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Impact of intrinsic properties of foulants on membrane performance in osmotic desalination applications

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Abstract

This study investigates the effect of intrinsic physico-chemical properties of polysaccharides and proteins on the performance of flat sheet and hollow fiber forward osmosis (FO) membranes in different modes. Results showed that the foulant hydrodynamic diameter, zeta potential and rheological behavior were essential characteristics that govern the osmotic desalination processes. Diffusivity was the dominant mechanism governing the performance of hollow fiber membranes in FO mode, while the performance of flat sheet membrane in pressure retarded osmosis (PRO) mode was controlled by a combination of three mechanisms: diffusivity, size exclusion and electrostatic forces.

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1. Introduction

Forward osmosis (FO) membranes are known to be less prone to fouling as compared to reverse osmosis membranes. This is due to the fact that there is no external pressure applied. Nevertheless, fouling remains an important issue in FO process as it affects the process performance and causes the decline in the permeate flux. Fouling is a complex phenomenon that can be governed by different parameters. The main factors affecting membrane fouling are: operating conditions, feed characteristics, as well as membrane properties and configuration [1]. At present, different types of FO membranes have been developed by various research groups [2-5]. These newly developed membranes have been reported to exhibit relatively high water fluxes. However, only limited researchers have tested their in-house fabricated membranes for fouling propensity [6-8]. Furthermore, the majority of existing FO fouling studies (either organic or inorganic) focus more on the effect of operating conditions [9, 10], membrane orientation [11, 12] and draw solution [13, 14]. The effect of physical and chemical properties of foulant on FO fouling behavior has not been thoroughly investigated. FO fouling behavior has been studied at various pH values [10, 13], with the addition of divalent cations [11, 15], with different foulant sizes [9, 13, 16] and concentrations [13]. The intermolecular adhesive forces between foulants (alginate, bovine serum albumin and humic acid) and the membrane have been studied with atomic force microscopy [15]. It was found that the fouling profiles of all foulants were almost identical. However, when calcium salt was added, significant differences in fouling rates were observed. The authors suggested that FO membrane fouling was related to foulant-foulant and foulant-membrane interfacial forces. The severity of fouling would depend on the amount of carboxylic groups of the foulant. This was due to the binding action of calcium ions to the

carboxylic functional groups of the organic foulants has increased the intermolecular adhesion and resulted in a more severe water flux decline.

Asymmetric membranes that consist of a dense active layer and a support layer are commonly used for forward osmosis processes. Hence, forward osmosis can be operated in two different membrane orientations: with the active layer of the membrane facing the feed solution (known as AL-FS or FO mode) and with the active layer of the membrane facing the draw solution (AL-DS or pressure retarded osmosis (PRO) mode). The selection of membrane orientation mainly depends on the feed characteristics and concentration [17, 18], as well as on the material and morphology of FO membranes [19, 20]. Due to its membrane structure, FO mode would be more suitable for feed with high fouling tendency, while PRO mode seems to be more favorable for feed with low fouling propensity. However, the selection of a suitable membrane orientation does not depend only on the above-mentioned factors, since there is a trade-off between the benefit of less severe membrane fouling and the cost effectiveness of the process (it is known that for the same draw solution concentration, higher membrane productivity could be achieved in PRO mode as compared to FO mode).

This work aimed to obtain better understanding of FO membrane fouling for osmotic desalination applications by taking into account the intrinsic physico-chemical properties of various foulants (polysaccharides and proteins). The filtration performance and fouling propensity of FO membranes were tested with two different FO membranes: a commercial flat sheet membrane manufactured by Hydration Technologies Inc. (HTI) and an in-house fabricated thin film composite hollow fiber membrane. A commercial FO flat sheet membrane

demonstrates high fouling resistance, but it has low productivity. A high concentration of draw solution is therefore required to achieve high water flux. On the other hand, thin film composite hollow fiber membrane exhibits superior water flux. However, it is more prone to fouling when used with its support layer facing the feed water, since foulants can easily gain entry to its highly porous sub-layer [21]. Since flat sheet and hollow fiber FO membranes appear to have different characteristics and have their own suitability for specific conditions, it would be more reasonable if these membranes were not studied under the same operation conditions. Therefore, these studies were not intended to compare the performances of both membranes. The performance of FO hollow fiber membrane was investigated in FO mode, while the flat sheet FO membrane was tested in PRO mode. The effect of foulants on each membrane was individually discussed.

