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RO membrane mineral scaling in the presence of a biofilm

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ABSTRACT

The influence of a pre-existing biofilm on RO membrane mineral scaling was evaluated using gypsum as a model scalant. The biofilm was established using microfiltered secondary treated wastewater effluent on-site in a wastewater treatment facility. Mineral scaling was then monitored via direct visual observation of crystal growth on the membrane surface in a transparent plate-and-frame RO cell. SEM imaging of the membrane surface and sectioned biofilm revealed gypsum crystals within the biofilm matrix, including the protrusion of crystal rods from within the biofilm. Both mineral scale surface coverage and crystal number density were greater in the presence of the biofilm. Moreover, individual mineral crystal growth rate within the biofilm was significantly higher relative to growth in the absence of a biofilm. Analyses of crystal growth and nucleation rates, within the biofilm and in its absence, suggest concentration polarization enhancement within the biofilm. The present study suggests that mineral scaling may not be restricted to tail elements in RO plants, but could also occur in lead elements where biofilms can enhance concentration polarization. Therefore, understanding of the coupling of biofouling and mineral scaling may be of particular significance to the operation and design of RO plants in water reuse applications.

1. Introduction

In recent years, increasing water reclamation and reuse efforts have emerged to help meet the rising demand and usage of fresh water supplies. Wastewater reuse could provide much needed supplementary water for populated areas such as central and southern California, the Middle East and other semi-arid regions, as well as populous urban areas around the world that experience water shortages [1–9]. In particular, reuse of secondary treated municipal wastewater requires desalting of this water source (containing ~500–1000 mg/L total dissolved solids (TDS); [4,10–12]). Reverse osmosis (RO) membrane technology has become an integral part of this water reuse scheme to produce highly purified water [13]. In order to maintain the economic viability of RO treatment, operation at high product water recoveries (typically >80%) is essential [14–19]. However, high recovery RO is often limited due to biological (biofouling) [20–27], organics [28–31], and colloidal [32–34] membrane fouling.

Membrane biofouling is of particular concern in the desalination of secondary treated municipal wastewater due to the significant presence of microorganisms [23,27]. A biofilm can form due to deposition, attachment and growth of microorganisms onto the membrane surface. Studies have shown that even after 99% removal of microorganisms from the RO raw feed (e.g., via microfiltration and ultrafiltration (MF/UF)), biofouling still occurs [35,36]. Scaling of sparingly soluble mineral salts (e.g., calcium carbonate, calcium sulfate and calcium phosphate) could also impose significant limitation on the achievable RO product water recovery. When the concentrations of such salts exceed their saturation levels, mineral salts can precipitate in the feed/brine channel and deposit as well as crystalize directly onto the membrane surface. Mineral scaling results in permeate flux decline, and shorten membrane life due to possible membrane damage and harsh chemical cleanings may be employed for scale removal. Mineral scaling has been the subject of numerous studies on seawater [37] and brackish desalination [18,38–43], and has also been reported in RO desalting of wastewater effluent [12,44,45].

A number of recent studies have suggested that biofouling can result in enhancement of concentration polarization [46,47] which in turn could exacerbate the occurrence of mineral scaling. Bacterial adhesion takes place on the RO membrane surface due to the deposition of biological material near the membrane surface [48]. Mineral crystallization occurs only when the concentration of the ion-pair of the mineral salt of concern is above saturation [49]. Therefore, it is expected that biofouling would take place toward the leading elements of the RO process train,

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whereas mineral scaling is typically encountered in the tail membrane elements. For example, the source water in the present study was from the Orange County Water District (OCWD) which operates a 70 MGD RO process as part of the Groundwater Replenishment System (GWRS) – an advanced wastewater purification facility located in Fountain Valley, CA. Through the course of operations in this facility, the first of three stages of each 5 MGD RO unit typically exhibits increasing differential pressures and reduced permeability over time – all signs associated with biological and organic fouling. The third stages have experienced mineral scaling, as reflected in reduced permeability and increasing salt passage. If biofouling indeed exacerbates membrane mineral scaling, it may occur in a more widespread manner and not be isolated to a unit's tail-end stages. Therefore, it is important to understand the coupling between biofouling and scaling, in order to develop proper fouling mitigation strategies. While it is of importance to ultimately elucidate the concomitant and complex processes of biofouling and mineral scaling, an essential first step is to evaluate the effect of a biofilm on local concentration polarization and the ensuing impact on mineral scaling.

The goal of the present study is to investigate RO membrane mineral scaling, using gypsum ($CaSO_4 \cdot 2H_2O$) as a model scalant, in the presence of a pre-existing biofilm. The biofilm was formed on a commercial RO membrane, in a plate-and-frame RO cell, using secondary wastewater effluent from OCWD. The RO membrane with the pre-existing biofilm was then subjected to mineral salt crystallization induced by desalting under conditions leading to supersaturation of the mineral scalant. The effect of the biofilm was monitored with respect to permeate water flux and the evolution of mineral scale on the membrane surface which was followed optically in real-time [50] to quantify crystals nucleation and growth rate.

