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Understanding the interaction between **biomacromolecules** and their influence on forward osmosis process

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Abstract

This paper presents studies on the interactions and effects of **biomacromolecules** compounds on forward osmosis (FO) membrane performance. Individual components and a combination of various organic substances such as bovine serum albumin (BSA), dextran, sodium alginate and xanthan gum were used as model feeds and tested for their influences on FO performance with the active layer of the FO hollow fiber membrane facing the feed solution (AL-FS). The interactions between foulants were examined by using fluorescence spectroscopy, rotational rheometry and laser doppler micro-electrophoresis techniques. **For a system containing combined organic foulants, it was found that viscosity was not the dominant factor governing FO membrane fouling as the decrease in viscosity did not always result in less fouling. The effect of divalent cations on the FO fouling behavior was also studied by adding CaCl₂. The presence of calcium ions has exacerbated the flux decline, this occurred particularly for any combined organic foulants containing alginate, due to intermolecular bridging among alginate molecules. It is interesting to note that combined BSA + alginate caused moderate flux decline, while BSA and alginate alone did not cause any observable water flux loss. The (BSA + alginate) fouling became more severe with the presence of calcium ions.**

Keywords: forward osmosis, **combined organic fouling, biomacromolecules, effect of divalent ions, viscosity effect**

1. Introduction

Research in forward osmosis (FO) process is steadily growing. This is due to great potential of direct osmosis technology for various applications such as desalination, power generation, wastewater treatment and concentration of liquid food. FO possesses a range of advantages, among which are low capital cost, less energy consumption, and low membrane fouling propensity.

Although FO fouling is generally less severe and more reversible as compared to pressure-driven membrane processes [1], fouling is still a critical issue that hampers the FO long-term performance, and thus deserves further investigation. Fouling can cause various adverse effects in a membrane system, the most common being the permeate flux decline. Depending on the type of membrane process, fouling can also alter the membrane rejection behavior [2] that affects the subsequent cleaning process [3], degrade the quality of reverse osmosis product water due to the increase of salt passage, and increase the energy demand to maintain the production rate [4]. Numerous studies on FO membrane fouling have been performed using organic [1, 5-8], inorganic [9-11], colloidal [12, 13] and bio- foulants [14, 15]. However, the majority of former works focused on either individual foulants [16-18] or complex substances in real feed such as seawater, municipal wastewater and sewage [19-21]. When more than one type of foulant presence in the solution, different fouling behavior and filtration performance could occur due to the synergetic effect of combined fouling [22, 23]. Despite this important issue, only limited studies on synergistic fouling in a FO system containing multiple foulants have been reported [2, 22, 24, 25].

In contrast to the above-mentioned issues, combined organic fouling in pressure driven membrane processes has attracted keen interest from research community. The influence of various combinations of humic substances, proteins, polysaccharides, peptides, enzymes and yeasts on water flux of ultra- [26, 27] and micro- [28, 29] filtration membranes can be easily found in literatures. It was claimed that the flux decline occurred in a pressure-driven membrane system containing mixed foulants was equal to the sum of flux declines caused by individual foulants [30]. Further to this, specific interaction between foulants would result in synergistic fouling, which could either alleviate [31] or intensify [32] the water flux loss. Nevertheless, this phenomenon has not been widely explored in FO process.

Divalent cations such as calcium ions are commonly observed in seawater desalination. The presence of calcium ions has been shown to play a prevalent role in organic fouling. Calcium ions could react with organic molecules to form complexes and create intermolecular bridging with carboxylic groups of organic foulants that significantly exacerbated the fouling of nanofiltration and reverse osmosis membranes [3, 23, 31, 33, 34]. Similar effect of calcium ions was reported for FO process with various single foulants [33, 35]. More prominent flux decline occurred at higher calcium ions concentration. However, unlike RO and NF, the organic fouling layer in FO was reported to be less dense/compact due to the absence of mechanical hydraulic pressure [33, 35]. It is of interest to examine whether divalent ions would cause the same effect in a system containing multiple organic foulants where synergistic fouling may occur.

