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Anti-scale effects of select organic macromolecules on gypsum bulk and surface crystallization during reverse osmosis desalination

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ABSTRACT

Reverse osmosis desalination is increasingly applied to address the global challenge of water scarcity and pollution of available water resources. This study investigates interactions of select organic macromolecules – sodium alginate, humic acid and bovine serum albumin – with the inherent operational limitation of membrane scaling caused by gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) bulk and surface crystallization. Tailored operation of a bench-scale reverse osmosis system demonstrated that severe concentration polarization provoked gypsum surface crystallization as opposed to bulk crystallization and vice versa. Gypsum bulk crystallization was significantly retarded by coexisting macromolecules. Macromolecular adsorption onto growth sites of crystals appeared to be the underlying mechanism of retardation. Supplemental crystallization experiments were performed to determine the prolongation of gypsum induction times in the presence of macromolecules. Macromolecular properties and concentration as well as crystallization kinetics determined the extent of retardation. Scaling by gypsum surface crystallization, however, was enhanced in the presence of sodium alginate and humic acid. The developed macromolecular fouling layers shifted gypsum scaling mechanisms from bulk to surface crystallization. This was most clearly observed for sodium alginate, which caused strongest membrane fouling. A correlation between the extent of fouling and the enhancement of surface crystallization is suggested. Hence, any potential anti-scale effects exhibited by various organic macromolecules, may be superposed by enhanced concentration polarization due to macromolecular fouling.

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1. Introduction

Population growth, urbanization and industrialization are continuously increasing the demand for reliable water resources [1,2]. Climate change and contamination of available freshwater resources further complicate this global challenge [2]. Besides important measures of water conservation and protection of water resources, the only methods to increase available water supply are water reuse and desalination [3]. Desalination by membrane technology contributes to reduce water stress in coastal and inland regions through the production of fresh water from seawater, saline groundwater, drainage water and treated wastewater [1]. Reverse osmosis (RO) has emerged as the leading and most energy-efficient technology for seawater desalination and is the benchmark for comparison for any new desalination technology [2].

An inherent challenge of membrane-based desalination processes is membrane scaling, especially at high water recoveries [4]. The process of membrane scaling is described as the undesired

deposition, accumulation and growth of sparingly soluble salts on the membrane surface [4,5]. Scaling may cause permeability loss [4], decreased rejection of charged solutes [6,7] and irreversible membrane deterioration [8]. Depending on water recovery, membrane rejection properties and operating conditions, the concentrations of sparingly soluble inorganic mineral ions may reach their solubility limit and crystallization of the respective salt can occur [4]. Due to the ubiquitous abundance of calcium and sulfate ions in natural waters, gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is one of the most common scale compounds in membrane processes for brackish water and seawater desalination [4,9–12]. Compared to other common scales, gypsum is especially problematic because of the pH insensitiveness of gypsum solubility [13] and the coherent ineffectiveness of acids in preventing or removing existing gypsum scale.

A prerequisite to crystallization is solution supersaturation with respect to the scale forming mineral salt. Theoretically, supersaturation at any level can cause nucleation, however, a spontaneous homogeneous nucleation of a crystal-free solution does not usually occur until supersaturation exceeds a certain threshold value [14]. Below this threshold value, nucleation only occurs after relatively long induction times have elapsed [15–17] or by being stimulated

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heterogeneously by exogenous surfaces, such as particles, impurities or membrane surfaces [14].

In membrane applications, two extreme scaling mechanisms are reported in literature: (I) surface crystallization and (II) bulk crystallization [18–22]. While the first mechanism (I) describes the heterogeneous nucleation and subsequent crystal growth directly on the membrane surface, the second mechanism (II) describes the homogeneous nucleation in the feed solution and the subsequent deposition and growth of crystals on the membrane surface.

Controversy exists with respect to the prevailing mechanism of scale formation in technical membrane systems. Pervov [23] suggests that crystal formation takes place in the bulk solution due to high supersaturations reached in deadlocks of the membrane module. Contrarily, Uchymiak et al. [24] and Radu [25] recall that observed induction times for bulk crystallization have been reported to be significantly longer than the convective residence time of water in spiral wound RO modules. They suggest that surface crystallization is the primary contributor to membrane scaling. Karabelas and Karanasiou [26] investigated gypsum scaling under comparably realistic conditions and summarize that there is strong indication that incipient gypsum scaling occurs due to growth of surface crystals and not due to deposition of crystals developing in the bulk solution. Obviously, some researchers suggest that scaling in membrane systems is a combination of both scaling mechanisms described above [4,27].

