



Ultrafiltration behaviors of alginate blocks at various calcium concentrations



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ARTICLE INFO

Article history:

Received 28 December 2014

Received in revised form

15 May 2015

Accepted 5 June 2015

Available online 9 June 2015

Keywords:

Alginate blocks

Transparent exopolymeric particles (TEP)

Calcium ion

Membrane fouling

ABSTRACT

Alginate, a linear copolymer, is composed of 1,4-linked β -D-mannuronic acid (M) and α -L-guluronic acid (G), which are combined into homopolymeric blocks (MM-block and GG-block) and heteropolymeric block (MG-block). It has been widely used as a model foulant in various studies of membrane fouling, thus this study investigated the impacts of calcium ion on MG-, MM- and GG-blocks of alginate and the filtration behaviors of the three types of alginate blocks at different concentrations of calcium ion. Results showed that calcium ion had the most serious effects on GG-blocks and significantly promotes the formation of transparent exopolymeric particles (TEP) from GG-blocks which in turn led to rapid formation of thick cake layer on membrane surface during the filtration of GG-blocks. As for MM-blocks, it was found that the formation of TEP was proportional to the Ca^{2+} concentration in MM-blocks solution, while the membrane fouling was enhanced by Ca^{2+} in the filtration of MM-blocks solution. Unlike MM- and GG-blocks, MG-blocks were nearly not affected by addition of calcium ion, as the result, there was no significant increase in TEP. The initial fouling rates and the mass of foulants deposited on the membrane surfaces further revealed a close correlation between the TEP concentration and the membrane fouling propensity. The observations by field emission scanning electron microscope (FESEM) and atomic force microscope (AFM) further confirmed the formation process of the cake layer by TEP on the membrane surface. This study offers deep insights into the development of membrane fouling by different alginate blocks in the presence of calcium ion, and suggests that TEP formed from alginate blocks played a very significant role in the fouling development.

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1. Introduction

Membrane technology has been intensively employed worldwide for clean water production and wastewater reclamation.

List of abbreviations: AFM, atomic force microscope; FESEM, field emission scanning electron microscope; G, α -L-guluronic acid; GG, homopolymeric alginate blocks composed of α -L-guluronic acids; M, β -D-mannuronic acid; MF, micro-filtration; MG, heteropolymeric alginate blocks composed of β -D-mannuronic acids and α -L-guluronic acids; MM, homopolymeric alginate blocks composed of β -D-mannuronic acids; MWCO, molecular weight cut off; PES, polyethersulfone; RO, reverse osmosis; TEP, transparent exopolymeric particles; TOC, total organic carbon; UF, ultrafiltration; XDLVO, extended Derjaguin-Landau-Verwey-Overbeek.

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However, membrane fouling has been known as a factor leading to increased operation and maintenance costs (Shannon et al., 2008; Elimelech and Phillip, 2011; Zhang et al., 2014). Alginate as a typical model foulant has often been used in study of membrane fouling under various conditions (Lee and Elimelech, 2006; van den Brink et al., 2009; Mi and Elimelech, 2010; Katsoufidou et al., 2010). Indeed, alginate is a linear copolymer composed of 1,4-linked β -D-mannuronic acid (M) and α -L-guluronic acid (G) which are combined into homopolymeric blocks (i.e. MM- and GG-blocks) and heteropolymeric block (i.e. MG-blocks) (Draget et al., 2005). The combinations and sequences of these blocks in alginate may vary widely, and determine the chemical and physical properties of alginate which in turn affect their filtration behaviors (Draget et al., 2005; Lee and Mooney, 2012; Meng and Liu, 2013). Evidence also showed that the filtration behaviors of alginates were also

significantly influenced by the presence of divalent cations, e.g. calcium ion (Katsoufidou et al., 2007; van de Ven et al., 2008; Listiari et al., 2009). For example, a strong correlation between calcium ion concentration and membrane fouling rate by alginate had been reported by van den Brink et al. (2009). Such an observation can be explained by the classic “egg-box” model according to which calcium ions tend to bind preferentially to the GG-blocks of alginate and form an egg-box-like structure with alginate molecules (Grant et al., 1973; Draget et al., 2005). In turn, the later may lead to the development of alginate cake layer on membrane surfaces (Katsoufidou et al., 2007; van den Brink et al., 2009). It should be realized that no study has explored the effects of calcium ion on membrane fouling development in consideration of alginate molecular composition. As MG-, MM- and GG-blocks of alginate have distinguished chemical and physical characteristics, it is reasonable to consider that these alginate blocks may possess highly different fouling propensities in the presence of calcium ion.

