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Ultrafiltration behaviors of alginate blocks at various calcium concentrations

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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.

Keywords: alginate blocks, transparent exopolymeric particles (TEP), calcium ion, membrane fouling

1. Introduction

Membrane technology has been intensively employed worldwide for clean water

production and wastewater reclamation. 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, Listiarini 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 Holenberg 2005, 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 (Alldredge 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 Alldredge 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 to 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 Alldredge 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 hours at 1,000 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 $^{\circ}\text{C}$ 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 1M 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 1M NaOH solution, then neutralized by 1M 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 Alldredge's method (Passow and Alldredge, 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 hours. 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 series of small beakers and were soaked in 5 mL of 80% H_2SO_4 solution for 2 hours. The beakers were gently swirled 3-5 times over 2 hours to ensure the complete dissolution of alcian blue in the H_2SO_4 solution. Lastly, the absorbance of the H_2SO_4 solution in each beaker with the eluted alcian blue was measured using a UV-Vis spectrophotometer (Shimadzu UV-2501PC, Japan) at the wavelength of 787 nm in a 1 cm cuvette, with ultra-pure water as reference. Three to five measurements were conducted for each sample and every sample was measured at least three times. The average absorbance was then used to calculate the TEP concentration in each sample. Gum xanthan (Sigma, USA) was used as a standard substance of TEP for calibration and the TEP concentration was finally expressed as mg gum xanthan equivalent per liter of water ($\text{mg X}_{\text{eq}}\cdot\text{L}^{-1}$). It should be noted that the term TEP used in this study was subjective to the definition by Villacorte et al. (2009a), i.e. alcian blue-stainable particles that can be retained by 0.05 μm polycarbonate filter.

2.2.2 Microscopic observation of TEP

The appearance of TEP derived from alginate blocks in the presence or absence of calcium ion was observed by a microscope (Keyence, Japan). The fresh TEP solutions were prepared prior to observation as described in Section 2.2.1. In order to visualize TEP with the bright-field microscope, alginate block solutions with or without presence of calcium ion were stained by freshly pre-filtered (0.05 μm polycarbonate filter) alcian blue solution as presented above (Passow and Alldredge, 1995). Stained samples were then observed under the microscope. For each sample, about 20 images

were randomly taken.

2.3 Field emission scanning electron microscope (FESEM) analysis and zeta potential measurements

The changes in the microstructures of alginate blocks due to addition of calcium ion were observed by an FESEM (Jeol JSM-7600F, Japan). For FESEM observation, MG-, MM- and GG-blocks in the absence and presence of calcium ion were first collected. 10-20 mL of the same sample solutions as used in above section were filtered through 0.1 μm polycarbonate filters (Whatman, United Kingdom) at 0.2 bars and then freeze dried completely in a freeze dryer (Christ, Germany) for further examination. All samples were observed at least three times and each time 5-10 pictures were randomly recorded.

The zeta potentials of alginate blocks in the absence and presence of calcium ion were also measured using a Malvern ZetaSizer Nano ZS. All samples were freshly prepared prior to the measurements and each measurement was repeated at least five times.

2.4 Cross-flow ultrafiltration experiments

The filtration behaviors of various alginate blocks solutions in the presence or absence of calcium ion were examined in a standard laboratory-scale cross-flow ultrafiltration module (Sterlitech, USA) at a constant pressure of 2 bars and a temperature of 25 ± 2 °C. Feed solutions were prepared as described in Section 2.2.1. A commercial polyethersulfone (PES) UF membrane (AMFOR INC, Beijing) with molecular weight cut off (MWCO) of 20 kDa was used in this study. The flat sheet PES membrane was soaked in the Milli-Q water for at least 12 hours for membrane wetting prior to use. Feed water was circulated in the close-loop module by a gear pump (Cole-Parmer, USA) at a cross-flow velocity of 10 cm/s. Permeate was collected in a beaker which was placed on an electronic balance. The weight of permeate was recorded at the time interval of 15 s by the data logger system which was connected to a computer. Before each filtration test run, Milli-Q water was first filtered for 24 hours to compact and equilibrate the membrane. Filtration test of each sample was repeated at least three

times. Furthermore, in order to determine the rejection rate of MG-, MM- and GG-blocks by the UF membrane, the total organic carbon (TOC) concentrations in the feed and the permeate were analyzed by a TOC analyzer (Shimadzu, Japan). The respective TOC concentrations in the feed water prepared from MG-, MM- and GG-blocks were found to be 18.0 ± 0.2 mg/L, 18.0 ± 0.1 mg/L and 17.9 ± 0.2 mg/L.