Scaling studies performed with bench-scale membrane systems come along with the inherent limitation of available membrane area. Achievable water recoveries are limited unless permeate is withdrawn and retentate recirculated. In this case, supersaturation may achieve levels where convective residence times exceed induction times and hence bulk crystallization becomes very likely to occur [28]. It has been demonstrated that the occurrence of the two scaling mechanisms depends strongly on the operating conditions of bench-scale membrane systems. Lee et al. [20] as well as Lee and Lee [18] investigated the effects of transmembrane pressure and crossflow velocity on gypsum scale formation using different nanofiltration membrane module configurations (plate-and-frame vs. spiral wound). Gypsum surface crystallization dominated at high transmembrane pressure and low crossflow velocity, whereas gypsum bulk crystallization occurred at low transmembrane pressure and high crossflow velocity. The authors conclude that the severity of concentration polarization, which is strongly dependent on crossflow velocity and permeate flux, i.e. transmembrane pressure, determines the dominating scaling mechanism. Mi and Elimelech [29] hypothesize that the surface chemistry and topography of the membrane surface influence the occurrence of gypsum scaling mechanisms using two membranes of different material (polyamide and cellulose acetate) in laboratory-scale forward osmosis experiments. A very similar study was recently published by Xie and Gray [30]. The importance of surface topography and surface chemical functionality of different polymeric substances on the kinetics of gypsum surface scaling has also been highlighted by Lin et al. [31]. A number of studies investigated the effect of membrane surface changes induced by different fouling layers on gypsum scaling. Thompson et al. [32] reported that established biofilms on RO membranes accelerate gypsum surface scaling by enhanced concentration polarization. The phenomenon of enhanced concentration polarization induced by hindered back diffusion of rejected ions through cake layers on the membrane surface was first described and modeled by Hoek et al. [33] as well as Hoek and Elimelech [34]. Vogel et al. [35] demonstrated the existence of cake enhanced concentration polarization induced by humic acid fouling layers in bench-scale nanofiltration experiments. Organic macromolecules, such as proteins, polysaccharides and humic and fulvic acids, are ubiquitously present in all natural

waters. Membrane fouling due to deposition and adsorption of natural organic matter is almost unavoidable and thus induces physicochemical changes of membrane surface properties [36,37]. Liu and Mi [36] investigated the effects of macromolecular conditioning on gypsum scaling in a bench-scale forward osmosis system. They hypothesize that the high density of carboxylic groups of humic acid and alginate fouling layers attract calcium ions and thereby accelerate gypsum surface crystallization. Additionally, enhanced concentration polarization is claimed responsible for accelerated surface crystallization. An inhibition of gypsum surface scaling by bovine serum albumin (BSA) is explained by the lower carboxylic acidity and steric obstruction. Similar experiments with almost identical conclusions were recently conducted by Wang et al. [37] using a bench-scale nanofiltration system. It is important to notice that Wang et al. [37] and Liu and Mi [36] used very high concentrations of organic macromolecules (200 mg/l and 100 mg/l, respectively) to enhance macromolecular fouling. Accordingly, desorption of macromolecules and their coexistence in solution during subsequent scaling experiments cannot be precluded.

If present in the feed water, organic macromolecules may directly interact with the gypsum crystallization process in aqueous solutions [38–42] and in feed waters of membrane systems [12,19,42]. Generally, an inhibitory anti-scale effect and a change of gypsum crystal size and morphology is observed in the coexistence of various organic macromolecules. Macromolecule adsorption and coverage of gypsum nuclei and active crystal sites is commonly believed to be the underlying mechanism of inhibition [39,41,43,44]. The macromolecule's properties, in particular, the density of surface carboxylic groups and their affinity to calcium ions, are believed to be the key parameters for the different extents of inhibition observed for various macromolecules [39,41].

So far, the complex interactions between organic macromolecules exhibiting distinctively different molecular properties and gypsum scaling have not been systematically investigated during reverse osmosis desalination. Owing to the dissent regarding the relevance of gypsum scaling mechanisms in technical RO systems, our study for the first time aims for an investigation of macromolecule-gypsum interactions individually during gypsum bulk and surface crystallization. This is achieved by tailored operation of a bench-scale reverse osmosis system and the use of three select model organic macromolecules – bovine serum albumin (BSA), humic acid (HA) and sodium alginate (SA). Results from RO experiments are further supplemented by determination of induction times in gypsum bulk crystallization experiments in the presence of the select macromolecules. The investigation of gypsum scaling in the coexistence of naturally occurring organic macromolecules is a fundamental, yet important field of research as both types of water constituents are ubiquitously present in natural waters. A better understanding of potential anti-scale effects of naturally occurring organic macromolecules may aid in optimizing scale prevention strategies and antiscalant dosages in RO systems. Additionally, membrane-assisted crystallization for mineral recovery from RO brines has gained increased attention [45]. Thereby, the identification of interactions between targeted minerals and natural organic matter is of crucial importance.

2. Material and methods

2.1. Reverse osmosis setup

The reverse osmosis experiments were conducted using a bench-scale cross-flow system operated under continuous permeate withdrawal and retentate recirculation. A constant volume of 3.0 L was maintained in the temperature-controlled feed water reservoir ($T = 25.0 \pm 0.1$ °C) by measurement of water level (capac-

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