In this study, the relationship between biomacromolecules interactions and the performance of FO membrane was explored. BSA, dextran, sodium alginate and xanthan gum were used as model foulants of organic matter. These substances are commonly present in real feed water [16, 27, 29, 31, 36]. The role of solution chemistry on FO fouling was studied by adding divalent

cations into the feed solution. The extents of water flux decline caused by various combined foulants were compared to the estimated additive flux decline percentages caused by individual foulants. The FO membrane was used with its active layer facing the feed solution. Fluorescence excitation-emission matrix, viscosity, hydrodynamic diameter and zeta potential measurements were conducted to examine the interaction between **biomacromolecules.**

2. Materials and Methods

2.1. FO membrane and foulants

In-house fabricated FO hollow fiber membranes of #C type were used in the study. Detailed description of membrane characteristics can be found elsewhere [37]. The active layer of the membrane was located on the inner surface of the hollow fiber. Each module consisted of fifteen hollow fibers with 1.3 mm outer diameter and 0.9 mm inner diameter. The effective filtration area was 119 cm². Prior to fouling experiments, the intrinsic separation properties, i.e. pure water (*A*) and salt (*B*) permeability values, as well as the salt rejection (*R*) of the membranes were measured. The tests were performed under cross-flow condition with a flow rate of 450 ml/min at 1 bar and room temperature (23 ± 1 °C). The salt rejection was measured by using 500 ppm NaCl solution as feed. BSA (Sigma-Aldrich), sodium alginate (ALG) (Hayashi Pure Chemical Industries), dextran of 200-300 kDa (DX) (MP Biomedicals) and xanthan gum (XG) (Sigma-Aldrich) were used as model foulants.

2.2. FO experiments

The experiments were conducted in FO mode for 360 minutes. This duration was selected based on our preliminary studies, which indicated that there was no significant flux decline occurred beyond 300 minutes of FO process. The feed solutions contained 70 ppm of each foulant and 10 mM NaCl with or without the addition of 1 mM CaCl₂. The feed solutions for baseline tests comprised sodium chloride or (sodium chloride + calcium chloride) only. The pH of the solutions was 6.25-6.5. A 5 M NaCl dosing solution was used to maintain a constant draw solution concentration of 1 M NaCl. The feed and draw solutions were circulated through the membrane at 6.5 cm/s cross-flow velocity in counter-current flow. The water flux was monitored at predetermined time intervals ($J(t)$) by using an electronic balance (Mettler Toledo, Switzerland) and a data logging system. The average water flux values of replicated experimental runs were then normalized to the initial water flux (J_0). In the presence of foulants, the decline in water flux occurred due to a combined effect of reverse salt flux (dilutive internal concentration polarization), feed concentration and fouling; therefore, the normalized water flux due to fouling alone was calculated as:

$$\text{Normalized Flux (fouling)} = \frac{J(t)}{J_0} + \Delta J_{bl(t)} \quad (1)$$

where $J(t)$ is the measured water flux at time t , J_0 is the initial water flux, $\Delta J_{bl(t)}$ is the normalized baseline flux at time t . The initial water flux of the membrane in both baseline and fouling experiments was 23 Lm⁻²h⁻¹ (LMH). It was found that the flux decline for baseline test was relatively low, i.e. only 9% over 6 hours of FO run. The percentages of water flux decline caused by various combined foulants were compared to the additive flux decline percentages (Table 1).

The additive flux decline was a sum of flux decline percentages obtained during filtration of single foulant solutions.

2.3. Analytical methods

Excitation-Emission Matrix (EEM) spectra were obtained by using a PerkinElmer LS55 fluorescence spectrometer equipped with a 10 mm cell. The measurements were performed at 280 nm excitation wavelength and 200-600 nm emission wavelength range [38]. Excitation and emission slits were set at 10 nm and the scanning speed was 1000 nm/min. Quenching data at the peak of the bell-like shape EEM spectra were used to generate the Stern-Volmer plots, which demonstrated the fluorescence intensity (expressed as F_0/F) as a function of quencher concentration [39]. F_0 and F are fluorescence intensities of the fluorophores in the absence and presence of quencher, respectively. The Stern-Volmer constant (K_{sv}) was obtained as the slope of the plot of F_0/F versus the concentration of quencher. EEM analyses were performed for all binary fouling solutions, except for BSA+ALG+calcium due to its non-stable fluorescent signal. The zeta potential and the hydrodynamic diameter of foulants were characterized by using Malvern Zetasizer Nano ZS, UK. All rheological data were obtained by using Physica MCR 101 rheometer (Anton Paar GmbH, Austria). The measurements were performed with a stainless steel cone of 49.973 mm diameter and 0.985° angle. The shear rate-dependent experiments were run by varying the shear rates between 0.01 and 1000 s⁻¹ at 23°C. The concentration of foulants used for size and charge measurements was similar to that used in FO experiments, while for viscosity measurements, the foulant concentration was increased by a factor of thirty to obtain more distinct rheological data. It is expected that the increase in concentration would increase the