2. Experimental

2.1. Materials

A low-pressure brackish water RO membrane (ESPA2; Hydranautics, Oceanside, CA) was used in this study to investigate the interaction between formed membrane biofilms and mineral scaling. This same membrane, which is also used in the OCWD GWRS RO system, was reported to have RMS surface roughness of 130 nm [51], permeability (based on DI water) of 0.04 ± 0.005 $m^3/(m^2\,h\,MPa)$, and NaCl salt rejection (based on 3000 mg/L feed solution) of 97%. Reagent grade calcium chloride ($CaCl_2\ 2H_2O$), sodium chloride (NaCl) and anhydrous sodium sulfate (Na_2SO_4) were used to prepare salt solutions (Fisher Scientific, Pittsburgh, PA) for membrane scaling tests. Dextran (12 kDa MW) and ammonium chloride (NH_4Cl) were used as nutrient sources to prevent bacterial detachment (Sigma-Aldrich, St. Louis, MO). Ethylenediamine-tetraacetic acid (EDTA) was used as a cleaning agent for the membrane monitoring system (Fisher Scientific, Pittsburgh, PA). Glutaraldehyde and phosphate buffered saline (PBS) solution were used during membrane fixation for sample preservation (Sigma Aldrich, St. Louis, MO). Propidium Iodide (PI) solution was used for membrane staining, while the LIVE/DEAD® BacLight Bacterial Viability Kit from Invitrogen (Carlsbad, CA) was used to assess bacterial viability. Scaling and cleaning solutions were prepared using de-ionized (DI) water (electrical conductivity of ≤ 0.2 μS/cm; Milli-Q Water System, Millipore, San Jose, CA).

Biofilm formation on the membrane was achieved using a mixture of unchlorinated secondary treated municipal wastewater (TMW) effluent and tertiary TMW effluent (Table 1) from OCWD's GWRS treatment facility. The secondary TMW effluent consisted of 80% activated sludge effluent and 20% trickling filter effluent (Table 1) with average total dissolved solids concentration of ~1100 mg/L, which was then mixed with tertiary TMW (Section 2.2.2). Mineral saturation indices for the various feed water sources and scaling solution were calculated as $SI_x = IAP_x/K_{sp,x}$, (where IAP_x and $K_{sp,x}$ are the ion activity and solubility products of mineral scalant x, respectively) using a multi-electrolyte thermodynamic simulation software (OLI Systems, Inc., Morris Plains, NJ).

Table 1
Secondary wastewater effluent quality.
Source: Orange County Water District (OCWD) Groundwater Replenishment System (GWRS) treatment facility, Orange County Water District Research Center, Fountain Valley, CA.

Analyte	Concentration (mg/L)
TDS	1100
pH	7.5 (pH units)
Total suspended solids	4
Turbidity	3 (NTU)
Major constituents	
Bicarbonate (as $CaCO_3$)	200
Ca^{2+}	80
Cl^-	250
Na^+	200
SO_4^{2-}	220
Total alkalinity	250
Minor constituents	
K^+	18
Mg^{2+}	20
NH_3–N	20
PO_4–P	1.5
SiO_2	20
Organic N	2
Total organic carbon	15
Bulk saturation indices	
Calcium orthophosphate ($Ca_3(PO_4)_2$) saturation index	5.92
Calcite ($CaCO_3$) saturation index	1.65
Silicon dioxide (SiO_2) saturation index	0.17
Gypsum ($CaSO_4\ 2H_2O$) saturation index	0.04

2.2. Biofouling and mineral scaling

2.2.1. Membrane system

The membrane system (Fig. 1) consisted of a transparent plate-and-frame RO (PFRO) cell allowing direct real-time imaging of the membrane surface. Details of the PFRO system and its hydrodynamics are available elsewhere [52,53]. Briefly, the PFRO cell dimensions were 2.81 cm (width) × 7.7 cm (length) × 0.25 cm (height) with an active membrane surface area of 21.6 cm^2. Water was fed to the PFRO channel from a mixed and temperature controlled 20-gallon feed tank via a high pressure 1/2 hp (373 W) positive displacement pump. Transmembrane pressure was adjusted using a back-pressure regulator with the pressure monitored using a pressure transducer. The feed and permeate flow rates were also monitored continuously.

The PFRO system was operated in two different modes during the biofilm growth (Section 2.2.2) and mineral scaling (Section 2.2.3) stages of the study (Fig. 1). During the inoculation phase of biofilm growth, the solution was circulated in total recycle mode to establish the initial biofilm attachment (with the drain valves closed and feed directly from a feed tank, Fig. 1). During the biofilm growth stage, the PFRO was operated in a single pass mode (with the feed provided directly from filtered secondary TMW effluent, Fig. 1) with the effluent streams and overflow from the feed tank discharged back to the municipal wastewater treatment facility. During this stage, secondary wastewater