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Studying the impact of RO membrane surface functional groups on alginate fouling in seawater desalination

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ABSTRACT

Despite extensive studies on the relationship between membrane surface properties and fouling, the roles of specific surface functional groups in RO membrane fouling under different solution conditions are still poorly understood. This research aims to elucidate how specific surface functional groups affect RO membrane fouling by alginate in solution conditions relevant to seawater desalination. Common RO membrane surface functionalities are represented by self-assembled mono-layers with –COOH, $-NH_2$, $-CONH_2$ and –OH ending groups. Alginate adsorption and removal was studied under relevant solution conditions using quartz crystal microbalance with dissipation monitoring (QCM-D). The results show that ionic composition has great impacts on alginate–alginate interaction, which is more important than membrane surface chemistry in determining alginate adsorption equilibrium at the high ionic strength of seawater. The initial adsorption rate is highly sensitive to surface chemistry. The $-NH_2$ group has strong affinity for alginate, yet the –COOH group exhibits the highest adsorption rate in simulated seawater. The reversibility of the adsorbed layer was influenced by both alginate–surface interaction and the structure of the layer. The large alginate aggregates formed in the presence of Ca^{2+} result in loosely packed and less viscous adsorbed layer on the surface, which is easier to remove by surfactant cleaning.

1. Introduction

Advances in thin film composite membranes in the past few decades have made reverse osmosis (RO) a prominent technology for seawater desalination [1]. However membrane fouling still remains a critical issue that impedes the wide application of RO desalination. Depending on the feed water quality and operating conditions, RO membranes can be fouled by mineral precipitation [2], attachment of colloids and dissolved organics [3,4], and growth of microbes on the membrane surface [5,6]. Amongst them, organic fouling is a major concern in seawater RO [7]. Organic fouling is rapid; organic foulants attached are difficult to remove completely by membrane cleaning, which causes continuing change in membrane surface properties and therefore easy re-fouling; the organic fouling layer can also serve as a conditioning layer for microbial attachment and growth, i.e., biofouling [8].

The composition of dissolved organic matter (DOM) in seawater is very complex. Most constituents of marine DOM have not been characterized at the molecular level [9]. Of the identified portion of marine DOM, carbohydrates are the major constituents [9,10]. Polysaccharides such as alginate, which is commonly produced by various algae and bacteria, are known to severely foul membrane surfaces [11]. Many studies have correlated organic fouling with the macroscopic physiochemical properties of the membrane surface. Membrane surface properties such as surface roughness, hydrophobicity and charge have been shown to largely control adhesion of organic foulants to the membrane surface [12]. In addition, specific interactions between functional groups on the foulant molecule and those on the membrane surface can contribute greatly to organic fouling. For example, many studies have shown evidence of bridging between carboxyl groups on the membrane surface and foulant molecules by divalent cations, which greatly increases fouling rate [13–15]. In the study by Li and Elimelech, the interaction forces between the surface of a commercial nanofiltration (NF) membrane and carboxylate modified latex particle were measured using atomic force microscopy (AFM) [13]. Measurements showed increased adhesion force between the two in the presence of Mg^{2+} or Ca^{2+} compared to Na^{+} alone, and the increase was much greater when Ca^{2+} was present; the greater adhesion in the presence of Ca^{2+} was attributed to the bridging of –COOH by Ca^{2}. The membrane flux decline correlated well with the measured interaction forces. Jin and coworkers correlated the flux decline rate during alginate

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fouling of an RO membrane at the initial and later stages with the free energy of adhesion (i.e., alginate-membrane) and the free energy of cohesion (i.e., alginate–alginate) respectively, and discovered significant increase in flux decline and decrease in both free energy values when Ca^{2+} was in the solution [14]. Mo et al. tested two laboratory-fabricated NF membranes with similar surface hydrophobicity and roughness under conditions when influence of surface charge is negligible, the membrane with fewer carboxyl groups showed better resistance to alginate fouling; this was attributed to the fewer surface sites for bridging with alginate by Ca^{2+} [15].

Besides the direct influence on adhesion of organic foulants, functional groups on the membrane surface are also closely related to the physicochemical properties of the membrane. The active layer of most commercial RO membranes is polyamide formed by interfacial polymerization of aromatic amine and aromatic acyl chloride monomers [16,17]. This gives the membrane surface carboxyl, amine and amide groups. Carboxyl and amine groups change their protonation states with pH, which largely determines membrane surface charge. The three groups have different hydrophobicity and therefore contribute to the macroscopic hydrophobicity of the membrane surface [18].

