Journal of Membrane Science 475 (2015) 395–405

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Calcium-mediated polysaccharide gel formation and breakage: Impact on membrane foulant hydraulic properties

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

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

ARTICLE INFO

Article history:
Received 9 June 2014
Received in revised form
14 October 2014
Accepted 17 October 2014
Available online 29 October 2014

Keywords:
Calcium
Alginate
Gelation
Membrane fouling
Filterability

ABSTRACT

The solution phase interaction between the polysaccharide alginate and calcium at various concentrations is examined in this paper. The observed gelation behavior and resulting hydraulic properties of the fouling layer deposited on flat sheet membranes can be directly related to the initial calcium concentration (in bulk solution). Particular attention is given to the effect of calcium concentration, with changes in calcium binding behavior of alginate in bulk solution shown to be closely related to the resistance of the cake layer formed on the membranes. At low calcium concentrations, Ca^{2+} ions interact strongly with guluronate (G) block functional groups forming a highly interconnected gel assemblage. This resulted in the fouling layer deposited on the membrane surface exhibiting high specific resistance despite being highly porous. Further increase in calcium concentration leads to enhanced calcium binding and significant aggregation of alginate in suspension with concomitant breakdown in the gel structure of the material accumulated on the membrane. The increased calcium concentration resulted in a cake that was characterized by a lower porosity and higher solid fraction and, most importantly, a markedly lower specific resistance to the passage of water. The materials properties of the alginate layers formed on flat sheet membranes were also determined under various pressures, with empirical expressions describing the hydraulic conductivity and compressibility of fouling layers developed as a function of trans-membrane pressure (TMP) for a range of calcium concentrations. The resulting materials properties expressions could be applied for the prediction of the filtration behavior of an alginate-rich solution for a range of calcium concentrations under constant flux (and thus time varying TMP) conditions.

1. Introduction

The use of submerged membrane bioreactor (MBR) technology has increased dramatically over the last 10 years due in part to its advantages over conventional activated sludge (AS) treatment including reduced footprint, superior effluent quality, and treatment efficiency independent of sludge-settling characteristics. However, significant challenges remain especially with regard to reducing the severity of membrane fouling. It is now recognized that organic compounds present in the sludge supernatant are the principal cause of severe fouling, particularly as operating procedures such as bubbling coupled with intermittent filtration are reasonably effective at removing sludge particulates from the membrane surface during routine operation [1–3]. Compounds present in the sludge supernatant include soluble and colloidal microbial products (SCMPs) such as proteins and polysaccharides with general consensus [1,4] that the polysaccharide component is a particularly significant contributor to fouling. Wang and Waite [4] have shown that the presence of calcium cations is critical to SCMP gelation and associated occurrence of severe membrane fouling with these divalent metal ions inducing bridging between polysaccharide groups, particularly as a result of binding to carboxylic acid sites present in the polysaccharides.

Polysaccharides make up 10–30% of the dissolved organic carbon (DOC) content in lakes [5], up to 50% of the DOC in marine waters [6] and typically constitute around 35% of the DOC in MBR supernatants [7]. The exopolysaccharide content of wastewater sludge supernatant is recognized to be a key to the formation of aerobic granules [8,9] and alginate-like exopolysaccharides (ALE) have recently been extracted from laboratory [10] and pilot-scale [11] reactors. This ALE has been shown to contain a high percentage of poly-guluronic acid (G) blocks that are also capable of forming rigid and non-deformable gels when linked by calcium cations. Alginate is a naturally derived linear anionic copolymer and consists of α-L-guluronate (G block) and 1,4-linked β-D-mannuronate (M block) residues arranged in a non-regular pattern by varying proportions and sequential distributions of GG, MM, and MG blocks along the polymer chain depending on the source of the alginate [12,13] and

---

* Corresponding author. Tel.: +61 2 9385 5060; fax: +61 2 9313 8341.
E-mail address: d.waite@unsw.edu.au (T. David Waite).

http://dx.doi.org/10.1016/j.memsci.2014.10.033

is recognized to form gel layers in the presence of divalent cations such as calcium. The interaction between calcium and alginate is generally conceptualized in terms of an "egg-box model" proposed by Grant et al. [14] where cooperative binding involving two or more rigid and buckled guluronic chains with the coordinated calcium ions "packed" into the sites are created between the chains.

The calcium content of wastewaters is typically in the range of 1.5 to 11 mM [15] with the actual content determined particularly by the hardness of the source drinking waters. In addition, lime ($Ca(OH)_2$) is used for pH adjustment in wastewater treatment with the required lime dosage depending primarily on the alkalinity of the wastewater [16]. As such, the polysaccharide content combined with the concentration of calcium present might be expected to play an important role with regard to the extent and severity of membrane fouling associated with gel formation.

