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Relating intrinsic membrane water permeability and fouling propensity in forward osmosis processes

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ABSTRACT

In this study, we determine the effect of different foulants on membrane permeability in a forward osmosis (FO) process. Each model foulant, including humic acid (HA) as an organic foulant, carboxylate-modified latex particles (CML) as a colloidal foulants and *Escherichia coli* as a bio-foulant, was added and fouled on the membrane surface. Two membranes with different flux, a low water permeable membrane (LPM) and a high water permeable membrane (HPM), were selected to study the effect of foulants on membrane permeability. Water flux, reverse salt flux and reverse flux selectivity were investigated. Furthermore, the performances of the membrane are described in terms of the solute selectivity coefficient (K). A larger K value indicates a decrease of the FO performance. After both membranes were fouled with HA molecules, an HA fouling layer promoted the FO performance due to the increase of hydrophilicity on the membrane surface. In addition, the charge screening effect in the HA fouling layer hindered the transportation of salt ions, which decreased the reverse salt flux and increased the reverse flux selectivity. On the other hand, CML and *E. coli* significantly decreased the FO performance because they strongly promoted external concentration polarization and internal concentration polarization. These effects hindered the salt diffusion to the bulk feed solution and increased the salt concentration near the active layer, which decreased the osmotic pressure gradient and decreased the water flux. Moreover, the fouling also affected the different flux membranes differently. The reverse flux selectivity of HPM changed more than that of LPM after they were fouled with foulants. Thus, our study confirmed that HPM was more sensitive to fouling than LPM, and more sophisticated state for fouling mitigation would be required.

Keywords: Forward osmosis; Membrane fouling; Membrane permeability; Concentration polarization

1. Introduction

The forward osmosis (FO) process is an osmotic pressure-driven process. The high osmotic pressure, generated by a high concentrate in draw solution, pulls water across a semi-permeable membrane from the low osmotic pressure side in feed solution [1,2]. The FO process has gained wider attention recently in many applications, such as desalination [3,4], wastewater treatment [5,6] and liquid food processing [7,8] due to the apparent advantages that emanate from its operation without applied hydraulic pressure, which has the potential for lower energy consumption and fouling propensity [9]. However, there are many factors that interrupt the performance of the system especially fouling. Lutchmiah et al. [10] stated that when foulants appear in the system and are deposited on the membrane surface, it decreases in the net driving force, enhances the concentration polarization (CP) and results in a flux decline.

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In an osmotic process, mass transfer is critical on both sides of the membrane, which is different from a pressure-driven membrane process in which mass transfer on the permeable side of membrane is unimportant [11]. The CP is considered as a critical drawback for lowering the water flux during the FO process, which is attributed to the convective permeate flow as being the same in a pressure-driven process and can occur on both sides of the membrane [12]. On the feed side of the FO process, the polarized layer is more concentrated than the bulk solution, which is called concentrative external concentration polarization (ECP), while on the permeable side, the layer is more diluted, which is called dilutive ECP. The presence of polarized layer inhibits the permeate flow due to the increased osmotic pressure at the membrane active layer surface, resulting in the decline of water flux. This effect has been controlled with cross flow and well-designed hydrodynamics [13]. Furthermore, when the membrane is asymmetric, one of the polarization effects occurs within the porous support layer. This phenomenon cannot be mitigated by shear turbulence and is referred to as internal concentration polarization (ICP) [11]. When the water molecules diffuse from the active layer and enter the porous support layer, the salt concentration in the supportive layer is diluted, which changes the osmotic pressure gradient. Hence, the quantity of water molecules transported to the supportive layer also affects the FO performance.

In addition, membrane development over the past 4 decades has been based on a pressure-driven process, rather than an osmotic-driven process. This has meant that the design of the membrane was very thin and had dense layers that rejected an undesirable solute, and a very thick porous support layer that mechanically supported the thin active layer under the hydraulic pressure required for operation [14]. Subsequently, the more recent membrane development has focused on increasing water permeability as well as on decreasing solute diffusion; thus, recent membranes have been designed to getting more high water permeability than the previous one.

Although many recent studies have investigated the fouling in the FO process [1,15,16], however, few studies have addressed the effect of foulants on membrane permeability using the solute resistivity coefficient (*K* value). Typically, the *K* value is used to determine the transportation of water molecules and salt ions for evaluating the FO performance. A larger *K* value indicates a decrease in the FO performance. Moreover, the mechanism in flux decline and the cause of it in flux decline are still not well understood, especially water molecules and draw solute transportation, and the quantity of water molecules transported to the supportive layer also affects the FO performance. The objective of this study was to investigate the effect of different foulants on membrane permeability in a low water permeable membrane (LPM) and a high water permeable membrane (HPM). We examined the water flux, the reverse salt flux and the reverse flux selectivity of both membranes before and after they fouled with different types of foulants.

