Comparison of Fouling by Extracellular Polymeric Substances and Polysaccharides in Forward Osmosis

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Abstract
Fouling caused by extracellular polymeric substances (EPS), the products secreted by bacteria, has been regarded as one of significant contributors to deteriorating membrane separation performances. Most current laboratory studies on membrane fouling use selected model foulants, such as alginate, which may not typically represent bacteria-produced EPS. This study aimed to compare the fouling caused by naturally occurring EPS and commercial polysaccharides in forward osmosis (FO) separation, thus possibly suggesting the ideal polysaccharide model in the research of membrane fouling. Three types of commercial polysaccharides, namely alginate, xanthan and pullulan, as well as two types of EPS (EPS-RSW and EPS-FSW) extracted from the bacteria in raw seawater and filtered seawater (RSW 14 and FSW 6) were selected herein. Our results showed that the commercial polysaccharides and the naturally occurring EPS behaved differently in the FO fouling tests, which could be largely attributed to the difference in their solution viscosities. Both of the solutions consisting of EPS exhibited lower viscosities and led to higher permeate fluxes, in comparison to those of the solutions with the commercial alginate and xanthan polysaccharides. The use of pullulan caused the most similar flux change in FO separation to that by utilizing the EPS; thereby we suggest that pullulan be the preferred model polysaccharide to represent EPS in FO fouling research.

Keywords
Forward osmosis; fouling; polysaccharide; extracellular polymeric substances; foulant model

INTRODUCTION

To date, an increasing demand for safe drinking water, caused by climate change, population growth, and environment pollution, has driven the widespread consideration and development of desalination technologies (Greenlee et al., 2009). In particular, membrane separation, such as reverse osmosis (RO) technology, has been commonly adopted in most desalination plants installed around the world.

In the membrane separation process, one of the critical issues is membrane biofouling, severely reducing water flux, affecting water product quality, and increasing energy

consumption. It is caused by the attachment of microorganisms in feed water onto membrane surfaces, followed by their multiplication by consuming nutrients from surrounding environment and the excretion of extracellular polymeric substances (EPS) (Kim et al., 2009; Matin et al., 2011). Especially, EPS form integral components of all biofilms, representing the majority of their biomass (Kim et al., 2009).

Dominant bacterial biofilm species identified in seawater systems vary between studies. Unfortunately, many controlled experiments in fouling research have used *Pseudomonas aeruginosa* biofilms and their associated EPS (bacterial alginates) which are atypical of most bacterial EPS, leading to the false impression that all EPS resemble algal alginates. Alginates are composed solely of uronic acid residues whereas most bacterial EPS are not (Sutherland, 1998). To study the EPS fouling, we selected two seawater isolates, RSW 14 which is a strain of *Achromobacter* (Beta proteobacteria) and FSW 6 which is *Xanthomonas citrii* (gammaproteobacteria), from our culture collection. Both of them appear prevalent in the samples from Western Australia and produce copious amounts of EPS (Nagaraja, 2013).

Our study aimed to investigate and compare the fouling behaviours of our laboratory produced EPS with different commercial polysaccharides in FO membrane separation, which shows great potential application in low-energy water desalination and treatment (Holloway et al., 2007). Herein, alginate, a commonly used model foulant, as well as xanthan and pullulan were chosen in our fouling work; whilst we isolated two kinds of EPS (EPS-RSW and EPS-FSW) produced from RSW 14 and FSW 6 in our laboratory for comparison (Nagaraja, 2013). The best polysaccharide representative of EPS in membrane separation process was suggested.

MATERIALS AND METHODS

Commercial polysaccharides and laboratory produced EPS

Three types of commercial polysaccharides were used as the foulant models in this study, namely sodium alginate (200 kDa), xanthan gum (1000 ~ 50,000 kDa) and pullulan (75 kDa), all of which were purchased from Sigma-Aldrich (USA) and used directly without any purification. Two types of pure EPS isolates were produced by the bacteria, RSW 14 in raw seawater and FSW 6 in filtered seawater, in our laboratory; which are denoted as EPS-RSW and EPS-FSW, respectively. Marine broth, which was used as the medium to grow bacteria cultures ascribed to its components being similar as the seawater, was purchased from BD (USA). Typically, the bacteria were grown on the liquid media which was shaken on IKA® KS 130 basic shaker orbital (Labtek Pty. Ltd, AU). The cultures were then centrifuged in a MSE Mistral 2000 centrifuge (DJB Labcare Ltd, UK) at 14,000 rpm for 30 min; after which the supernatant was collected, followed by the addition of cold acetone with the volume ratio of 3:1 between acetone and supernatant to precipitate EPS. Finally, the precipitated EPS was collected and then dissolved in a small amount of distilled water, followed by the dialysis in distilled water for 48 h.