While the importance of the polysaccharide and calcium content of wastewaters to gel formation and resultant membrane fouling is now well-recognized, limited insight into the effect of the relative polysaccharide and calcium content on the severity of membrane fouling is available. Important questions include "What is the relationship between suspension characteristics and filtration behavior?", "Does the gelling propensity of polysaccharides increase linearly with an increase in calcium or alginate concentration?" and "How does the resistance of the fouling layer vary as calcium is added in excess of the polysaccharide binding capacity?". Here, we aim to further the understanding of Ca–alginate interactions and implications of these interactions to filtration using alginate as a model of polysaccharides present in wastewaters. Ca–alginate solutions exhibiting a range of calcium concentrations have been characterized in terms of calcium binding behavior and assemblage size with the resultant fouling layers formed on membranes investigated using dead-end filtration methods, with the specific purpose of linking the interactions occurring in bulk solution to filtration properties.

2. Materials and methods

2.1. Materials

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 Ca-binding and filtration experiments. Sodium alginate solutions of 0.1, 0.4 and 1.0 g/L were prepared in high-purity water (Milli-Q, Millipore) with 50 mM NaCl background electrolyte and 2 mM morpholinepropanesulfonic acid (MOPS) and 1 mM $NaHCO_3$ as buffer (resulting in pH ~7) and were mechanically stirred until well dispersed. Ca–alginate solutions were prepared by adding the desired amount of $CaCl_2$ followed by overnight stirring. The pH of the solution was then adjusted by acid or 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. Bulk solution

2.2.1. Calcium binding to alginate

The binding of calcium to alginate 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 Ca–alginate solutions after overnight equilibration. The calibration curves for the ion selective electrode were derived using $CaCl_2$ solutions of known concentrations. Free calcium measurements were also carried out using dialysis bags with the results from these studies confirming that interference of the probe by either the alginate or Ca–alginate complex was not occurring.

2.2.2. Viscosity

Viscosity measurements of samples prepared in the same manner as for the Ca–alginate binding experiments were undertaken using a DV-79 digital viscometer (Shanghai Bilon Instrument Co. Ltd.).

2.2.3. Size

The sizes of aggregates in the Ca–alginate solutions were measured using dynamic light scattering (DLS) (Malvern Zetasizer Nano S). Sodium alginate solutions after overnight stirring were adjusted to pH 7.5 and filtered (0.45um Millex-HN syringe) prior to calcium addition in order to remove dust and large aggregates. The concentration of alginate in the solutions was unchanged by filtration as determined by total organic carbon (TOC) (Shimadzu TOC-500) measurements. Size was measured immediately after calcium addition with no significant change evident after sitting for 24 h.

2.3. Filtration studies

2.3.1. Filtration setup and procedures

The filtration set-up consisted of a small acrylic filtration cell (2 cm in height with an effective filtration area of 1.52×10^{-3} m^2) connected by a short Teflon tube to a 2 L reservoir containing a magnetic stirrer bar and pressurized with high purity nitrogen gas. A pressure controller (Bronkhorst P-602C) was used to set and maintain precise and constant required pressures in the range from 10 to 150 kPa (±0.1%). Durapore polyvinylidene fluoride (PVDF) 0.1 μm pore size flat sheet membrane (Millipore, Bedford, MA) was inserted in the base of the filtration cell to retain the Ca–alginate gel, and accumulated filtrate mass was logged using an electronic balance connected to a personal computer. While the reservoir was stirred in order to prevent settling of particles when large aggregates were formed in some filtration runs, stirring of the filtration cell was avoided in order to minimize disturbance of the gel layer forming on the membrane. Prior to a filtration run, a clean membrane was placed in the filtration cell, the reservoir filled with Milli-Q water, and the filtrate flux through the non-fouled membrane at the desired pressure was measured in order to determine the membrane resistance (R_m). The reservoir was then emptied and filled with Ca–alginate solution and re-pressurized to the same applied pressure as used in the R_m measurement. Filtration was then initiated and logging of the accumulated filtrate mass commenced.

2.3.2. Experimental filtration pressures

MBRs are typically operated at about 10–50 kPa. However, in order to determine properties of high resistance cakes using this operational pressure, extremely long filtration runs would have been required making the collection of a comprehensive data set impractical. Therefore, constant pressure filtration studies investigating the effects of calcium and alginate concentrations were conducted at 135 kPa in order to facilitate the development of a large data set. The applicability of these data to lower operating pressures was confirmed via a second set of constant pressure filtration studies conducted over a range of pressures at one alginate concentration and selected calcium concentrations. As described below (and presented in more detail elsewhere [17,18]), empirical expressions describing the manner in which both the hydraulic conductivity and compressibility of the cakes vary with both pressure and calcium concentration were then obtained.

2.3.3. Determination of material properties

Constant pressure dead-end filtration reaches a steady state condition when the deposited cake layer is fully consolidated and there exists a linear relationship between the cumulative permeate