viscosity value. Nevertheless, this concentration range did not seem to cause any significant effect since our earlier study showed that the fouling tendencies of more concentrated and dilute foulant solutions were relatively similar within this concentration range (data not shown).

3. Results and Discussion

3.1 Flux decline caused by various combined foulants

Figure 1 illustrates the water flux profile during filtration of ALG, XG, DX and BSA in the absence and presence of calcium chloride. By looking at this figure, it can be seen that more severe fouling occurred with XG (with and without calcium) and ALG + calcium. Fouling caused by other foulants was either minor (~ 6% flux decline for DX) or negligible. Although ALG alone did not cause any observable fouling, the flux decline reached 22% with the addition of calcium salt. The percentages of flux decline caused by XG were 22% (in NaCl solution) and 28% (in NaCl + CaCl₂ solution). These trends are similar to our previous work [16]. However, values obtained in present study are lower than those reported earlier. This is due to the fact that the concentration of foulants used in current research was approximately three times lower than the one used in our previous work. Our earlier findings suggested that the increased fouling by ALG in the presence of calcium chloride was a result of the formation of highly viscous egg-box structure [24]. Based on data presented in Figure 1, the extent of fouling caused by various combinations of ALG, XG, DX and BSA can be determined (Table 1).

Figure 2 depicts water flux profiles obtained during filtration of binary feed solutions. Except for BSA+DX, whose fouling was negligible (~1% flux decline), all other feed solutions showed \geq

10% water flux decline. It is interesting to observe that a combined BSA+ALG as feed caused approximately 10% flux decline, although no observable fouling occurred with feed containing BSA or ALG alone (Figure 1). Similar phenomena occurred with ALG+DX. ALG alone did not appear to be a fouling precursor in FO process, while DX alone caused only 6% flux decline. However, when these **biomacromolecules** were combined in the same feed solution, the flux decline became 17%. These phenomena suggested that interaction between foulants might occur.

Figure 3 indicates flux declines during filtration of binary solutions in the presence of calcium chloride. It is clear that the addition of calcium salt did not cause any significant effect during filtration of BSA+DX solution, since the flux declines with and without CaCl_2 were relatively the same. The flux declines caused by other binary foulants ranged between 23 – 36%. By comparing these results with data presented in Figure 2, it can be seen that calcium salt significantly intensified the membrane fouling (up to 72% difference in flux decline) for combined foulants containing alginate (BSA+ALG, ALG+DX, and ALG+XG). The impact of calcium addition was either negligible or minor for non-alginate foulant mixtures (0-12.5% difference in flux decline). These phenomena signify the reactivity of alginate with calcium ions as stated above.

The flux profiles obtained from filtration of ternary and quaternary foulants are illustrated in Figures 4 and 5. Without the presence of calcium (Figure 4), the percentages of flux decline caused by ternary and quaternary foulants ranged between 15% (for BSA+ALG+DX) to 36% (for ALG+DX+XG), while flux decline percentages with the addition of calcium (Figure 5) varied from 25% (for BSA+ALG+DX) to 39% (for ALG+DX+XG+BSA). Again, these results also indicated that the addition of calcium had aggravated the membrane fouling for alginate containing solutions. The addition of calcium to foulants containing alginate increased the

severity of flux decline by up to 66%, while for non-alginate fouling solution (BSA+DX+XG) no further flux decline was observed.