2. Materials and methods

2.1. Membrane and foulants

We used two types of membrane based on water permeability, a commercial low water permeable membrane provided by GE (South Korea) and a commercial high water permeable membrane provided by Toray (South Korea). All membrane samples were stored and soaked in deionized water before use to remove the chemical covering and any contaminants attached on the membrane surface.

The humic acid (HA; Sigma-Aldrich, USA), carboxylate-modified latex particles (CML; Magsphere, Pasadena, CA) and *Escherichia coli* BL21 pET-25 (*E. coli*), which had a green fluorescence, were used as the organic foulants, colloidal foulants and bio-foulants, respectively.

2.2. FO fouling and flux test

All experiments were conducted in a laboratory-scale FO unit [17]. Each membrane sample was placed with the active layer facing the feed solution in the membrane cell with a length, width and channel height of 7.75, 2.60, and 0.30 cm, respectively. The total effective membrane area was 20.15 cm^2. Two speed gear pumps (Longer Pump WT3000-1FA) were used to flow the feed and draw solutions with 702.0 mL/min (corresponding to a cross-flow velocity of 15.0 cm/s). The initial volume of the solution was 4 L in the feed solution and 2 L in the draw solution. The draw solution was placed on a digital balance (AND GF-4000 digital weighing scale), and weight changes were recorded by a computer to calculate the permeation flux. The conductivity of the draw solution was continuously measured using a conductivity probe (Vernier LabPro, USA) that was connected to a computer during the entire experiment.

For the fouling experiment, 10 mM NaCl was used as feed solution, and then, each foulant was added in the feed solution, including 50 mg/L of HA, 10^7/mL of CML or 10^7/mL of *E. coli*. The experiment was run for 8 h. The fouling protocol can be found in elsewhere [18]. The controlled temperature was 21°C ± 0.5°C using custom-made temperature controller. To determine the membrane surface properties, the water contact angles of each membrane surfaces were measured by a contact angle analyzer (Phoenix, South Korea).

3. Results and discussion

To investigate the water permeability of each membrane at difference draw concentrations in the FO mode, we used types of membrane based on the water permeability: one was a low water permeable membrane (LPM), and the other was a high water permeable membrane (HPM). According to Figs. 1(a) and (b), water flux and salt flux in both membranes increased with an increase in the draw concentration. However, the water flux and salt flux of HPM were larger than that of LPM. The reason was that the membrane structure of HPM formed like macrovoids as represented in Fig. 2(b), which helped reduce the mass transfer resistance and increased the water molecule and salt ion transportation. In addition, the macrovoids structure in HPM reduced the increase in ICP in the supporting layer; thus, the water flux and salt flux of HPM were larger than that of LPM. On the other hand, the membrane structure of LPM was asymmetric and more tortuous than HPM as represented in Fig. 2(a). McCutcheon and Elimelech [11] stated that one of these boundary layers occurs within the porous support layer, protecting it from the shear and turbulence associated with cross flow along the membrane surface. The water molecules were transported with difficulty through the membrane structure, which caused an increased ICP, which in turn reduced the osmotic pressure gradient, resulting in the low water flux and salt flux.

Moreover, Loeb et al. [19] introduced a simplified equation to model CP based on the model that was developed by Lee et al. [20], to calculate the water flux in the FO process without consideration of the membrane orientation or any applied hydraulic pressure as expressed in Eq. (1):

$$K=\left(\frac{1}{J_w}\right)\ln\left(\frac{B+A\pi_{D,b}}{B+J_w+A\pi_{F,m}}\right) \tag{1}$$

where K is the solute resistivity coefficient within the membrane support layer; A and B are pure water and the solute permeability coefficient, respectively [21,22]; $\pi_{D,b}$ is the osmotic pressure of draw solution in the bulk; and $\pi_{F,m}$ is the osmotic pressure of the feed solution at the membrane surface. From Eq. (1), the water flux decreased in the osmotic pressure difference and the increase of the K value. In addition, the K value is also defined as:

$$K=\frac{t\tau}{D\varepsilon} \tag{2}$$

where t is the thickness; τ is the tortuosity; ε is the porosity; and D is the diffusion coefficient of the membrane [23]. These values are important intrinsic parameters of the membrane because they directly affect the ICP, which also affects the water flux. On this basis, we used the K value to determine the intrinsic membrane properties and transportation of water molecules and salt ions for evaluation the FO performance in this research. A lower K value indicates the more water transportation, which produces a better FO performance.