2. Materials and Methods

2.1. FO membranes and foulants

Two types of FO membranes were used in the study: an in-house fabricated thin film composite FO hollow fiber membrane (#C type) [22] and an asymmetric mesh embedded FO flat sheet membrane manufactured by HTI [23]. The characteristic parameters of both membranes can be found in Table 1. The active layer of the membrane was located on the inner surface of the hollow fiber substrate. Each module consisted of fifteen hollow fibers with 1.3 mm outer diameter and 0.9 mm inner diameter. The effective filtration areas were 37 cm^2 for flat sheet membrane and 119 cm^2 for hollow fibers. Prior to fouling experiments, the intrinsic separation properties, i.e. pure water (A) and salt (B) permeability, 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. Details on foulants used in this study are shown in Table 2.

2.2. *Membrane fouling experiments*

The individual performance of flat sheet (in PRO mode) and hollow fiber membranes (in FO mode) was studied by conducting 360 minutes of fouling experiments. Baseline tests were performed to evaluate the membranes' flux behavior without the presence of foulant. The feed solution for baseline tests contained 10 mM NaCl with pH of 6.25-6.5. All feed solutions used for fouling experiments contained 10 mM NaCl and 200 ppm of foulants. 200 ppm of foulant concentration was selected to approximate the concentration of soluble organics in seawater that have been reported as major fouling precursors [24]. Similar concentration of organic foulants was also used in various former studies on FO fouling [9, 15, 25]. 3 mM $CaCl_2$ was added to the feed in selected experiments (DX 250, ALG and XG). The working volume of the feed solution in the tank was 5 L. In order to generate an identical initial water flux, 3 and 2.25 M NaCl draw solutions were used for flat sheet and hollow fiber membranes, respectively. 5 M NaCl dosing solution was used to maintain a constant draw solution concentration. During experiment, feed and draw solutions were circulated on each side of the membrane at 6.5 cm/s cross-flow velocity in countercurrent configuration. An electronic balance (Mettler Toledo, Switzerland) connected to a data logging system was used to record the water flux at predetermined time intervals ($J(t)$). The average water flux values of replicated experimental runs were then normalized to the initial water flux (J_0). With the presence of foulants, the decline of water flux during FO process could be due to a combined effect of concentration polarization and fouling. Hence, the normalized water flux due to fouling (($J(t)'/J_0)_{fouling}$) can be calculated as:

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$$\left(\frac{J_{(t)}'}{J_0} \right)_{fouling} = \frac{J_{(t)}}{J_0} + \Delta J_{bl(t)} \tag{1}$$

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 recorded data (not shown) indicated that 15 and 5 % flux drop occurred during 360 minutes of baseline tests for flat sheet and hollow fiber membranes, respectively. The initial water fluxes in baseline and fouling experiments for both membranes were approximately the same ($\sim$ 28 L/m^2-h).

2.3. Characterization of foulants and FO membranes

The performance of FO membrane can be affected by the intrinsic physico-chemical properties of foulants such as rheological behavior, size and charge. In order to study the FO membrane fouling behavior, various foulants were characterized to provide better understanding and relationship between foulant properties and FO membrane performance. The zeta potential and the hydrodynamic diameter of foulants were characterized by using Malvern Zetasizer Nano ZS, UK. The rheological behavior (shear stress-shear rate and viscosity-shear rate dependence) of foulants was studied 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 0.985º angle. The shear rate dependent experiments were run by varying the shear rates between 0.1 and 1000 s^{-1} at 23 ºC. The concentration of foulants used for viscosity, size and charge measurements was identical to that used in FO experiments. SurPASS electrokinetic analyzer (Anton Paar GmbH, Austria) was used to determine the zeta potential of the membranes. 10 mM KCl solution was pumped through an adjustable gap sample holder. The streaming potential was detected by Ag/AgCl electrodes located at both ends of the sample holder. Measurements were

performed at 3-10 pH range. The pH of electrolyte was adjusted by using 0.1 M NaOH or HCl solution. The zeta potential of hollow fiber membrane was measured by cutting the fibers longwise and fixing them onto the sample holder. Several cut fibers were arranged in parallel with their active layers facing up so that they fully covered the surface of the sample holder. The contact angle of the membranes was measured with the sessile drop method, using a goniometer (Contact Angle System OCA, DataPhysics Instruments GmbH, Germany).

