Effect of iron on membrane fouling by alginate in the absence and presence of calcium

Yongjia Xin, Mark W. Bligh, Andrew S. Kinsela, T. David Waite *

School of Civil and Environmental Engineering, The University of New South Wales, Sydney, NSW 2052, Australia

A B S T R A C T

While the effects of calcium addition on membrane fouling by alginate have been extensively investigated, there exists little research into the impact of iron concentrations on the fouling behavior of this model polysaccharide. In this paper, the bulk solution characteristics of Fe-alginate assemblages such as size and zeta-potential were determined as were the properties of the materials deposited on flat sheet membranes at different iron and alginate concentrations under steady-state constant pressure filtration conditions. Biphasic filtration behavior of Fe-alginate was observed with highly impermeable gels formed at low iron concentrations, and reduced fouling at high iron concentrations with increased particle sizes observed in bulk solution. Any beneficial effects of iron addition, however, were strongly dependent on the concentration of alginate present. Increased alginate concentrations led to increased Fe-alginate complexation, stabilization of Fe-alginate aggregates and thus more severe fouling. Furthermore, calcium additions were found to strongly influence the properties of the Fe-alginate fouling layer with the presence of calcium inducing the formation of larger aggregates which formed fouling layers with greater surface roughness and lower specific cake resistance and porosity. The material properties of the Fe-alginate, Ca-alginate and Fe–Ca-alginate assemblages formed on flat sheet membranes were also compared and empirical expressions describing the hydraulic conductivity and compressibility of fouling layers developed as a function of trans-membrane pressure.

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1. Introduction

Although the use of membrane bioreactors (MBR) has increased dramatically in recent years as a result of both the effectiveness of the treatment and the decreasing cost of membranes, significant issues remain with regard to managing membrane fouling. While coarse bubbling in the membrane zone is reasonably effective at removal of large sludge particulates from the membrane surface, particular problems are experienced with the gelatinous assemblages that are formed on retention of soluble microbial products (SMP) present in the MBR supernatant [1–3]. The well-recognized, limited removal of soluble contaminants such as phosphorus is another disadvantage of MBR technology. Commonly, chemicals such as ferric and ferrous chloride are added to assist in phosphorus removal (and are also widely used for odor control) with the most appropriate chemical dependent upon both precise treatment configuration and local chemical costs [4]. However, iron addition often increases the severity of membrane fouling.

The polysaccharide component of SMP is generally considered to be the major source of membrane fouling [2,5] due to the formation of gelatinous assemblages as a result of the strong association between carboxylic acid functional groups present in the SMP and divalent or multi-valent metal ions [5]. Alginate has been commonly used as a model polysaccharide in membrane fouling studies [6,7] and is used to investigate the effect of iron addition on membrane fouling in the studies described here. The algae-derived polysaccharide, alginic acid, is a linear anionic copolymer and consists of α-L-guluronate (G) and 1,4-linked β-D-mannuronate (M) residues arranged in a non-regular pattern of varying proportions [8,9]. Furthermore, inconsistent sequential distributions of GG, MM, and MG blocks exist along the polymer chain depending on the source of the alginate, with the flexibility (elasticity) of the polymer series increasing in the order GG < MM < MG [10,11]. The alginate carboxyl groups play a key role in the gelation of this polysaccharide with the presence of divalent or multi-valent cations critical to the nature and extent of the gels formed [12]. Ca-alginate gels have been widely studied with a strong focus on the nature of calcium binding by the G blocks and the resultant "egg-box" structure that is formed [13]. Interest in the formation and nature of Ca-alginate gels has been high because of their widespread use in cell encapsulation [14],

* Corresponding author.
E-mail address: d.waite@unsw.edu.au (T.D. Waite).

wound dressing [15,16] and other areas including food, cosmetics and agriculture [17].

Fe-alginate gels are of emerging interest as a result of their existing and potential application in the field of drug delivery systems, particularly given their biocompatibility [18–21]. Furthermore, the formation and properties of these gels may provide important insights into fouling behavior in MBR wastewater treatment given their likely similarity to the Fe-polysaccharide assemblages that will be present in such systems. Fe-alginate ionic cross-links are established between negatively charged alginate carboxyl groups and positively charged iron through electrostatic interactions. Recent studies of the gelation mechanism of alginate solutions in the presence of ferrous (Fe(II)) iron using confocal Raman spectroscopy and viscoelastic measurements indicate relatively low binding ability of iron cations to alginate urinate chains, with the formation of random aggregates observed to occur, in contrast to the rod-like structure exhibited by high-affinity Ca-alginate gels [22]. While these insights are useful, they provide little information on the interaction of alginate with ferric (Fe(III)) iron, especially in the circum-neutral pH range where the solubility of ferric iron (Fe(III)) is extremely limited.