A comparison of the average K value between LPM and HPM from Tables 1 and 2 reveals that the average K value of HPM was lower than that of LPM. That indicates that the membrane structure of HPM was less tortuous and more porous than LPM, which helped the water molecules be transported through the membrane more easily, resulting in a higher water flux in HPM.

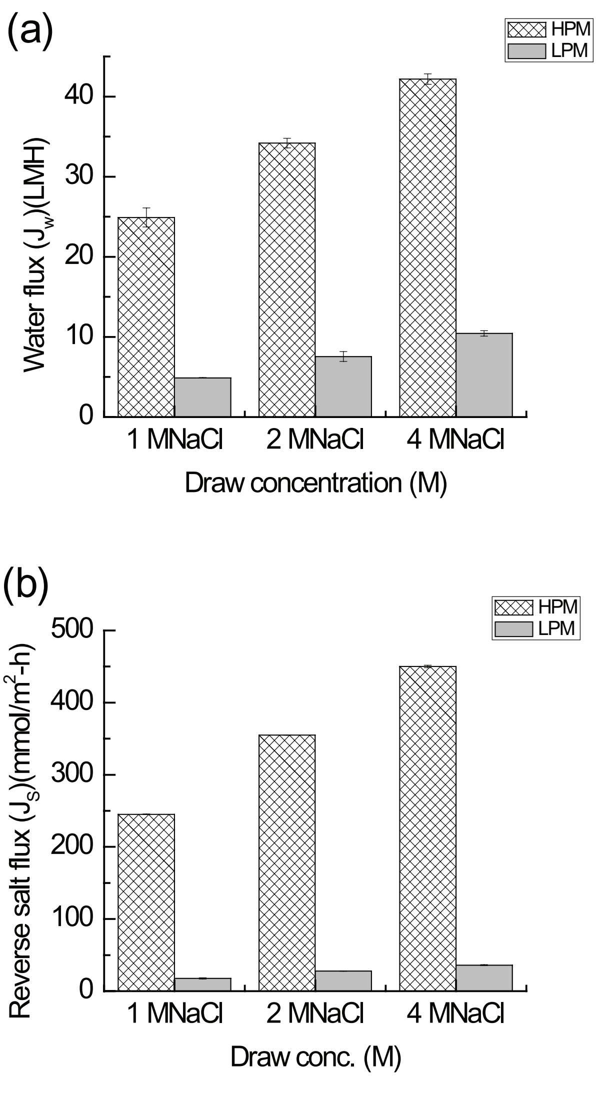

Fig. 1. The water flux (a) and reverse salt flux (b) of LPM and HPM at different draw concentration.

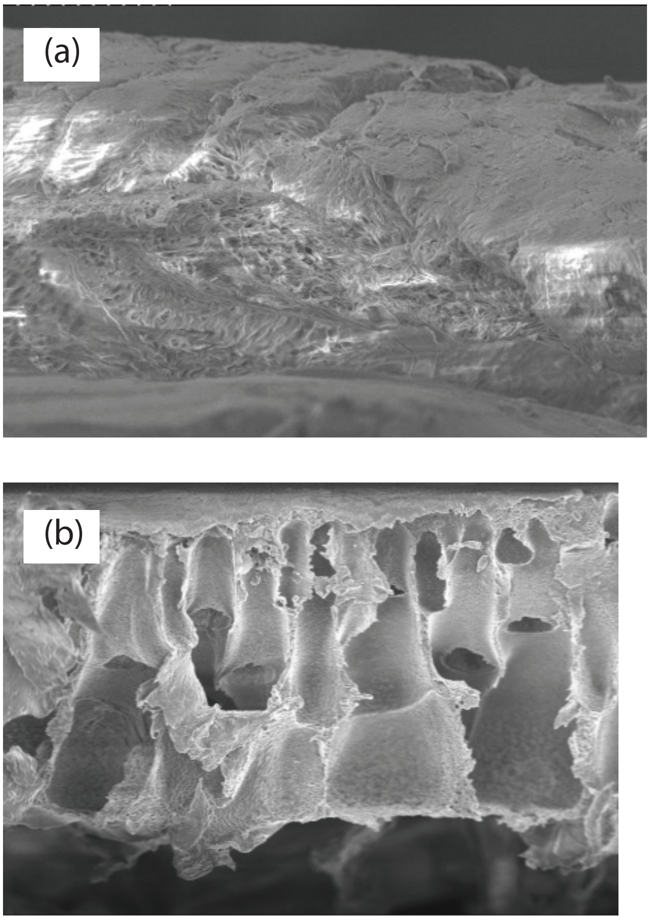

Fig. 2. Cross section of LPM (a) and HPM (b).