3. Results and Discussion

The following sections describe results from characterization of foulants and FO membranes. These outcomes were then linked to the performances of both FO hollow fiber and flat sheet membranes and discussed.

3.1. Characterization of foulants

Figure 1 shows the rheological behavior of various polysaccharides and proteins. It can be seen that certain foulant solutions were Newtonian fluids, while others exhibited pseudoplastic behavior. In contrast to Newtonian fluids, in which the shear stress is a linear function of the velocity gradient, pseudoplastic fluids undergo shear thinning effect [26]. Among all foulants, XG and XG + calcium solutions exhibited pseudoplastic behavior at $0.1 - 70$ s^{-1} shear rate range. Decrease in shear stress of ALG + calcium solution was observed within $0.1 - 3$ s^{-1} shear rate range, while at shear rate greater than 3 s^{-1} no change in shear stress was observed.

Figure 2 illustrates the effect of shear rate on the viscosity of non-Newtonian foulants. XG and XG + calcium exhibited identical viscosity-shear rate profiles. The viscosity values of these

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As mentioned earlier, all biopolymers used in this study were characterized in terms of their

hydrodynamic diameters and zeta potential values. The hydrodynamic diameters of DX 250,

ALG and XG were 11, 15 and 13 nm, respectively (Table 3). The addition of calcium salt to DX

250 did not significantly alter its hydrodynamic diameter (14 nm). In contrast to DX250, the

presence of Ca^{2+} in XG and ALG solutions led to significant increase in hydrodynamic diameter

of the polysaccharides. The hydrodynamic diameter of XG increased to 34 nm, while the

hydrodynamic diameter of ALG magnified to 57 nm. The hydrodynamic diameters of proteins

were 3-6 nm [27]. The data also indicated a non-linear relationship between dextran sizes and

their molecular weights. For instance, the hydrodynamic diameters of DX 6 and DX 70 were 3

and 7 nm, respectively, while the hydrodynamic diameter of DX 500 was only slightly higher

(15 nm).

Table 3 presents the zeta potential values of foulants. It can be seen that all species were

negatively charged, except for LYS. The zeta potential values of all dextrans were relatively

close to zero, except for DX 70. For example, the zeta potential values of DX 6, DX 250 and DX

500 were – 9, – 2 and – 3 mV, respectively, while DX 70 was slightly more negative (– 17 mV). It appears that the addition of calcium to DX 250 did not alter its charge. The zeta potential values of protein substances were – 16 mV for BSA, + 14 mV for LYS and – 7 mV for OVL [28]. Among all foulants, XG (– 50 mV) [29] and ALG (– 45 mV) [30] had the most negative values. The addition of calcium chloride to XG and ALG reduced the electronegativity of both substances to – 29 mV.

According to literatures, dextrans are neutral polysaccharides with no charged moieties [31]. A slightly negative charge of dextrans observed in the study could be due to the presence of sulfate groups in the polymer chain [32]. The charge of proteins was originated from protonation of amino groups and dissociation of carboxylic functional groups [33], while the charges of XG and ALG were due to the latter mechanism only [33, 34]. When salt was added, the ionized functional groups of XG and ALG would interact with cations. The increased viscosity of ALG in the presence of Ca^{2+} was a result of the formation of a highly organized gel with a structure resembling an egg-box [35]. The viscosity of XG solution should also increase in the presence of divalent cations, however it would depend on XG and salt concentrations [36]. XG and ALG became less negative with the addition of calcium, this could be attributed to a reduced thickness of the electric double layer of the biopolymers. The increase of the hydrodynamic diameters of ALG and XG in the presence of calcium indicated the entrapment of cations by the polymer chain. In contrast to XG, results from viscosity measurements suggested that the entrapment of calcium by ALG led to the gelation of the solution. Based on rheological measurements, XG + calcium and XG demonstrated pseudoplastic behavior. The non-Newtonian behavior of XG has also been reported elsewhere [37]. The shear-thinning of XG could be due to the ability of

polymer molecules to form aggregates through hydrogen bonding and polymer entanglement. These aggregates were progressively disrupted during shearing, resulting in a lower solution viscosity [36, 38]. Newtonian behavior of low concentration BSA, LYS and OVL solutions is in agreement with previous studies [39-41]. The decrease of ALG + calcium shear stress within 0.1 - 3 s^{-1} shear rate range was due to the rupture of the egg-box polymer network.