2.5 Analyses of fouling rate and foulant mass

The total membrane filtration resistances were calculated according to Darcy's law:

$$J = \frac{\Delta P}{\mu R_t} \quad (1)$$

where J is the permeate flux ($\text{m}^3 \text{m}^{-2} \text{s}^{-1}$); R_t is the total filtration resistance (m^{-1}); ΔP is the applied pressure (Pa); and μ is the solution viscosity (Pa·s). Fouling rates were determined from the slope of the plot of total resistance versus time, whereas the initial fouling rate was calculated from the initial linear part in the plot of total resistance against filtration time. In addition, total foulant mass deposited on the membrane surface was measured as the difference between the initial amount of alginate blocks in the feed and that left in the solution after the filtration.

2.6 Characterization of fouled membrane

Surface morphology and topography of the fouled membranes were examined by the FESEM and a XE 100 atomic force microscope (AFM, Park Systems, Korea) respectively. In order to track of the development of cake layer on the membrane surface, membrane samples taken at different filtration times of 10 min, 30 min and 1,500 min were examined. The sampled membranes were completely dried in a freeze dryer (Christ, Germany) prior to observation. For the purpose of comparison, samples used for respective FESEM and AFM observations were cut from the same location of fouled membranes. For each observation, at least 16-20 pictures were randomly recorded.

3. Results and discussion

3.1 TEP derived from alginate blocks

Fig. 1 shows the concentrations of TEP derived from the MG-, MM- and GG-blocks in the absence and presence of calcium ion. Without addition of calcium ion, the MM-blocks exhibited greatest tendency of self-aggregation, as the result, the highest concentration of TEP was recorded among three alginate blocks, whereas the lowest-concentration TEP was observed in the solution of MG-blocks. These can be reasonably explained by different cohesive interaction energies between alginate block molecules that can be calculated by extended Derjaguin-Landau-Verwey-Overbeek (XDLVO) theory (Meng and Liu 2013). For example, the cohesive interaction energies of MG-, MM- and GG-blocks are all positive and tend to decrease in the order of $MG > GG > MM$. A positive cohesion free energy indeed reflects a repulsive force between interfacial surfaces. Therefore, MG-blocks should have the lowest self-aggregation tendency for TEP formation, whereas TEP would likely be easily formed from self-aggregation of MM-blocks as observed.

It should be noted that the formation of TEP in the presence of calcium ion appeared to be different from those observed in the cases without addition of calcium ion. In sense of chemical coagulation, calcium ion can enhance the aggregation of all the alginate blocks, leading to more TEP production as shown in Fig. 1. It was found that the concentrations of TEP derived from alginate blocks tended to increase in the order $MG < MM < GG$ in the presence of calcium ion. In fact, it was not surprising to observe that GG-blocks generated the highest-concentration TEP. As documented in the literature, there is a strong binding between GG-block and calcium ion, resulting in a three dimensional network of alginate strands held together through ionic interactions, known as “egg-box” structure (Grant et al. 1973, Draget et al. 2005). The biaxially linked G residues in GG-blocks form a cavity that can accommodate divalent calcium ion, i.e. GG-blocks can easily link together through the bridging of calcium ion. As such, more TEP can develop from GG-blocks in the presence of calcium ion as observed in Fig. 1. Although the TEP produced from MG- and MM-blocks was also enhanced by addition of calcium ion, it was much lower than that from GG-blocks. The binding mechanisms of MG- and MM-blocks with calcium