The above studies suggest that membrane surface functional groups could play important roles in membrane fouling during seawater desalination. To date there has been little research on the influence of surface functional groups on the adsorptive fouling by dissolved organic matter, largely because of the physical and chemical heterogeneity on typical RO membrane surfaces. In a previous study, we used self-assembled monolayers (SAMs) with desired ending functional groups to create chemically homogeneous surfaces and investigated the influence of seven specific functional groups (–CH_3, –O-phenyl, –NH_2, ethylene-glycol, –COOH, –$CONH_2$, and –OH) on the adsorption of alginate and BSA at a low ionic strength of 10 mM [18]. Results show that specific interactions between the organic foulants and SAM surface functional groups, such as hydrogen bonding, play a more important role than the non-specific electrostatic and hydrophobic interactions; the organic foulant adsorption equilibrium and kinetics as well as the dynamic structure of the adsorbed foulant layer strongly depends on the specific surface functional groups. These measurements provide important insight on interactions between protein and polysaccharide foulants and various membrane surface functional groups in solution conditions relevant to surface water purification and wastewater reclamation applications. However, because the range of solution conditions (e.g., ionic strength and ionic composition) tested in this study was limited, the impact of membrane surface chemical functionality on organic fouling in other important applications such as seawater desalination is still unclear. Solution condition is known to strongly influence fouling behavior by altering the physicochemical properties of the surface as well as those of the foulants [19,20].

In the study reported here, we use a similar approach to study the influence of RO membrane surface chemistry on alginate adsorptive fouling under solution conditions relevant to seawater desalination. Surface functional groups commonly found in polyamide RO membranes (–COOH, –NH_2, –$CONH_2$) were studied using SAMs with corresponding ending functional groups, and alginate adsorption and subsequent desorption during chemical cleaning were characterized using the quartz crystal microbalance with the dissipation (QCM-D) monitoring technique. The roles of major surface functional groups on polyamide membranes as well as solution condition, namely ionic strength and composition, in alginate adsorption equilibrium, kinetics and reversibility were elucidated and the implication on alginate fouling during seawater RO was discussed.

2. Experimental

2.1. Materials

Five alkanethiols, namely 1- Dodecanethiol, 11-Mercaptoundecanoic acid, 11-Mercaptoundecanamide, 11-Hydroxy-1-Undecanethiol and 11-Amino-1-undecanethiol hydrochloride, were purchased from Asemblon (Remond, WA) in powder form, and were stored in 4 °C. Reagent grade NaCl, $MgCl_2 \cdot 6H_2O$, $CaCl_2 \cdot 2H_2O$, HCl, and sodium alginate derived from brown algae (A2158) were purchased from Sigma Aldrich (St. Louis, MO). A commercial sea salt Instant Ocean (Spectrum Brand, Inc., Madison, WI) was used to prepare synthetic seawater. Sodium dodecyl sulfate ($\geq 99\%$) was purchased from IBI Scientific (Peosta, IA). Organic solvents used include ethanol (200 proof, Decon Laboratories, Inc., King of Prussia, PA), Toluene (andydrous, 99.8%, Sigma-Aldrich, St. Louis, MO), and Acetone (99.7%, Fisher Scientific, Pittsburgh, PA). The gold coated crystal QCM-D sensors were purchased from Q-sense (Glen Burnie, MD). Ultrapure water (≥ 18.1 MΩ cm) produced by an E-Pure system (Barnstead, Batavia, IL) was used for all aqueous solutions.

2.2. Methods

2.2.1. SAM preparation and characterization

SAMs, each with a different ending functional group, were prepared on gold-coated quartz crystal QCM-D sensors via a two-step immersion procedure. The functionalities studied include –COOH, –NH_2, –$CONH_2$ and –OH. The first three are essential functionalities in polyamide based membranes while –OH is commonly found in surface coatings for hydrophilic or antifouling modification. Prior to SAM preparation, the crystal sensors were cleaned by sonicating twice in toluene, acetone and ethanol, respectively, in a sonication bath (Bendeline Sonorex, London, England) for 10 min in each step. After cleaning the crystals were dried with ultra-pure nitrogen and cleaned in an UV/ozone chamber (ProCleaner Chamber, Bioforce Nanoscience, Ames, IA) for 30 min. Cleaned crystals were first immersed in 1 mM alkanethiol solutions of desired end groups for 24 h. The pH of the 11-Mercaptoundecanoic acid and 11-Amino-1-undecanethiol solutions was adjusted to 2 and 11 respectively using 0.2 M HCl and 30% NH_4OH to reduce the electrostatic repulsion between the alkanethiol chains in order to form an ordered SAM. After the first immersion step, the crystals were transferred to 1 mM dodecanethiol solutions and immersed for another 24 h to obtain better SAM coverage. The crystals were then thoroughly rinsed with 200-proof ethanol and dried with ultrapure nitrogen. For each immersion steps the thiol solutions were freshly prepared immediately before the experiment and purged with pure argon to remove dissolved oxygen that could oxidize the alkanethiols.

Static water contact angle in air was measured on each SAM-layer using the sessile drop method with a CAM 200 contact angle analyzer (KSV instrument Ltd., Helsinki, Finland). Measurements were conducted immediately after formation of SAMs and contact angle values reported were averages of five measurements on each crystal.

2.2.2. Salt solutions

The recipes of the four salt solutions used in the experiments are summarized in Table 1. The solutions were designed to simulate seawater ionic strength and study the impacts of major cations. Synthetic seawater was made by dissolving 32 g Instant Ocean sea salt in 1 L of water. The ionic concentrations of Na^{+}, Mg^{2+} and Ca^{2+} in the synthetic seawater were measured by ICP-OES (Optima 4300, Perkin Elmer). The total ionic strength of the Instant Ocean solution was calculated based on these major ions, assuming Cl^{-} was the only anion. The calculated value is