3.2. Relationship between fouling behavior and foulant characteristics

3.2.1. Hollow fiber membrane

Figure 4 presents the effect of foulants (DX 250, ALG, XG with and without calcium) on the hollow fiber membrane performance in FO mode. The presence of calcium ions did not cause any observable impact, since the flux declines of DX 250 with and without calcium were insignificant (9 and 2 %). In contrast, severe flux drop occurred for both XG and XG with calcium. The percentages of flux decline caused by XG and XG + calcium were 37 and 43 %, respectively. Results obtained from all fouling experiments are summarized in Table 4. ALG demonstrated distinct fouling patterns. In the presence of calcium ions, the flux decline was prominent (similar to the flux decline of XG) ~ 52 %, the flux drop was insignificant in the absence of calcium (comparable to the flux decline of DX 250 solution) ~ 2 %. Figure 5 illustrates the impact of dextrans (Figure 5a) and proteins (Figure 5b) on the performance of hollow fiber membranes. It is clear that dextrans and proteins influenced the FO process in a similar manner with insignificant water flux decline.

The highest flux decline occurred for filtration of ALG + calcium (52 %). In relation to its rheological behavior, the viscosity of ALG + calcium was significantly higher than the viscosity

of other solutions. Furthermore, it was found that the magnitude of water flux decline increased with the increase of foulant viscosity. This indicates that rheological behavior could be a factor determining the severity of membrane fouling in FO mode.

Stokes-Einstein equation relates viscosity to the diffusivity [42]:

$$D_s = \frac{kT}{6r\pi\eta} \tag{2}$$

where D_s is the diffusion coefficient, κ is Boltzmann's constant, T is the absolute temperature, r is the particle diameter and η is the viscosity.

Stokes-Einstein equation indicates that the increase in viscosity at constant temperature would result in the decrease of diffusion coefficient. Since FO relies on the osmotic pressure difference as a driving force to induce the diffusion of water across a dense membrane, lower diffusivity would cause lower water flux. Results from experiment confirmed that the most viscous foulants caused the highest flux decline.

The shear rate at the inner wall of a Newtonian fluid flowing inside a channel can be calculated according to Poiseuille's law [43]:

$$\gamma = \frac{8V}{h} \tag{3}$$

where V is the tangential flow velocity in the feed channel and h is the height of the feed channel;

For FO hollow fiber module, h = d. For calculation of shear rate of liquid outside the hollow fiber, d = inner diameter of the shell (tubing); for shear rate of liquid inside the hollow fiber, d = inner diameter of the hollow fiber.

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The shear rate of Newtonian fluids at the inner wall of the hollow fiber calculated with equation (3) was found to be 580 s^{-1}. The fluid shear stress at shear rate of 580 s^{-1} was determined by using shear rate-shear stress relationship (Figure 1). The shear stress values of various Newtonian fluids are shown in Table 3. ALG had the highest shear stress of 0.75 Pa, while the shear stress of other foulant solutions (DX 250, DX 250 + calcium, DX 6, DX 70, DX 500, BSA, LYS and OVL) ranged between 0.58-0.65 Pa. As expected, results from fouling tests suggested that less fouling occurred at higher shear stress.

The zeta potential values of the active layer of the hollow fiber membrane can be seen in Figure 6. The active layer of the hollow fiber membrane appeared to become more negatively charged with the increase of pH. The membrane had a slightly negative charge (the zeta potential was – 4.5 mV) at the pH value of FO experiment (6.25-6.5). Since the membrane did not obtain a strong charge, the surface interaction between the membrane and charged foulants could be weak. Hence, the flux decline caused by both negatively and positively charged foulants was negligible (Figure 5b).