By comparing the experimental and additive flux declines (Table 1), it can be seen that **there are discrepancies between experimental and additive values (12.5% to 100% difference)**, which suggests possible interactions between foulants that synergistically affect the fouling behavior. In order to confirm this, further analyses of foulants were performed. Results from these analyses are discussed in sections 3.2-3.4.

3.2 Rheological behavior

Our previous work showed that the viscosity of feed solution was an important parameter governing the FO membrane fouling in a system containing a single foulant [16]. In order to determine whether this concept would be applicable to complex organic fouling, the rheological behavior of various mixed solutions was examined (Figures 6 – 9). When several substances present in the mixture, it is expected that the viscosity of the mixture would be in between the viscosity of the most viscous and the least viscous substances. However, our viscosity measurement results are different from common presumption. By looking at the viscosity – shear rate profiles, these feed solutions can be classified into three groups: 1) the viscosity of the mixture was dominated by the most viscous component in the solution (Figures 6b, 6c, 6e, 6f, Figures 7a-e, Figures 8a-d, 8f, and Figures 9a, 9c; 2) the viscosity of the mixture was lower than the viscosity of individual foulants (Figure 6a); and 3) the viscosity of the mixture was in between the maximum and minimum viscosity values of components present in the solution (Figure 6d, Figure 8e, Figures 9b, 9d, 9e). **This indicated that there could be a certain degree of**

interactions or chemical bonding between these organic substances that changed the physico-chemical properties of the combined foulants in groups 1 and 2.

It is known that the decrease in viscosity could improve the FO water flux [6]. However, by relating our viscosity measurement values to the FO performances, it seemed that a reduced viscosity did not always result in the alleviation of membrane fouling. It is interesting to observe that the decrease in viscosity of BSA+ALG mixture (group two) caused even more severe fouling. This suggested that viscosity was not the dominant factor that governed FO membrane fouling when mixed organic substances was used as feed. There could be other factors that exacerbated the fouling. Further works are needed to investigate this.

3.3 Fluorescence spectroscopy analysis

Chemical bonding between foulants could alter the fluorescence intensity. Fluorescence excitation-emission matrix measurements were conducted to confirm this. Figure 10 and Figure 11 represent Stern-Volmer plots of EEM measurements, which show the relationship between fluorescence intensity (F_0/F) and the concentration of the quencher (added foulant). It can be seen that F_0/F increased with the increase of quencher concentration for BSA+ALG, BSA+DX, BSA+XG, BSA+DX+calcium, BSA+XG+calcium. This behavior indicates the quenching of fluorophore by the added foulant (quencher). The loss of fluorescent signal (F) (quenching) indicates **bonding** between foulants [39]. The Stern-Volmer plot reaches a plateau at high quencher concentration, which indicates the presence of more than one fluorophore populations; one being accessible to quencher, while the others may be inaccessible, partially accessible or buried [40]. It means that the above-mentioned solutions may contain pure fluorophore and

fluorophore-quencher aggregates. The Stern-Volmer plot can also provide useful information on relative sensitivity of the fluorophore-quencher system; a higher K_{sv} value indicates more sensitive system. In the presence and absence of calcium, BSA+DX and BSA+XG solutions obtained relatively similar sensitivities, while BSA+ALG exhibited the lowest sensitivity (Figures 10a and 11a). The K_{sv} of BSA+ALG was approximately four times lower than the K_{sv} of other solutions. The lower the K_{sv} , the higher the quencher concentration is needed to quench the fluorescence. DX+XG, ALG+XG, ALG+DX (Figure 10b) and those with calcium chloride (Figure 11b) showed the reduction in F_0/F with the increase of quencher concentration. Such pattern indicates fluorophore destruction (no chemical bonding was formed) [41].

3.4 Zeta potential and hydrodynamic diameter measurements

The measurements of hydrodynamic diameter and zeta potential were also conducted to elucidate characteristics of foulants and foulant complexes. Sizes and charges of single and selected binary foulant solutions were analyzed to determine any inter-foulant interactions and/or synergistic fouling effect.