are currently unclear. It had been reported that hydrogels formed by alginates rich in M residues were softer, less porous and unstable towards disintegration with time as compared with those developed from alginates rich in G residues (De Vos et al. 1996, Simpson et al. 2004). These imply that MG- and MM-blocks can't firmly bind to calcium ion, evidenced by differences in the stiffness of alginate blocks which are in the order $MG < MM < GG$ (Smidsrød, 1974, Vold et al. 2006). The highly flexible MG-blocks preferably tend to bind to water molecules instead of forming complexes with calcium ion (Smidsrød, 1974). Therefore, such behavior of MG-blocks indeed unfavors the formation of TEP even in the presence of calcium ion. This is further supported by the observation of that the TEP concentration was increased insignificantly with increasing the calcium concentration from 1 mM to 2 mM (Fig. 1). As the rigidity of MM-blocks was higher than that of MG-blocks, MM-blocks should preferably react with calcium ion, as a result, more TEP was produced (Fig. 1). In addition, the positive correlation between TEP in different size ranges and calcium concentrations in solutions of MM-blocks are observed in Fig. 2, suggesting the dependence of the TEP formation on the level of calcium ion in the solution MM-blocks.

TEP formed from MG-, MM- and GG-blocks in the presence or absence of calcium ion were visualized by a light-field microscope. Fig. 3 provides direct observation of the morphology and structure of TEP derived from alginate blocks. In the absence of calcium ion (Fig. 3 a-c), only few small TEP were observed. However, much more and large TEP with complex structures were captured in the vision field of the microscope in the presence of calcium ion, as indicated by strong blue color (Figs. 3 d-f). For example, both the concentration and the size of TEP derived from GG-blocks were significantly increased in the presence of calcium ion. These indeed are in good agreement with the TEP results presented in Fig. 1. As discussed above, GG-blocks can generate more TEP through the formation of the complex "egg-box" structure among GG-blocks and calcium ion.

3.2 Structural changes of alginate blocks

FESEM images revealed the changes in microstructure of alginate blocks induced by calcium ion. The filament-type alginate blocks were observed in the absence of calcium ion (Fig. 4 a-c), whereas much bigger and more compact structure was developed for all the three alginate blocks after addition of calcium ion (Fig. 4 d-f). Moreover, the microscopic morphologies of MG-, MM- and GG-blocks were completely altered by calcium ion. Such changes in the microstructure of alginate blocks are likely due to the binding with calcium ion as discussed above.

Table 1 summarizes the zeta potentials of MG-, MM- and GG-blocks solutions at various concentrations of calcium ion. With the addition of calcium ion, the zeta potentials of alginate blocks all tended to decrease, indicating that alginate blocks became less stable and had greater tendency of aggregation among themselves. Consequently, this may affect their fouling propensity during membrane filtration.

3.3 Filtration behaviors of alginate blocks at various calcium concentrations

3.3.1 Flux profiles of MG-, MM- and GG-blocks

As presented above, it is obvious that calcium ion has significant effects on the physic-chemical properties and microstructures of MG-, MM- and GG-blocks, subsequently their potentials to form TEP. Fig. 5a shows the permeate flux profiles observed during the ultrafiltration of MG-blocks at various concentrations of calcium ion. The higher of the calcium concentration, the severer membrane fouling is observed. In the absence of calcium ion, the initial flux declines slowly. However, in the presence of 1 mM and 2 mM calcium ion, a rapid decline was observed at the initial phase. The TOC concentration of the permeate further revealed that the rejection rate of MG-blocks (Table 2) by the membrane was only about 28.8% without calcium ion, however it increased to 56.9% and 57.2% with the addition of 1 mM and 2 mM Ca^{2+} , respectively. These results indicate that most of MG-blocks were smaller than the pores of membrane, thus could pass through the membrane. On the contrary, with the addition of calcium ion, calcium ion promoted the self-aggregation of MG-blocks (Fig. 1), leading to the formation of large MG-blocks complexes that can be effectively retained by the ultrafiltration membrane used in this study.

