charge was determined using a SurPASS electrokinetic analyser (Anton Paar GmbH, Graz, Austria). The zeta potential of each membrane surface was calculated from the measured streaming potential using the Fairbrother-Mastin approach [26]. All streaming potential measurements were conducted in a background electrolyte solution containing 10 mM KCl. Hydrochloric acid and potassium hydroxide were used to adjust pH by means of automatic titration. The test solution was used to

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