3.1. The effect of different foulants on the membrane permeability

We selected HA, CML and *E. coli* as the organic foulants, colloidal foulants and bio-foulants, respectively, to investigate the effect of foulants on membrane permeability. The water flux of LPM and HPM in the presence of each foulant is shown in Fig. 3(a). The water flux of the membrane fouled with HA was slightly higher than the controlled one, while the water flux of the membrane fouled with CML and *E. coli* was lower. The functional groups that contribute most to the surface charge and reactivity of HA are carboxylic and phenolic, which consist of a hydroxyl group. These functional groups are polar groups that can change the membrane surface property to become more hydrophilic as can be seen in the decrease of water contact angle results in Fig. 4 [24]. That indicates favorable surface properties for the access of water molecules. In addition, the reverse salt flux of the membrane fouled with HA significantly decreased (Fig. 3(b)). HA molecules consisted of various charged organic compounds especially negatively charged organic matter. That means that when HA fouled the membrane surface more, the charged organic matter deposited on the membrane surface increased. This charged organic matter hindered the ions diffusion through the membrane by the enhanced electrostatic interaction, resulting in the salt flux decrease [25].

On the other hand, CML as a colloidal foulant and *E. coli* as a bio-foulant decreased the water flux (Fig. 3(a)). During the deposition of colloidal particles on the membrane surface, the cake-enhanced osmotic pressure (CEOP) occurred. Under CEOP conditions, the salts accumulated near the membrane surface needed to diffuse through the tortuous paths within the colloidal layer but were unable to, and these salts could not be exposed to the bulk by tangential flow, leading to the enhanced salt CP layer near the membrane surface, which reduced the osmotic pressure gradient and resulted in a water flux decrease [16]. When the membrane was fouled with bio-foulants, this phenomenon also occurred but it was attributed to the bio-enhanced osmotic pressure (BEOP). Bacterial cells deposited on the membrane surface

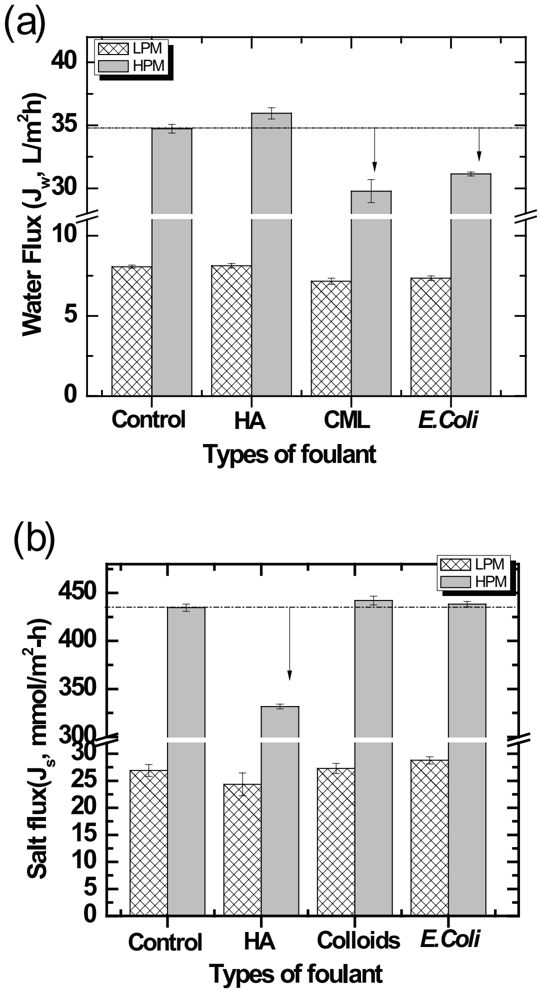

Fig. 3. The water flux (a) and reverse salt flux (b) results of LPM and HPM fouled with the different types of foulants.