It can be seen from the data in Table 2 that BSA (6 nm diameter) and XG (54 nm diameter) interacted to form compact aggregates of 8 nm. The binding occurred through the amino-groups of the albumin and the carboxyl groups of the gum [42]. The addition of calcium chloride did not affect the BSA hydrodynamic diameter (6 nm), but slightly altered its charge (from -14 to -11 mV), while the size and zeta potential of XG increased significantly from 54 nm and -59 mV to 71 nm and -41 mV, respectively, with the addition of calcium chloride. This could be due to the attachment of calcium to carboxylic groups of BSA and XG. In the presence of calcium chloride,

the carboxyl-Ca²⁺-carboxyl bond linked the BSA and XG resulting in the formation of more complex substances.

The sizes of BSA+DX complex (7 nm without calcium and 8 nm with Ca addition) were comparable to the sizes of BSA and DX alone (Table 2). The zeta potential analysis results indicated that the binding of neutral DX with negatively charged BSA had resulted in the formation of a negatively charged BSA+DX complex (Table 2). According to literatures, BSA and DX could interact through the hydroxyl groups of the polysaccharide and the tryptophan residues of the protein, forming hydrogen bond [43]. The addition of calcium salt might diminish the negative charge of BSA+DX due to cation binding. Significant reduction in foulant size could also occur when foulants interacted with each other. For example, the size of XG was 54 nm, while the size of combined BSA+XG was only 8 nm.

BSA interacted with XG and ALG in similar manner, i.e. through its amino groups and the carboxyl groups of the polysaccharide [44]. The interactions of BSA-ALG were described in details in our previous work [24]. In brief, BSA interacted with ALG to form compact aggregates of 6 nm. The zeta potential measurement data indicated that there were two different types of aggregates formed in the solution, i.e. BSA-ALG complex (-32 mV) and unbound ALG (-47 mV). The addition of calcium initiated the formation of viscous ALG+calcium network with a structure resembling an egg-box. The linking between carboxyl groups of ALG and those of BSA occurred via calcium bridging.

Interesting phenomena were observed with ALG+DX foulant mixture. Both rheological test (Figure 6d) and EEM measurement results (Figure 11b) indicated no chemical bonds between ALG and DX as the viscosity of (ALG+DX) mixture fell between the viscosity values of ALG

and DX. On the contrary, data obtained from zeta potential and size measurements indicated that the ALG-DX solution contained two different types of particulates, i.e. particulates that had undergone conformational changes: (1) 16 nm hydrodynamic diameter with +3 mV zeta potential, which were closed to the size of ALG and DX (14 and 13 nm) and the charge of DX (-1 mV); (2) the 25 nm size and -34 mV charge, which represented foulants with altered morphology. One possible explanation of these contradictory results could be due to the fact that the ALG viscosity was relatively close to DX viscosity (Figure 6d). Hence, any viscosity change that might occur as a result of molecular interaction between ALG+DX could be too weak to be measurable. Furthermore, it can be seen in Figure 6d that the viscosity of (ALG+DX) was close to DX viscosity at 0–1 1/s shear rate; the viscosity of (ALG+DX) mixture was approaching ALG viscosity value at shear rate greater than 1 1/s. This seems to indicate that a certain degree of interaction might occur.

In the presence of calcium ions, the EEM and rheological test results of this mixture exhibited fluorophore destruction and the viscosity that was dominated by the most viscous component in the solution, respectively. Such data suggest that in the presence of calcium ions, ALG and DX formed highly viscous complex. With the absence of calcium ions, the EEM test indicated no chemical bond between ALG and XG molecules, while increased in viscosity was detected. In contrast, data from zeta potential and size measurements demonstrated the formation of 20 nm and -58 mV complexes. Similar contradictive results also occurred for DX+XG (negative EEM test, while the rheological test result was classified as group 1 as described in section 3.2.). Without the presence of calcium salt, the charge of DX+XG was -58 mV. The charge became less negative (-38 mV) with the addition of calcium salt. Further discussion on these conflicting results can be found at the end of this section.