Fig. 5b shows the filtration profiles of MM-blocks in the absence and presence of calcium ion. Without addition of calcium ion, the flux decline during the ultrafiltration of MM-blocks was much less than that observed for MG-block. The TOC concentration of the permeate shows that 88.7% of MM-blocks was retained by the ultrafiltration membrane used in this study. According to the filtration data of MM- and MG-blocks, it is reasonable to consider that most of MM-blocks had a size bigger than MG-blocks. This indeed is supported by the prediction by the XDLVO theory, i.e. MM-blocks possess the highest self-aggregation potential to form bigger TEP in water (Meng and Liu 2013). Furthermore, the addition of calcium ion significantly promotes the self-aggregation of MM-blocks and the formation of TEP. As the result, much severer decline in the permeate flux was observed. As can be seen in Fig. 5 b, the severity of the flux decline is proportionally related to the concentration of calcium ion added to the MM-block solutions. For example, the filtration flux of MM-block solution in the absence of calcium ion only decreased to 82.7% of its initial flux after 48-hour ultrafiltration. However, with the addition of 1 mM and 2 mM calcium ion to the MM-block solutions, the respective fluxes significantly dropped to 23.9% and 14.7% of the initial flux. In addition, the measured TOC concentrations in the permeates further indicate that 96.0% and 97.2% of MM-blocks were rejected in the presence of 1 mM and 2 mM of calcium ion, respectively. Previous study also showed that the formation of cake layer on the membrane surface was the main cause of membrane fouling in the filtration of MM-blocks with a 0.2- μm microfiltration membrane (Meng and Liu 2013). Similarly, it is reasonable to consider that the formation of cake layer by MM-blocks was mainly responsible for the observed fouling during the ultrafiltration with a membrane of 20,000 Daltons. As shown in Fig. 1, the addition of 1 mM and 2 mM of calcium ion greatly promoted the formation of TEP ($>0.05\ \mu\text{m}$) in the MM-blocks solutions from 4.0 mg Xeq/L without calcium ion to 9.6 and 17.1 mg Xeq/L) respectively. On the other hand, Fig. 3 also reveals that TEP formed in the presence of calcium had more complex structure than TEP developed in the absence of calcium. Obviously, these calcium-induced physical changes to TEP inevitably expedite the formation of cake layer on the UF membrane.

Fig. 5c shows the effects of calcium ion on the ultrafiltration behaviors of GG-blocks. Compared to the MG- and MM-blocks, calcium ion had a much greater effect on the ultrafiltration of GG-blocks. The permeate flux of GG-blocks in the absence of without calcium, only declined 89.7% of its initial value after 24-hour filtration. However, in the presence of 1 mM and 2 mM of calcium, an extremely quick drop in the respective filtration fluxes of GG-blocks was observed in the initial phase, and only 6.8% and 5.6% of the initial flux remained after 24-hour ultrafiltration. Such severe membrane fouling can be explained by the highest concentration of TEP obtained in the GG-blocks solutions after the addition of calcium (Fig. 1), as compared to MM- and MG-blocks. For example, only about 3.6 mg Xeq/L TEP > 0.05 μ m was determined in the GG-block solution without addition of calcium, whereas 71.1 and 72.2 mg Xeq/L were obtained at the calcium concentrations of 1 mM and 2 mM respectively. Meanwhile, Fig. 3 showed the structure of TEP derived from GG-blocks in the presence of calcium also became larger and more complex. Furthermore, the TOC concentration in the permeate showed 93.7% and 95.3% of GG-blocks were rejected after the addition of 1 mM and 2 mM calcium. Therefore, the increases in concentration and size of TEP derived from the GG-blocks solutions in the presence of calcium are definitely responsible for the observed quick and severe membrane fouling (Fig. 5c).

3.3.2 Analysis of fouling rate and foulant deposited on membrane surface

The initial fouling rate and total foulant mass on the membrane surface deposition were calculated in order to establish the relationship between TEP concentration and the fouling development. The ultrafiltration membrane used in this study has a MWCO of 20 kDa, thus TEP measured with a size >0.05 μ m should not result in the pore blocking of membrane. Fig. 6 shows a positive correlation between the TEP concentration (>0.05 μ m) and the initial fouling rate. It appears that TEP plays a critical role in the initial development of membrane fouling. These results also suggest that TEP can adhere onto the membrane surface very quickly to form a gel-like layer as also reported by Bar-Zeev et al. (2012).

The foulant mass deposited on the membrane surface offers direct insights into the cake layer formed by TEP (TEP>0.05 μm). It can be seen in Fig. 7 that the amount of foulants is proportionally correlated to the TEP concentration in the feed water. Figs. 6 and 7 offer a much clearer understanding of the role of TEP in the development of membrane fouling. In fact, such an observation is supported by the study of Bar-Zeev et al. (2012) showing that TEP preferably tend to attach to solid surfaces.