Results from experiments also showed that the performance of FO hollow fiber membrane was not affected by the size of biopolymers (Figure 5a). This was due to the hollow fiber membrane was operated with its active layer facing the feed, therefore, foulants could not enter the dense active layer of the membrane.

3.2.2. Flat sheet membrane

Figure 7 shows the influence of DX 250, ALG, and XG on the flat sheet membrane performance in PRO mode. The water flux drops caused by DX 250 and XG were 36 and 44 %, respectively, while the flux loss of ALG was less prominent (14 %). In the presence of calcium, the flux declines for all foulants ranged between 40 to 50 %. It can be clearly seen that calcium did not significantly affect the water fluxes of DX 250 and XG. Flux decline caused by DX 250 + calcium or XG + calcium was only 6-7 % more severe than the flux drop without the presence of calcium. In contrast, the addition of Ca^{2+} to ALG aggravated the membrane fouling by 28 %. Figure 8 depicts the membrane performance during filtration of various dextrans and proteins. DX 6 exhibited the most severe flux decline of 56 %. Filtration of DX 70 and DX 500 solutions resulted in 31 and 36 % flux loss, respectively. LYS and OVL demonstrated identical fouling behavior with the final flux drop of around 45 %. Flux decline caused by BSA solution was 21 %.

Experimental results indicated that the performance of flat sheet membrane in PRO mode could be affected by foulant charge and hydrodynamic diameter. Fouling induced by positively charged foulant (LYS) was approximately two times higher than the one caused by the negatively charged foulant (BSA). Although flat sheet membrane was positively charged (+ 4 mV) at pH 6.25-6.5 (Figure 6), the membrane showed affinity to positively charged foulant during filtration. It is known that cellulose triacetate membrane is a neutrally charged polymer that may possess hydroxyl and carboxylic functional groups [44]. Therefore, the negatively charged segments of the membrane would attract the positively charged LYS and repel negatively charged BSA and OVL. The fouling profile of OVL, however, was in fact identical to LYS. These proteins have been shown to have similar hydrodynamic diameters (Table 3), while

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the zeta potential values indicated that OVL was less negative than BSA. Hence, it can be assumed that membrane fouling due to protein compounds could be ruled by charge repulsion/attraction.

Biopolymers with smaller sizes caused higher fouling rates. The flux decline with feed containing 3 nm DX 6 was 20 % higher than the flux drop of feed with 15 nm DX 500 (Figure 8a). Since the pore size of membrane support layer (Table 1) was larger than the size of the foulants, smaller biopolymers could easily gain entry and accumulate inside the porous support layer, hence fouling would be more severe. Interestingly, fouling caused by 15 nm dextran (DX 500) was more pronounced than fouling induced by 7 nm dextran (DX 70). Such behavior could be due to DX 70 was more negatively charged than DX 500. This suggests that foulant hydrodynamic diameters and charge are essential parameters for flat sheet membrane operated in PRO mode.

As mentioned earlier, fouling caused by ALG was negligible (Figure 7). Fouling generated by DX 250 solution was similar to fouling caused by XG (36 % and 44 %, respectively). Data from dynamic light scattering measurements indicated that the hydrodynamic diameters of polysaccharides were almost identical to those of a neutral DX 250 and strong negative charges of ALG and XG. Results from rheological tests suggested that the viscosity of XG was higher than the viscosity values of DX 250 and ALG. Viscous foulant would have lower diffusivity coefficient (equation 2), hence fouling would be more severe. These findings suggest that fouling of DX 250, ALG and XG may be dominated by electrostatic and diffusivity mechanisms.

The addition of calcium ions to the feed solution containing alginate had drastically reduced the water flux (Figure 7). No significant further flux decline occurred with the addition of calcium into the feed containing DX 250, as well as XG. The addition of Ca^{2+} ions did not affect the viscosity, hydrodynamic diameter and charge of DX 250. In contrast, the hydrodynamic diameters of XG and ALG increased when their charges became less negative. The viscosity of XG was unaffected by calcium. ALG, however, underwent a huge viscosity escalation. This observation confirms that foulant charge and viscosity are critical characteristics for flat sheet membrane in PRO mode.