The data from FO experiments showed that certain feed solutions exhibited different fouling behavior in the presence and absence of calcium chloride. For example, the addition of calcium salt into BSA+ALG, ALG+DX, ALG+XG, BSA+ALG+DX, BSA+ALG+XG, ALG+DX+XG+BSA solutions had caused moderate to significant flux decline. This could be due to the increased viscosity values of these solutions upon addition of calcium ions. No observable further flux decline occurred when calcium ions were added to BSA+DX and BSA+DX+XG solutions; this can be linked to unchanged rheological behavior with the addition of calcium ions. There were cases where fouling became slightly less severe with the addition of calcium (BSA+XG and DX+XG), this can be correlated to the reduction of zeta potential values of BSA+XG and DX+XG complex in the presence of calcium ions (-58 vs. (-37) – (-38) mV).

Results obtained from permeate flux, rheological measurement, EEM, molecular size and zeta potential analyses for various combinations of binary foulants are summarized in Table 3. The symbol “✓” for water flux indicates that the system with binary foulants (for example BSA+ALG) caused further flux decline in comparison to the flux decline obtained with single foulants (BSA and ALG alone). The symbol “x” indicates that the flux decline obtained with binary foulants is the same as those with single foulants (no further flux decline was observed when both foulants were combined). Similar context applies for EEM, viscosity and zeta potential results. As mentioned earlier, the results are rather contradictory. Based on these results, it can be assumed that positive results for all measurements indicate strong interaction between foulant molecules, while this is certainly not the case for partially positive results. It can be seen in Table 3 that the EEM, viscosity and zeta potential measurements suggest changes in physico-chemical properties when BSA was combined with DX. However, the water flux measurement result suggests otherwise. It appears that changes in physico-chemical properties of

organic foulants do not always aggravate the fouling. No chemical bonding was detected between ALG+DX, ALG+XG and DX+XG molecules, while all other measurements indicate positive results (except for viscosity measurement of ALG+DX). This could be due to the binary foulants formed relatively weak chemical bonds (non-covalent bond) that could mediate specific interactions between molecules to become undetectable [45]. Further study is required to confirm this.

4. Conclusions

Findings from this study suggested that viscosity was not the dominant factor that governed organic fouling in FO process as the decrease in viscosity did not always result in less fouling.

FO membrane fouling became more severe with the presence of calcium ions, particularly for combined organic foulants containing alginate. This was due to the reaction between calcium ions and alginate molecules via intermolecular bridging.

Complex organic fouling in FO process is governed by both physico-chemical properties of the feed and chemical bonding between foulants. It is not possible to determine the FO performance based on single parameter due to a possible interplay between the governing factors. Similar physico-chemical properties, for example aggregates of similar size (BSA+ALG, BSA+DX, BSA+XG) could result in different filtration behavior, while relatively weak chemical bonds could mediate specific interactions between molecules,

causing the changes to become undetectable. It was also found that the changes in physico-chemical properties of organic foulants do not always exacerbated the fouling.

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Figure 2.	Normalized water flux profiles obtained with various binary foulants. The feed contained 66.7 ppm of each foulant and 10 mM NaCl. Experimental conditions: FO mode; cross-flow velocity 6.5 cm/s; draw solution 1 M NaCl; pH 6.25-6.5; temperature 23 °C.
Figure 3.	The effect of calcium chloride addition on the performance of FO process with binary foulants. The feed contained 66.7 ppm of each foulant, 10 mM NaCl and 1 mM CaCl ₂ . Experimental conditions: FO mode; cross-flow velocity 6.5 cm/s; draw solution 1 M NaCl; pH 6.25-6.5; temperature 23 °C.
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	<p>fluorescence intensity of quenched and unquenched substance decreasing and increasing, respectively. Pre-experiments were carried out to understand fluorescent behavior of mixtures (i.e. whether fluorescence signal increasing or decreasing) (data not shown). Concentration of quencher was gradually increased from 12.5 to 32000 ppm. Sodium and calcium chloride concentrations were adjusted accordingly to fluorophore concentration to maintain same foulant-NaCl-CaCl₂ ratio utilized in FO experiments. K_{sv} was calculated as a slope of Stern-Volmer plot.</p>
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Table 1. Experimental and theoretical (additive) flux declines.

Table 2. Hydrodynamic diameter and zeta potential of single foulants and selected foulant complexes.

Table 3. Changes in flux and physico-chemical properties of binary foulants as opposed to the changes obtained with individual foulants without the presence of calcium.