Increasing evidence suggests that transparent exopolymeric particles (TEP) are responsible for the development of membrane fouling (Berman and Hohenberg, 2005; Berman and Passow, 2007; Meng et al., 2013; Bar-Zeev et al., 2015). TEP originally found in marine environment is a class of transparent particulate acidic polysaccharides that can be stained by alcian blue (Aldredge et al., 1993). Operationally, TEP has been defined as particles retained by 0.4 μm polycarbonate filter that can be stained by alcian blue (Passow and Aldredge, 1995). This pore size 0.4 μm was chosen due to the fact that in limnological research, substances passing through 0.2–0.4 μm filters are usually considered as “soluble” (Discart et al., 2015). Concurrently, polysaccharide materials stained by alcian blue and passing through 0.4 μm polycarbonate filters are considered as precursors of TEP, which can further form TEP (Passow, 2000). Subsequently, to better understand the role of TEP in the development of membrane fouling, Villacorte et al. (2009a) further fractionated TEP according to their sizes by using in-series filtrations with filters of different pore sizes (i.e. 0.05–0.4 μm). So far, the involvement of TEP in the fouling development in various membrane systems including microfiltration (MF), ultrafiltration (UF) and reverse osmosis (RO) had been reported (Villacorte et al., 2009a,b; 2010a,b, 2012). Alginate as a common and widespread polysaccharide has been reported to generate TEP-like particles that can be stained by alcian blue and was used as standard calibration substance for TEP determination (Passow and Aldredge, 1995; Thornton et al. 2007). Previous study showed that TEP can form from alginate blocks (e.g. MG-, MM- and GG-blocks) (Meng and Liu, 2013). Therefore, it is reasonable to use alginate blocks as a model of TEP and this study mainly aimed to explore the effects of calcium ion on the formation of TEP from MG-, MM- and GG-blocks as well as the specific roles of the formed TEP in the development of membrane fouling.

2. Materials and methods

2.1. Alginate fractionation

Sodium alginate (Wako, Japan) was fractionated according to the method used by Leal et al. (2008). 10 g/L of sodium alginate solution was stirred for 2 h at 1000 rpm. 3 M of HCl solution was then slowly added into the above alginate solution to reach a final concentration of 0.3 M HCl, and the later was heated at 100 °C in oil bath for 30 min with slow stirring. The cooled solution was centrifuged at 13,420 g for 30 min. The supernatant was harvested and neutralized with 1 M NaOH solution and then poured into the equal-volume ethanol solution, yielding a white precipitate. This precipitate was collected by centrifugation at 13,420 g-force for 30 min and was finally freeze-dried to obtain the fraction of MG-

blocks. The insoluble fraction from the first centrifugation was re-dissolved in 1 M of NaOH solution under rapid vortex condition. The pH of this solution was then readjusted to 2.85 by addition of 1 M of HCl solution. At pH 2.85, a precipitate appeared and was further separated out by centrifugation. After neutralization by 1 M of NaOH solution, the remaining soluble fraction was precipitated out by adding ethanol, and resulting precipitate was harvested by centrifugation and freeze-dried to obtain the fraction of MM-blocks. Again, the insoluble fraction was similarly dissolved in 1 M NaOH solution, then neutralized by 1 M HCl and finally was precipitated out by addition of ethanol to obtain the fraction of GG-blocks. All the freeze dried alginate blocks were grinded into powder form in an agate mortar and were then stored in a copper sulfate dryer to prevent them from being exposed to the damp room condition. All the solutions used were prepared with ultrapure Milli-Q water. The above fractionation was repeated three times. Results showed that the sodium alginate used was composed of $13.8 \pm 1.9\%$ MG-blocks, $53.5 \pm 1.3\%$ MM-blocks and $32.7 \pm 0.6\%$ GG-blocks, respectively, which was consistent with that reported by Draget et al. (2005).

2.2. TEP formation from alginate blocks at different levels of calcium ion

2.2.1. Determination of TEP

TEP formed in respective MG-, MM-, and GG-blocks solutions with and without the presence of calcium ion were determined with the modified Passow and Aldredge's method (Passow and Aldredge, 1995; Villacorte et al., 2009a). 50 mg/L of sample solutions were prepared by dissolving the required amount of MG-, MM- and GG-blocks into ultrapure Milli-Q water with continuous stirring for 2 h. The ionic strengths of all solutions were adjusted to 10 mM by NaCl (Wako, Japan), while CaCl_2 (Sigma, USA) was used to make up solutions with different calcium ion concentration. All sample solutions were freshly prepared just before the determination of TEP. The above prepared sample solutions were first filtered at a constant pressure of 0.2 bars through a series of polycarbonate filters (Whatman, United Kingdom) of pore size 0.05, 0.10, 0.2 and 0.4 μm respectively (Villacorte et al., 2009a). The TEP retained on the filters were further stained using 1 mL of pre-filtered (0.05 μm polycarbonate filter) alcian blue solution which contained 0.02% of alcian blue 8 GX (Sigma, USA) in 0.06% acetic acid (pH 2.5). After 5-s reaction, excess dye was removed by filtration of 1 mL of ultrapure water (Milli-Q) through each filter at a pressure ≤ 0.2 bars. The washed filters were then transferred into a

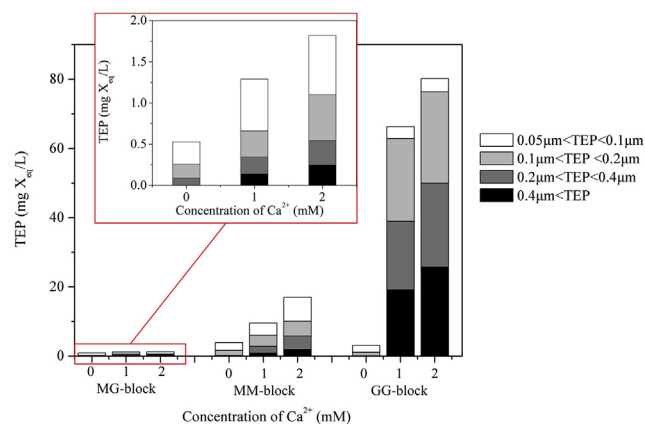


Fig. 1. TEP formation in MG-, MM- and GG-blocks solutions at various calcium concentrations.

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