The shear rate of Newtonian fluids for experiments with flat sheet membrane was 520 s^{-1}. Depending on the viscosity values, the shear stress at 520 s^{-1} shear rate ranged between 0.52 – 0.67 Pa. By relating results in Table 3 and Table 4, it can be seen that the lowest flux decline of 14% was achieved at the highest shear stress (0.67 Pa). This indicates that the increase in shear stress could minimize the extent of water flux decline. Hence, in addition to other parameters (viscosity, zeta potential and hydrodynamic diameter), shear stress also played an important role in controlling fouling of flat sheet membrane. This finding was similar to that of the hollow fiber and was in agreement with previous studies, which suggested that high shear stress could minimize the foulant-membrane and foulant-foulant interactions resulting in a less severe fouling [45, 46].

4. Conclusions

This research aimed to study the effect of foulants intrinsic characteristics on direct osmosis process performance. By relating the characteristics of foulant with membrane fouling behavior,

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it was found that the increase in feed viscosity caused more severe membrane fouling. The reduction of foulant size, shear stress and electronegativity depression magnified the fouling of flat sheet membrane in PRO mode. Based on these findings, it can be concluded that diffusivity was the dominant fouling mechanism governing the performance of hollow fiber membranes in FO mode; and the performance of flat sheet membrane in PRO mode was controlled by a combination of three fouling mechanisms: diffusivity, size exclusion and electrostatic forces.

References

[1] C. Tang, T. H. Chong, A. Fane, Colloidal interactions and fouling of NF and RO membranes: A review, Advances in Colloid and Interface Science 164 (2011) 126-143.

[2] R. Wang, L. Shi, C. Tang, S. Chou, C. Qiu, A. Fane, Characterization of novel forward osmosis hollow fiber membranes, Journal of Membrane Science 355 (2010) 158-167.

[3] N. Y. Yip, A. Tiraferri, W. Phillip, J. Schiffman, M. Elimelech, High performance thin-film composite forward osmosis membrane, Environmental Science & Technology 44 (2010) 3812-3818.

[4] N. Bui, M. L. Lind, E. Hoek, J. McCutcheon, Electrospun nanofiber supported thin film composite membranes for engineered osmosis, Journal of Membrane Science 385-386 (2011) 10-19.

[5] K. Y. Wang, T.-S. Chung, G. Amy, Developing thin-film composite forward osmosis membranes on the PES/SPSf substrate through interfacial polymerization, AICHE Journal 58 (2012) 770-781.

[6] Y. Gu, Y. Wang, J. Wei, C. Tang, Organic fouling of thin-film composite polyamide and cellulose triacetate forward osmosis membranes by oppositely charged macromolecules, Water Research 47 (2013) 1867-1874.

[7] S. Zhang, K. Y. Wang, T.-S. Chung, H. Chen, Y. C. Jean, G. Amy, Well-constructed cellulose acetate membranes for forward osmosis: Minimized internal concentration polarization with an ultra-thin selective layer, Journal of Membrane Science 360 (2010) 522-535.

[8]   E. Arkhangelsky, F. Wicaksana, C. Tang, A. Al-Rabiah, S. Al-Zahrani, R. Wang, Combined organic-inorganic fouling of forward osmosis hollow fiber membranes, Water Research 46 (2012) 6329-6338.

[9]   S. Lee, C. Boo, M. Elimelech, S. Hong, Comparison of fouling behavior in forward osmosis (FO) and reverse osmosis (RO), Journal of Membrane Science 365 (2010) 34-39.

[10]   S. Zou, Y. Gu, D. Xiao, C. Tang, The role of physical and chemical parameters on forward osmosis membrane fouling during algae separation, Journal of Membrane Science 366 (2011) 356-362.

[11]   C. Tang, Q. She, W. Lay, R. Wang, A. Fane, Coupled effects of internal concentration polarization and fouling on flux behavior of forward osmosis membranes during humic acid filtration, Journal of Membrane Science 354 (2010) 123-133.

[12]   V. Parida, H. Y. Ng, Forward osmosis organic fouling: Effects of organic loading, calcium and membrane orientation, Desalination 312 (2013) 88-98.

[13]   C. Boo, S. Lee, M. Elimelech, Z. Meng, S. Hong, Colloidal fouling in forward osmosis: role of reverse salt diffusion, Journal of Membrane Science 390-391 (2012) 277-284.

