Rheological and permeability characteristics of alginate fouling layers developing on reverse osmosis membranes during desalination

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ABSTRACT

Rheological property data (practically and theoretically significant) of typical desalination-membrane fouling layers are reported for the first time in this study, involving two stages. First, desalination of brackish water (with 30 mg/L sodium alginate) was carried out under constant flux; Ca^{2+}-ion concentration 1 mM–8 mM was used. Linear temporal trans-membrane pressure increase, associated with constant specific fouling resistance α, indicated uniformity of growing alginate layers. Fouling resistance α increased with calcium concentration. Subsequently, fouled membrane segments were tested in a parallel-plate rheometer, operating in oscillatory and steady shearing modes. Key rheological parameters of fouling layers, including storage (G') and loss (G'') moduli, complex and shear viscosities, were assessed in relation to their permeability and other characteristics. Alginate fouling layers possess viscoelastic properties characteristic of rather stiff gels; moreover, they belong in the class of thixotropic materials with yield stress. Layers from feed-water of small Ca^{+2}-ion concentration exhibit strong elastic character, high viscosities and yield stresses; the elastic character and rheological parameter values are reduced with increasing Ca^{2+}-ion concentration. The high Na-ion concentration in the fouling layers appears to significantly influence their structure; however, considering the complicated dynamics of developing layers, the relative significance of the abundant Na-ions compared to Ca^{2+}-ions is unclear.

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1. Introduction

Polysaccharides are hydrophilic poly-hydroxyl compounds, which (together with proteins and lipids) are present in seawater [1], surface waters [2,3] and biologically treated effluents [4,5], commonly processed by RO, NF and UF membranes for desalination and water purification [1–5]. There is plenty of evidence [6,7] that polysaccharides, even at rather small concentration in the aforementioned feed-waters to membrane processes, play a key role in membrane fouling and performance degradation. In fact, there is evidence (e.g. [8–10]) that polysaccharides tend to form coherent fouling layers and to act as "binders" in deposits with other foulants such as humic acids and colloidal particles [8–11]. Of particular interest are the following recent results [12], based on autopsies of leading spiral wound membrane (SWM) elements in pressure vessels from two seawater RO plants (located in different geographical areas):

– Gelatinous material, comprised of hydrophilic high molecular weight compounds with high water content ($\sim$95%) was responsible for membrane fouling.
– Approximately 70% of the dried foulants were organic matter. LC-OCD/ OND analyses showed C and N elemental membrane surface density 77.6 mg-C/m^2 and 11.5 mg-N/m^2. The main "biopolymers"-foulants identified were polysaccharides and proteins.

It is noted that the aforementioned high water content of membrane fouling layers is characteristic of polysaccharide gels [13]. Sodium alginate (SA) used in the present tests is a typical polysaccharide, commonly employed in membrane fouling studies [3,4].

Alginate fouling layers forming on RO membranes during desalination, and the expected concomitant enhancement of concentration-polarization effects [14], can cause significant pressure increase in constant flux filtration as well as degradation of membrane ion rejection. Knowledge of the rheological properties of fouling layers is crucial to understanding their behavior, under the flow conditions and prevailing stresses within the narrow channels of SWM

elements; such information can also offer valuable insights into the membrane fouling mechanism. In particular, correlation of key rheological parameters with the bulk fluid (i.e. feedwater or retentate) composition and flow field properties is considered essential for the development of efficient methods to mitigate fouling and/or clean the membranes. To the best of the authors' knowledge, rheological properties of thin organic layers developing on membranes are presented here for the first time. Indeed, the rheological characteristics of organic layers on RO membrane, formed in a highly dynamic environment characterized by tangential shear stresses due to cross-flow and compressive stresses due to trans-membrane pressure [15] are largely unknown. Although a significant amount of rheological data are available, they exclusively concern alginate gels prepared in the laboratory by various protocols (e.g. [16–19]) and not gels from membrane—filtered dilute solutions as in the present study.

The physical properties of alginate gels, including rheological properties, have been extensively studied. Alginates are linear unbranched copolymers composed of (1–4) linked b-D-mannuronic acid (*M-block*) and a-L-guluronic acid (*G-block*). The mannuronic to guluronic ratio appears to have a significant impact on complexation with cations and on gel structure [20–22]. Great attention have received Ca^{2+}-alginate gels, characterized by ion-mediated junction zones [23,24] holding polymer chains together through physical forces, ionic interactions, and hydrogen or van der Walls bindings. There is evidence that the Ca^{2+} ions bind preferentially to the guluronate units (G-blocks) than to M-blocks [25,26]. In addition, it has been reported [27] that Ca^{2+} ions can replace hydrogen of the carboxyl functional group of the G-blocks, which can physically fold to develop a cavity; this is apparently not the case for the carboxyl functional group of the M-blocks. The so-called "egg-box" gel-structure model [28], where alginate chains adopt a helical conformation, has been used to describe the association between alginate polymer chains and divalent cations such as calcium, which is located in the aforementioned cavity of a pair of guluronate chains [27,28]. Regarding the rheological behavior of alginate gels, it has been reported that non-Newtonian behavior exists even at low concentrations of about 1 to 2 w/v%, with extensive lower Newtonian plateau before the shear thinning region; however, the corresponding viscosity exhibits a remarkable increase, more than an order of magnitude, with alginate concentration increasing to 5% [16]. Accordingly, the elastic modulus G' of the 2% alginate gels increases by approx. an order of magnitude, from 10 Pa to 100 Pa for the same frequency (1 Hz), with concentration increasing to 5% [16]. It should be noted that the grade of the raw material is apparently of importance since it has recently been reported that an increase of an order of magnitude of the viscosity (shear or complex) might be expected for the same wt% alginate concentration, for different grades of raw material [29]. The results of these and other similar studies are generally helpful for interpreting the properties of gel layers developing under different conditions.