3.3.3 Development of cake layer at different TEP concentrations

As discussed above, the formation of cake layer on the membrane surfaces was of critical importance in the ultrafiltration of MM- and GG-blocks. In the present study, FESEM and AFM techniques were employed to visualize the membrane surfaces fouled at two different TEP concentrations. Although TEP were freeze-dried prior to microscopic observation, these visualization techniques could still provide direct evidence of the TEP attachment on the membrane surfaces.

As can be seen in Fig. 8a, only few and small TEP were deposited on the membrane surface after 10-minute filtration at the low TEP concentration, while remarkable accumulation of TEP on the membrane surface was observed at the high concentration (Fig. 8b). After 30-minute filtration, some membrane still remained blank in the ultrafiltration of low-concentration TEP solution, but the entire membrane surface was eventually completely covered by TEP in the filtration of the high-concentration TEP solution (Figs. 8c and 8d). These observations indeed are in good agreement with the results in Fig. 6 showing high-concentration TEP resulted in high initial fouling rate. Figs. 8e and 8f further show the fouled membrane surface after 1500-minute filtration. It should be noted that crafts in these two figures were created by the freeze dry process in the preparation of the samples for FESEM. Fortunately, these crafts revealed that the thicker cake layer was developed at the higher TEP concentration.

In addition, three dimensional AFM images (Fig. 9) also revealed the phenomena similar to those by FESEM. The roughness was evaluated from AFM images on different locations of the same fouled membrane and the average values were reported in Fig 9. It appears that the roughness of the fouled membrane surfaces tended to

increase with the successive accumulation of TEP, and the changes in the surface roughness was also related to the TEP concentration, e.g. the surface roughness was found to increase rapidly during the filtration of high-concentration TEP solution.

3.4 Effects of calcium ion on the cross-linking of MG-, MM and GG-blocks

It is demonstrated above that despite derived from the same source of alginate, MG-, MM- and GG-blocks behaved totally differently in the reactions with calcium ion. Fig. 10 schematically illustrates possible interactions between various alginate blocks and calcium ion. As discussed above, most of MG-blocks are small enough to pass through the membrane used in present study. After the addition of calcium ion, only few TEP were form from MG-blocks, i.e. the interaction or reaction between MG-blocks and calcium ion is insignificant. Unlike MG-blocks, the binding between MM-blocks and calcium ion appeared to be much stronger and seemingly Ca^{2+} -dependent. As a result, the TEP concentration in the MM-block solution was much higher than that observed in the MG-block solution. The most notable reaction was found between GG-blocks and calcium ion, and the addition of calcium ion to the GG-block solution significantly enhanced the production of TEP, resulting in a quick formation of cake later on the membrane surface.

So far, more than 200 kinds of commercial alginates derived from different sources are available in the market and the MG-, MM and GG-blocks contents in alginates vary largely (Tonnesen and Karlsen 2002; Lee and Mooney 2012). In the literature, alginate from various suppliers has been commonly employed as a model foulant, but with no consideration of possible differences in their molecular compositions and structures. As shown in Fig. 10, MG-, MM- and GG-blocks indeed exhibit different cross-linking structures with calcium ion which exists extensively in various water and wastewater environments. Therefore, it appears to be necessary to characterize the molecular compositions and structures of alginates from various sources which would be useful for better interpretation of filtration results from different types of membranes.

4. Conclusions

Although derived from the same source alginate, MG-, MM and GG-blocks exhibited distinguished properties, and such differences were further intensified by the presence of calcium ion. The reaction between calcium ion and GG-blocks was found to be strongest, and more TEP was thus produced. As the result, ultrafiltration membrane was quickly fouled by accumulated TEP on its surface. Although the formation of TEP from MM-blocks was enhanced by the addition of calcium ion, it was not as intensive as that observed for GG-blocks. As such, the development of membrane fouling during the ultrafiltration of MM-block solution was slowed down. The effect of calcium ion on MG-blocks was slightest, and only very limited amount of TEP was produced. Thus, the membrane fouling by MG-blocks was not as serious as those observed during the ultrafiltration of MM- and GG-blocks. More importantly, this study provided experimental evidence showing the critical role of TEP in the development of membrane fouling.

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