FO separation

The FO system consisted of a cross-flow FO membrane cell (an effective membrane area of 42 cm^2; Sterlitech, US), two peristaltic pumps (Cole-Parmer, US), a refrigerated circulated water bath (Thermoline Scientific, AU), and a digital balance (A&D Australasia Pty. Ltd,

AU) (Mi and Elimelech, 2008). In a typical test, the cross-flow velocity was set at 8.5 cm/s. The temperature of the solution was controlled at 25 ± 1 °C. The saturated NaCl (AR grade, Chem-Supply Pty. Ltd, AU) solution was used as the draw solution, generating an initial flux of ~ 9.5 LMH. The concentration of Ca^{2+} in the feed solution was adjusted to be 1 mM by using $CaCl_2$ (LR grade, Chem-Supply Pty. Ltd, AU). The ionic strength of feed solution was adjusted to 50 mM by adding NaCl (Lee et al., 2010). All the concentrations of model polysaccharides and isolated EPS used as the foulants in this study were 0.20 g/L. The viscosities of feed solution consisting of different foulants were measured by using Gilmont® Instruments falling-ball viscometer Model GV-2200 (glass ball size #3, GF-1332-P; Thermoline Scientific Pty. Ltd, AU).

The commercial FO pouch membrane, which was provided by Hydration Technologies and made of cellulose triacetate on top of a non-woven backing, was used in all of the fouling tests. Before starting experiment, the membrane sample was immersed in deionized (DI) water overnight. In the FO fouling test, the membrane was firstly compacted with DI water for 2 h, followed by the stabilization and equilibration process *via* circulating the foulant-free electrolyte solution (1 mM Ca^{2+} and 50 mM ionic strength) for another 2 h. After stable permeate fluxes were observed, the foulant was added into the feed solution; the separation lasted for 12 h. During 24 h FO separation, the weight change of the draw solution tank was recorded in real time and used to calculate the permeate fluxes as shown (Cornelissen et al., 2008; Nataraj et al., 2008):

$$J_t = \frac{1}{A_m}\frac{dV}{dt}$$

J_t is the permeate flux in litre per square meter per hour (LMH) at a selected time interval t (h); V is the volume of collected permeate (L), which was estimated based on the weight change of the draw solution tank; and A_m is the effective membrane area (m^2).

RESULTS AND DISCUSSION

Figure 1 compares the permeate fluxes obtained from fouling tests with the use of different commercial polysaccharides (alginate, xanthan, and pullulan) and EPS (EPS-RSW and EPS-FSW) in FO separations. As seen, the fouling behaviors caused by the commercial polysaccharides and EPS differ greatly. The fluxes in FO separation with the addition of the EPS, e.g. EPS-RSW or EPS-FSW, are close to those in the baseline test. Among three selected commercial polysaccharides, the pullulan behaves most similarly to that of our produced EPS in the FO fouling tests. In contrast, xanthan caused the highest fouling with a significant flux decline (~20%) after 12 h.

The varying fouling behaviors of commercial polysaccharides and EPS could be attributed to the difference in their solution viscosities, as presented in Figure 2. Based on the literature (Choi et al., 2005; Madaeni et al., 2011; Cath et al., 2013), permeate flux is dependent on the trans-membrane pressure, solution viscosity and total hydraulic resistance; that undoubtedly, the solution with higher viscosity caused severer fouling. In Figure 2, xanthan solution was observed with the highest viscosity, 13.7×10^{-4} Pa.s. It likely reduces the shear force by the cross-flow velocity, increasing the xanthan accumulation on the membrane and subsequently causing severe fouling (Mattaraj et al.; Ang et al., 2011).

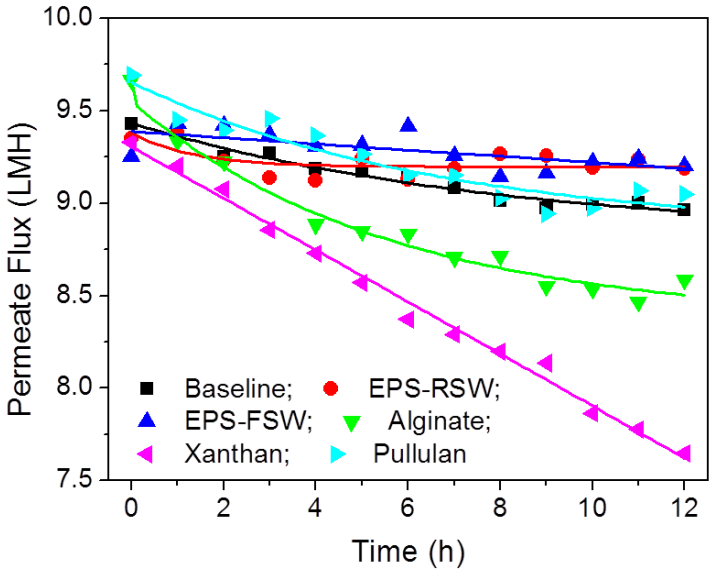

Figure 1. Permeate fluxes *versus* time in the FO fouling tests with the use of different commercial polysaccharide (alginate, xanthan, or pullulan) and our laboratory produced EPS (EPS-RSW or EPS-FSW).