Table 1
Data for osmotic runs in FO mode with different draw concentration of LPM

Active layer		Supportive layer		Flux (LMH)	K (10^6 s/m)
Concentration (M)	Osmotic pressure (atm)	Concentration (M)	Osmotic pressure (atm)		
0.01	0.48	1.00	48.25	4.89	1.72
0.01	0.48	2.00	96.50	7.55	1.26
0.01	0.48	4.00	193.01	10.45	1.75
				Average	1.34

Table 2
Data for osmotic runs in FO mode with different draw concentration of HPM

Active layer		Supportive layer		Flux (LMH)	K (10^6 s/m)
Concentration (M)	Osmotic pressure (atm)	Concentration (M)	Osmotic pressure (atm)		
0.01	0.48	1.00	48.25	24.91	0.35
0.01	0.48	2.00	96.50	34.21	0.30
0.01	0.48	4.00	193.01	42.17	0.28
				Average	0.31

and held together by the extracellular polymeric substance matrix layer, hindered the back diffusion of salt; thus, the osmotic pressure gradient between both sides of the membrane decreased and resulted in a water flux decrease [26]. However, there were no significant changes in the membrane surface properties of the membrane fouled with CML and *E. coli* as shown in Fig. 4. The water contact angle of membrane fouled with CML and *E. coli* were quite similar to the controlled one. Because the water flux decreased by CEOP/BEOP phenomena, the dilution effect in the ICP was not severe, and the formation of colloidal particles or *E. coli* only encouraged the ECP, so there was no significant change in the reverse salt flux results, as can be seen in Fig. 3(b).

For the investigation of changes in membrane selectivity due to the fouling layer, the reverse flux selectivity (J_w/J_s) was calculated and is shown in Fig. 5. The value of the reverse flux selectivity is independent of the structure of the membrane support layer and is solely determined by the selectivity of the membrane active layer [27]. The difference in salt concentration at the active layer and support layer interfaces is necessary to generate a large osmotic gradient, which enhances the high water flux. Nevertheless, this higher concentration of salts also increases the concentration gradient across the active layer, which enhances the salt flux. Therefore, the value of reverse flux selectivity should remain constant [28]. However, after the membrane surface was fouled with different foulants, the reverse flux selectivity changed. That indicates that the membrane surface properties changed. The results showed that the increase in the reverse flux selectivity after the membrane surface was fouled with HA was due to an increase in hydrophilicity and the charge screening effect, while after fouling with CML and *E. coli*, the reverse flux selectivity decreased due to strong promotion of ECP and ICP as described above.

Furthermore, the solute resistivity coefficient (K) could be used to determine the FO performance. The increased K value indicates a decrease in the FO performance or a decrease in reverse flux selectivity. According to Tables 3 and 4, when a membrane was fouled with HA, the K value decreased in both LPM and HPM, while the K value increased when the membrane was fouled with CML or *E. coli*. That means that the effect of CML and *E. coli* to reduce the membrane permeability is stronger than HA. HA molecules could promote the FO performance while CML and *E. coli* significantly decreased the FO performance.

Interestingly, the reverse flux selectivity of HPM significantly changed more than that of LPM as can be seen in Fig. 6. Due to the lower water flux in LPM, while the dilution effect in ICP was small and ECP was less concentrative, there was no significant change in the water flux and salt flux. However, with a higher water flux in HPM, there was a more severe dilution effect in ICP, and ECP was more concentrative; thus, the water flux and salt flux were more severely changed than in LPM.

In addition, the change in the K value was determined as the sensitivity of the membrane surface as determined

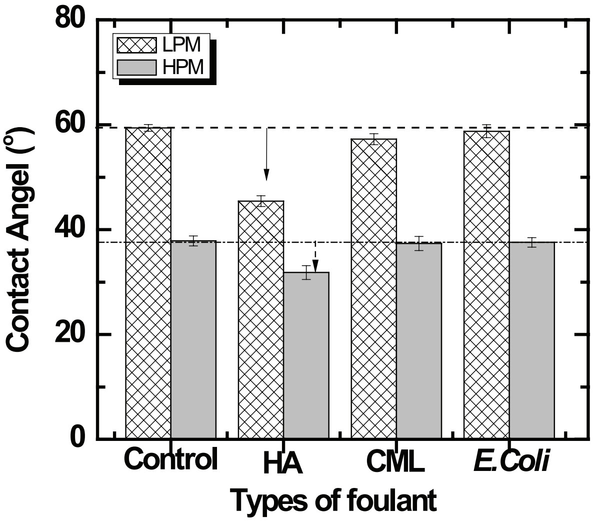

Fig. 4. The contact angles of LPM and HPM fouled with different types of foulants.