In the following section, the RO desalination experiments, to develop the membrane fouling layers, and the subsequent rheological measurements are described in fair detail. Presentation and discussion of results is made in the next section; RO fouling layer characteristics including specific resistance to permeation are presented first, followed by the measured rheological properties. A comparative assessment of the new data is made in relation to relevant literature; finally, conclusions and further research needs are outlined.

2. Experimental part

2.1. RO membrane fouling tests

The experimental set-up is described elsewhere [30,31] and only a summary is provided here. The experiments are performed in a laboratory-scale unit with a stainless steel cross-flow filtration section where flat sheet membrane pieces are fitted. This unit is comprised of two steel plates; in the bottom plate a porous stainless steel sheet is embedded on which the membrane rests. By means of a spacer/flange, a rectangular channel is formed of uniform ~1 mm gap. The effective membrane area is 1.30×10^{-2} m^2. No retentate-side spacer was employed in order to obtain a smooth surface of the fouling layer, facilitating the ensuing rheological measurements. A brackish water RO desalination membrane (Hydranautics CPA2) was used in all tests; this is a polyamide thin-film composite membrane with an average salt rejection 99.5%, as reported by the manufacturer.

Pressure and cross-flow rate were monitored through sensors at the entrance and exit of the test section, respectively. The permeate volume was continuously recorded, and transformed to flow rate, via the program GeniDAQ 4.25. *Constant flux operation* was maintained through the GeniDAQ software, using an inverter to adjust the high pressure pump motor [15]. Thus, the permeate flow rate was the continuously measured control variable, whereas the imposed pressure increased with fouling layer growth. Moreover, in all RO tests, needle valves were manually adjusted to maintain constant superficial retentate cross flow velocity at 30 cm/s. For this cross-flow velocity, the mean shear stress at the membrane surface in the test channel is 2.57 Pa, which is the same as the space-averaged wall stress prevailing in a spacer-filled channel at a superficial velocity ~21 cm/s [32,33]. In operating RO plants, cross-flow velocity approx. 20 cm/s usually prevails at the entry SWM elements of a pressure vessel, where the most severe conditions for colloidal fouling are encountered. Temperature of feed stream is controlled at 25 ± 0.1 °C through a cooling coil submerged in the feed water vessel and, together with pH and conductivity, it is recorded via a multimeter (InoLab 750 pH/Ion/Cond multilab-WTW). To better simulate real systems, an *open loop operation* is implemented by the continuous introduction of water with foulants into the test section and subsequent disposal of both permeate and retentate. A fresh concentrated solution of sodium alginate in deionized water is injected into the feed water mixing tank (of capacity 27 L) at a rate such that a final feed water concentration of ~30 mg/L is obtained, whereas pH is adjusted to 7.0. The feed water flow rate in the mixing vessel is 1.8 L/min, and thus the mean residence time of water and fouling species therein is approximately 15 min. Tap water is used as the basic feed water, which passes sequentially through a ~1 m high sand filter and a 1 μm cartridge filter to reach a turbidity less than 0.1 NTU. A typical analysis of this water is reported elsewhere [15]. Concentrated solutions of re-crystallized natural salt and of CaCl$_2$, were injected in the feed vessel at appropriate rates to achieve the desired final solution composition.

The salinity of feed-water for the present experiments was 2000 mg/L TDS, with addition of NaCl only; the corresponding natural water Ca^{2+} was 1 mM. With CaCl$_2$ addition, the Ca^{2+} concentration was adjusted within the range 1 mM to 8 mM. In all tests, the RO permeate flux was kept constant at a typical value ~20 L/m^2 h (Table 1). An important consideration in this study was to establish a stable membrane performance (in terms of pressure and rejection) before addition of the fouling species. Thus, prior to a RO fouling test, there was a membrane setting period using solution composition and testing conditions similar to those in the ensuing fouling experiment. Consequently, the observed changes in system performance (i.e. increasing trans-membrane pressure) could be safely attributed to the net effect of foulant addition. In each experimental run, usually ~3 h were dedicated to membrane setting with clean feed water.

Commercial sodium alginate (A-2158, Sigma–Aldrich, St. Louis, MO) extracted from brown algae was used as received. For this SA