While we have recently made progress in understanding the relationship between suspension properties of Ca-alginate assemblages and the corresponding membrane fouling behavior for different alginate and calcium concentrations [23], limited insight into the relationship between relative polysaccharide and iron content and membrane fouling is available. For example, how do the gel layer properties of Fe-alginate assemblages differ from those of Ca-alginate assemblages? Does Fe-alginate show similar biphasic fouling behavior to that recently observed for Ca-alginate [23]? Furthermore, how does the presence of calcium influence the Fe-alginate interaction and the associated fouling behavior? Considering the almost ubiquitous use of iron as coagulant, the amount of information available with regard to its contribution to, or mitigation of, fouling behavior in the treatment of wastewaters is surprisingly small. This paper addresses the issues raised above by examining the characteristics of the fouling layer formed from solutions containing various alginate and iron concentrations in the absence and presence of calcium, using constant pressure dead-end filtration methods, material properties characterization and electron micrograph imaging.

2. Materials and methods

2.1. Materials

Depending on the required iron concentration, stock solutions of 0.3, 10, 50 and 100 mM Fe(III) were prepared by dissolving an appropriate amount of $FeCl_3 \cdot 6H_2O$ (Sigma) in 2, 10 and 50 mM HCl with stock solutions retained for no longer than one week. Sodium alginate (Sigma-Aldrich Product no. 180947) that was mannuronate-rich (61% M, 39% G) with molecular weight (MW) ranging between 120,000 and 190,000 g mol^{-1} was used as received in all filtration experiments. Sodium alginate solutions of 0.1 and 0.4 g L^{-1} were prepared in high-purity water (Milli-Q, Millipore) containing 50 mM NaCl background electrolyte and 2 mM morpholinepropanesulfonic acid (MOPS) and 1 mM $NaHCO_3$ as buffer (resulting in pH ~7) with mechanical stirring until well dispersed. If investigating the effect of calcium, Ca-alginate solutions were prepared by adding the desired amount of $CaCl_2$ to alginate solution followed by overnight stirring. Fe(III) stock solution was subsequently pipetted into the solution of interest to achieve the required iron concentration, followed by fast mixing. The pH was adjusted by acid/base addition to 7.50 with the pH measured using an Orion 5 Star multifunctional meter (Thermo Electro Corporation, USA) prior to filtration.

2.2. Analytical methods

2.2.1. Zeta-potential and size

Sodium (or, in some cases, calcium) alginate solutions were stirred overnight, the pH adjusted to 7.50 after iron addition then the zeta-potential and size of Fe-alginate aggregates measured by laser Doppler micro-electrophoresis and dynamic light scattering (DLS) respectively using a Malvern Zetasizer Nano ZS. A Malvern 2000 Mastersizer was used when alginate sizes were too large (> 0.5 μm) for DLS measurement.

2.2.2. Viscosity

The viscosity of samples (prepared in the same manner as for the Fe-alginate size measurements) was determined using a DV-79 digital viscometer (Shanghai Bilon Instrument Co. Ltd.).

2.2.3. Determination of extent of adsorbed alginate

Thirty minutes after the addition of ferric iron to the alginate solution, an aliquot of the supernatant was removed by syringe and filtered through a 0.45 μm Millex-HN filter. The total organic carbon (TOC) content of the filtrate was determined using a Shimadzu TOC-5000 analyzer and the concentration of alginate in the supernatant determined from the TOC content by reference to a calibration curve relating alginate concentration to TOC content. The concentration of alginate adsorbed to any iron oxyhydroxides formed (in the 30 min following ferric iron addition) and which did not pass through the 0.45 μm filters was determined by subtracting the supernatant alginate concentration from the total concentration of alginate used. While particles of size less than 0.45 μm may pass through the filter and the organic content of these particles be determined in the TOC analysis, the extent to which this occurs is expected to be minimal in view of the relatively large size of assemblages formed under the conditions used in these studies.

2.2.4. Kinetics of Fe(III) complexation by alginate

The competitive ligand method was used to determine the rate of complexation of ferric iron by alginate [24]. Sulfosalicylic (SSA) was used as the competing ligand as it binds Fe(III) with a known rate constant of $k_{SSA} = 3.5 \times 10^4 \, M^{-1} \, s^{-1}$ [24] and forms a colored complex, the rate of formation of which, at different alginate concentrations, can be used to determine the rate constant for formation of the Fe-alginate complex. An appropriate amount of alginate was mixed with 100 mM SSA stock solution in 10 mM MOPS buffer solution (with 50 mM NaCl) to create a 2 mM SSA solution with alginate concentrations of 0.2, 0.5, 0.75, 1 and 2 g L^{-1}. After adjusting solution pH to 7.5 by acid/base addition, a 10 mL aliquot was transferred to a 10 cm pathlength reduced volume cuvette in a Cary 50 Bio UV-vis spectrophotometer and the instrument zeroed. The solution in the cuvette was then spiked with 0.3 mM Fe(III) stock to generate a final concentration of 1.5 μM Fe and mixed by shaking. The concentration of the Fe(III) SSA complex formed over time was then determined spectrophotometrically. Further details of the competitive ligand method are provided in Supporting Information.

2.2.5. Calcium binding to alginate

The binding of calcium to alginate during iron addition was examined by measuring the activity of free calcium ions (using an Orion ion selective electrode in conjunction with an Orion 5 Star multifunctional meter) in the Fe–Ca-alginate solutions. The calibration curves for the ion selective electrode were developed using $CaCl_2$ solutions of known concentration. The possible effect of alginate (or other solution components) on free calcium