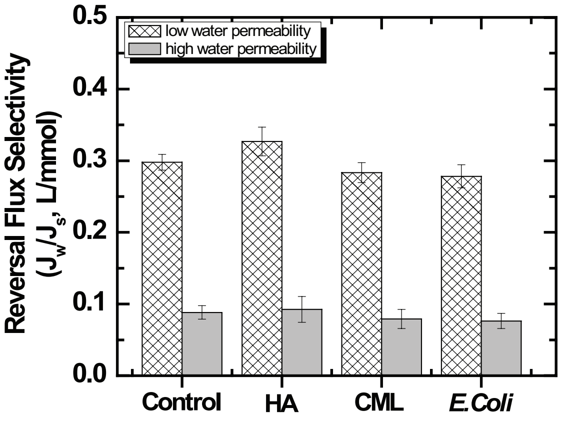

Fig. 5. The reverse flux selectivity of LPM and HPM fouled with different types of foulants.

Table 3
Data for osmotic runs in FO mode with different foulants addition of LPM

Conditions	Active layer		Supportive layer		Flux (LMH)	K (10^6 s/m)	ΔK (%)
	Concentration (M)	π (atm)	Concentration (M)	π (atm)			
Control	0.01	0.48	2.70	130.28	7.50	1.42	0.00
HA	0.01	0.48	2.70	130.28	7.60	1.39	2.11
CML	0.01	0.48	2.70	130.28	7.30	1.47	3.52
E. coli	0.01	0.48	2.70	130.28	7.40	1.44	1.41

Table 4
Data for osmotic runs in FO mode with different foulants addition of HPM

Conditions	Active layer		Supportive layer		Flux (LMH)	K (10^6 s/m)	ΔK (%)
	Concentration (M)	π (atm)	Concentration (M)	π (atm)			
Control	0.01	0.48	2.70	130.28	34.50	0.33	0.00
HA	0.01	0.48	2.70	130.28	36.00	0.31	6.06
CML	0.01	0.48	2.70	130.28	29.50	0.40	21.21
E. coli	0.01	0.48	2.70	130.28	31.25	0.37	12.12

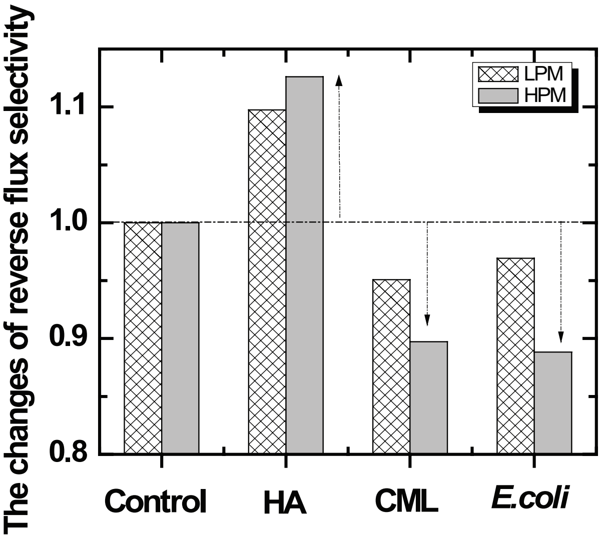

Fig. 6. The changes of reverse flux selectivity with different types of foulants.

by the changes in reverse flux selectivity between LPM and HPM. The K value of HPM was more changed than that of LPM, especially when the membrane was fouled with CML and *E. coli*. That indicates that HPM was more sensitive to fouling than LPM. This type of membrane must be carefully used, when fouling occurs.

4. Conclusions

In this study, we investigated the effects of different foulants on membrane permeability. We found that the HA fouling layer promoted the FO performance due to an increase of hydrophilicity on the membrane surface and the charge screening effect, which led to an increase in water flux and a decrease in reverse salt flux. On the other hand, CML and *E. coli* significantly decreased the FO performance due to the strong promotion of the ECP and ICP. These effects hindered the salt diffusion and increased the salt concentration near the active layer, resulting in the water flux decrease. Moreover, the fouling also was affected different by the membrane permeability. After both membranes were fouled with foulants, various membrane surface properties of HPM significantly changed more than that of LPM, as can be seen in the change of the reverse flux selectivity and the change of the calculated K value. Consequently, HPM was more sensitive to fouling than LPM and high flux FO membrane should be used carefully in operation, especially when fouling occurs.

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