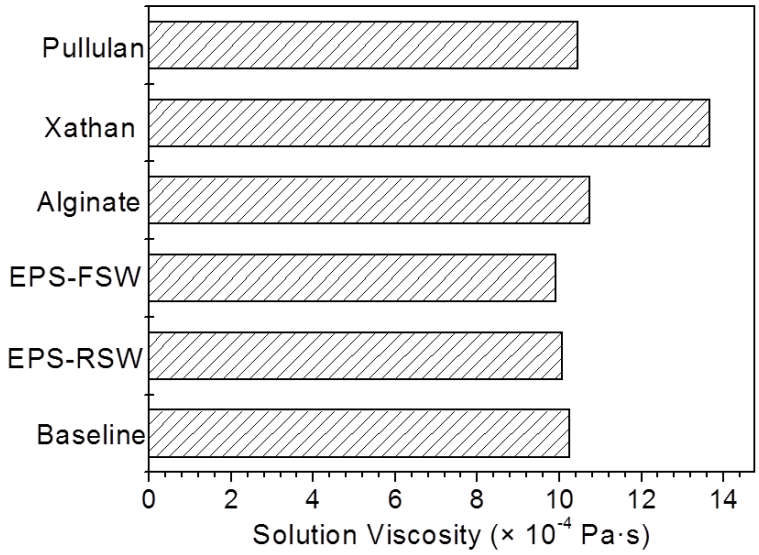

Figure 2. Solution viscosities in the absence (baseline) and presence of different polysaccharides (alginate, xanthan, or pullulan) or our isolated EPS (EPS-RSW or EPS-FSW).

Both of viscosities of alginate (10.7×10^{-4} Pa.s) and pullulan solutions (10.5×10^{-4} Pa.s) are slightly greater than those of the EPS solutions, 10.1×10^{-4} Pa.s (EPS-RSW) and 9.9×10^{-4} Pa.s (EPS-FSW), respectively. However, it is interesting to find that alginate caused severer fouling, relative to that by pullulan or our laboratory produced EPS. We attribute that to the formation of loose Ca-alginate gels in the presence of Ca^{2+} ions in the feed solution. Alginate molecule contains a large amount of carboxylic functional groups, which Ca^{2+} ions preferentially interact with. The Ca^{2+} ions in the feed solution can bridge alginate molecules and enhance the intermolecular adhesion between alginate molecules, thus accelerating the alginate accumulation on the membrane surface (Mi and Elimelech, 2008; Ang et al., 2011). In contrast, pullulan does not possess carboxylic groups along their polymer chains, resulting

in much less quantity of gel deposited on the membrane surface, in conjunction with its low solution viscosity. On the basis of that the use of pullulan causing a similar change of permeate fluxes to those of EPS during FO separation, we suggest it be selected as the ideal polysaccharide representative of the EPS relative to alginate and xanthan.

In the laboratory preparation of EPS-RSW and EPS-FSW, it is noted that the utilized marine broth contains a large amount of Mg^{2+} and Ca^{2+} ions, 0.089 mol/L and 0.016 mol/L, respectively. These ions may gel the EPS during the centrifugation of the cultures, leading to the low production of EPS in the supernatant. In addition, the use of acetone might vary the EPS chain structures during the precipitation of EPS and then impact on the solution viscosity after it was re-dissolved in the feed solution. Therefore, our future work will investigate the preparation of EPS without the use of acetone. That might largely minimize the modification or change on polymer structures and help us confirm the use of pullulan as the preferred representative of the EPS in FO fouling test. Moreover, the FO fouling test with the use of EPS produced by mixed bacterial species will be carried out in our future research; it will facilitate the design and selection of an ideal polysaccharide model which can well simulate the real foulants in desalination. In addition to FO separation, the investigation and comparison of our isolated EPS and commercial polysaccharides can be further expanded to other membrane separation processes, such as reverse osmosis and nanofiltration.

CONCLUSIONS

FO fouling tests by selecting three types of model polysaccharides and two types of isolated EPS were investigated in this paper. It was found that the polysaccharides and the EPS fouled the membrane to different degrees, which could largely be explained by the difference in their solution viscosities. The xanthan solution exhibited the highest viscosity and thus caused the severest fouling. The presence of alginate in FO separation caused a reduction in permeate fluxes, which could be attributed to the formation of Ca-alginate gels. However, its fouling level was less than that of xanthan, which was possibly due to the lower solution viscosity. Based on our results by using three different commercial polysaccharides, pullulan is suggested as the preferred model representative of our isolated EPS in FO membrane separation.

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