[14]   E. Cornelissen, D. Harmsen, , K. F. de Korte, C. J. Ruiken, J. J. Qin, H. Oo, L. P. Wessels, Membrane fouling and process performance of forward osmosis membranes on activated sludge, Journal of Membrane Science 319 (2008) 158-168.

[15]   B. Mi, M. Elimelech, Chemical and physical aspects of organic fouling of forward osmosis membranes, Journal of Membrane Science 320 (2008) 292-302.

[16]   C. Nayak, S. S. Valluri, N. Rastogi, Effect of high or low molecular weight of components of feed on transmembrane flux during forward osmosis, Journal of Food Engineering 106 (2011) 48-52.

[17] S. Zhao, L. Zou, D. Mulcahy, Effects of membrane orientation on process performance in forward osmosis, Journal of Membrane Science 382 (2011) 308-315.

[18] S. Zhao, L. Zou, C. Tang, D. Mulcahy, Recent developments in forward osmosis: Opportunities and challenges, Journal of Membrane Science 396 (2012) 1-21.

[19] A. Tiraferri, N. Y. Yip, W. Phillip, J. Schiffman, M. Elimelech, Relating performance of thin-film composite forward osmosis membranes to support layer formation and structure, Journal of Membrane Science 367 (2011) 340-352.

[20] L. Shi, S. Chou, R. Wang, W. X. Fang, C. Tang, A. Fane, Effect of substrate structure on the performance of thin-film composite forward osmosis hollow fiber membranes, Journal of Membrane Science 382 (2011) 116-123.

[21] E. Arkhangelsky, F. Wicaksana, S. Chou, A. Al-Rabiah, S. Al-Zahrani, R. Wang, Effects of scaling and cleaning on the performance of forward osmosis hollow fiber membranes, Journal of Membrane Science 415-416 (2012) 101-108.

[22] S. Chou, L. Shi, R. Wang, C. Tang, C. Qiu, A. Fane, Characteristics and potential applications of a novel forward osmosis hollow fiber membrane, Desalination 261 (2010) 365-372.

[23] J. Herron, Asymmetric forward osmosis membranes, US Patent 7,445,712, Hydration Technologies Inc., Albany, OR, USA, 2005.

[24] C. Fritzmann, J. Löwenberg, T. Wintgens, T. Melin, State-of-the-art of reverse osmosis desalination, Desalination 216 (2007) 1-76.

[25] B. Mi, M. Elimelech, Organic fouling of forward osmosis membranes: Fouling reversibility and cleaning without chemical reagents, Journal of Membrane Science 348 (2010) 337-345.

[26] F. Durst, Fluid mechanics: an introduction to the theory of fluid flows, Springer Berlin, Germany, 2008.

[27] A. Valstar, M. Almgren, W. Brown, The interaction of Bovine Serum Albumin with surfactants studied by light scattering, Langmuir 16 (2000) 922-927.

[28] Y. Wang, C. Tang, Fouling of nanofiltration, reverse osmosis, and ultrafiltration membranes by protein mixtures: the role of inter-foulant-species interaction, Environmental Science and Technology 45 (2011) 6373-6379.

[29] A. Benichou, A. Aserin, R. Lutz, N. Garti, Formation and characterization of amphiphilic conjugates of whey protein isolate (WPI) / xanthan to improve surface activity, Food Hydrocolloids 21 (2007) 379-391.

[30] A. Contreras, A. Kim, Q. Li, Combined fouling of nanofiltration membranes: Mechanism and effect of organic matter, Journal of Membrane Science 327 (2009) 87-95.

[31] T. Heinze, T. Liebert, B. Heublein, S. Hornig, Functional polymers based on dextran, Polysaccharides II 205 (2006) 199-291.

[32] C. Chauvierre, D. Labarre, P. Couvreur, C. Vauthier, Novel polysaccharide-decorated poly(isobutyl cyanoacrylate) nanoparticles, Pharmaceutical Research 20 (2003) 1786-1793.

[33] Y. Zhao, F. Li, T. Carvajal, M. Harris, Interactions between bovine serum albumin and alginate: an evaluation of alginate as protein carrier, Journal of Colloid and Interface Science 332 (2009) 345-353.

[34] F. Garcia-Ochoa, V. E. Santos, , J. A. Casas, E. Gomez, Xanthan gum: production, recovery, and properties, Biotechnology Advances 7 (2000) 549-579.

[35] G. Grant, E. Morris, D. Rees, P. Smith, D. Thom, Biological interactions between polysaccharides and divalent cations: the egg-box model, FEBS Letters 32 (1973) 195-198.

[36] M. Sworn, Xanthan gum, in: G. Phillips, P. Williams, Handbook of hydrocolloids, Woodhead Publishing, Cambridge, 2000, pp. 103-115.

[37] L. Smolka, A. Belmonte, Charge screening effects on filament dynamics in xanthan gum solutions, Journal of Non-Newtonian Fluid Mechanics 137 (2006) 103-109.

[38] B. Katzbauer, Properties and applications of xanthan gum, Polymer Degradation and Stability 59 (1998) 81-84.

[39] W. R. Bowen, J. I. Calvo, A. Hernandez, Steps of membrane blocking in flux decline during protein microfiltration, Journal of Membrane Science 101 (1995) 153-165.

[40] A. Szymanska, T. Hornowski, G. Slosarek, Denaturation and aggregation of lysozyme in water-ethanol solution, Acta Biochimica Polonica 59 (2012) 317-321.

[41] T. Matsumoto, J. Chiba, Rheological and small-angle X-ray scattering investigations on the shape and order arrangement of native ovalbumin molecules in aqueous colloids, Journal of Chemical Society, Faraday Transactions 86 (1990) 2877-2882.

[42] B. van der Bruggen, C.Vandecasteele, Modelling of the retention of uncharged molecules with nanofiltration, Water Research 36 (2002) 1360-1368.

[43] M. Frappart, A. Massé, M. Jaffrin, J. Pruvost, P. Jaouen, Influence of hydrodynamics in tangential and dynamic ultrafiltration systems for microalgae separation, Desalination 265 (2011) 279–283.

[44] A. Tiraferri, M. Elimelech, Direct quantification of negatively charged functional groups on membrane surfaces, Journal of Membrane Science 389 (2012) 499-508.

[45] O. Le Berre, G. Daufin, Skimmilk crossflow microfiltration performance versus permeation flux to wall shear stress ratio, Journal of Membrane Science 117 (1996) 261-270.

[46] D. Jermann, W. Pronk, S. Meylan, M. Boller, Interplay of different NOM fouling mechanisms during ultrafiltration for drinking water production, Water Research 41 (2007) 1713-1722.

[47] J. Wei, C. Qiu, C. Tang, R. Wang, A. Fane, Synthesis and characterization of flat-sheet thin film composite forward osmosis membranes, Journal of Membrane Science 372 (2011) 292-302.

[48] Y. Wang, F. Wicaksana, C. Tang, A. Fane, Direct microscopic observation of forward osmosis membrane fouling, Environmental Science and Technology 44 (2010) 7102-7109.

List of Figures and Tables

Figure 6.	Zeta potential of flat sheet and hollow fiber membranes in 10 mM KCl as a function of pH.
Figure 7.	The effect of calcium addition on the performance of flat sheet membrane in PRO mode with (a) DX 250, (b) ALG and (c) XG. Feed solution contained 10 mM NaCl + 200 mg/L foulant + 0 or 3 mM CaCl$_2$. Experimental conditions: cross-flow velocity 6.5 cm/s; draw solution 2.25 M NaCl; pH 6.25-6.5; temperature 23 °C.
Figure 8.	Effect of (a) DX 6, DX 70, DX 500 and (b) BSA, LYS, OVL on flat sheet membrane performances in PRO mode. Feed solution contained 10 mM NaCl + 200 mg/L foulant. Experimental conditions: cross-flow velocity 6.5 cm/s; draw solution 3 M NaCl; pH 6.25-6.5; temperature 23 °C.

Table 1. Characteristics of FO membranes.

Table 2. Foulants used in the study.

Table 3. Shear stress, hydrodynamic diameter and zeta potential of studied polysaccharides and proteins.

Table 4. Flux declines due to fouling measured at the end of experiments.