

Organic and Colloidal Fouling of Thin-film Composite Polyamide Membrane through Forward Osmosis

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Abstract

The main focus of this research is to investigate the mechanisms of flux decline during the organic and colloidal fouling of a thin-film composite (TFC) polyamide membrane operated in osmotically driven membrane process (forward osmosis). It has been found that flux decline by humic acid was minimal while the attachment of colloidal particles resulted the gradual decline in forward osmosis. The main mechanism of the flux decline in forward osmosis is due to the colloid-enhanced osmotic pressure (CEOP) due to the salt build-up near the membrane surface and was reversible by the removal of attached particles. Combined organic and colloidal fouling did not cause any flux decline which showed similar results with humic acid fouling alone due to the increase of negative charge on the membrane surface by adsorbed humic acids.

Keywords- *Forward osmosis; membrane; humic acid; colloidal fouling; organic fouling*

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I.

II. Introduction

Forward osmosis (FO) is one of the latest membrane technologies that become the focus of studies apart from the

well-known reverse osmosis (RO) process. It has gained interests due to its lower cost and low energy consumption, because it uses natural osmotic pressure as its driving force in contrast to the hydraulic pressure being used in RO (McGinnis and Elimelech, 2007; Phuntsho et al., 2011; Yoon et al., 2013). Both membrane processes encounters a great challenge which is fouling. Membrane fouling includes organic fouling, inorganic fouling, colloidal fouling and biofouling (Pan et al., 2010; Yoon et al., 2013). In the case of organic fouling of salt-rejecting membranes, the decline in the permeate flux is generally attributed to the increase in the total hydraulic resistance brought by the organic fouling layer (Lee et al., 2010). Organic fouling has been reported to be dependent upon specific membrane physiological factors such as hydrophilicity, zeta potential, membrane materials membrane roughness and others. However, in addition to these factors, organic loading has also been stated to have an impact on flux decline in FO based on the study of Parida and Ng (2013). Lower organic loading resulted in lower flux decline. Colloidal fouling in FO, on the otherhand, is governed by concentration polarization and cake layer formation on the non-porous membrane surface (Li and Elimelech, 2006). Furthermore, Boo et al. (2012) demonstrated that significant flux decline rates were observed with large particles (139 nm) as compared to small particles (24 nm) due to the thick or less porous fouling layers formed.

The main objective of this paper is to study the mechanism of organic and colloidal fouling through direct microscopic observation as well as to know the fouling effect of combined organic and colloidal fouling.

III. Materials and Methods

A. Membrane and Model foulants.

The membrane used in the entire experiment was a thin-film composite (TFC) polyamide membrane for desalination (GE PRO-RO 4040 LE series). The membrane was cut according to the size of the membrane cell (2.6 cm x 7.75 cm). Humic acid (Sigma Aldrich) was used as model organic foulant at 100 mg/L, while 10⁷/ml yellow-green fluorescent carboxylated modified latex (CML) particles (1µm diameter; Magsphere, Pasadena, CA) were used as model colloidal particles.

B. Bench-scale cross-flow experiment

1. Forward osmosis set-up

The system is comprised of two independent closed loops for the feed and draw solutions which is similar to the typical bench-scale setup in the previous studies (Kang et al., 2008; Mi and Elimelech, 2008). The feed and draw solution were both recirculated back to the reservoir by two individual gear pumps (LongerPump WT3000-1FA). The volume changes in the draw solution measured by AND GF-4000 digital weighing scale were automatically transmitted to the computer for a minimum of 8 h. The feed conductivity was monitored by using a device (LabPro, Vernier). The cross-flow membrane cell used was customized with equally structured channels on both sides of the membrane. The dimensions of the rectangular, cross-flow, channel membrane unit were 2.60 cm × 7.75 cm with a channel height of 0.30 cm. The clear membrane cell was placed under the microscope (Olympus BX43, Japan) at 100x magnification on the feed side.

2. Fouling protocol

Pure water and 10 mM NaCl feed solution were used with corresponding draw solution concentrations of 2 M and 2.4 M of NaCl respectively, which were designed to produce around 6 LMH ($L/m^2 \cdot h$) of initial flux.

The protocol for fouling experiment could be found elsewhere (Mi and Elimelech, 2010). Initially, baseline experiments were performed for 100 minutes with no foulants added. After the flux has become stable, humic acid and CML particles were added in the feed solution to attain 100 mg/L and $10^7/ml$, respectively. The graphical representation of the fouling experiment is shown in Fig.1.

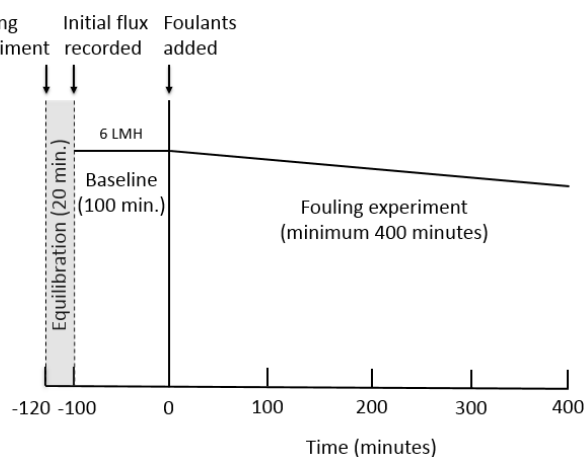
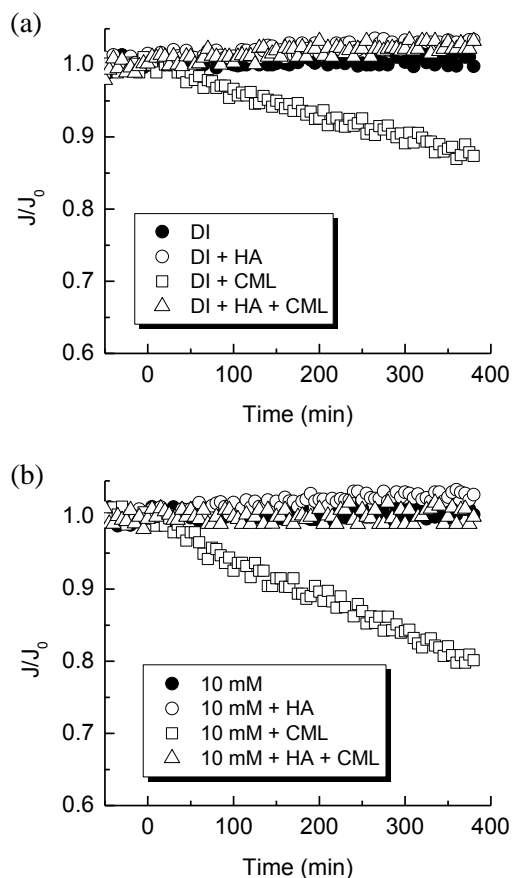


Figure 1: Graphical representation of the fouling experiment

IV. Results and Discussions

A. Impact of humic acid and colloids

Fig. 2 shows the flux decline curves with humic acid and CML particles as foulants. The FO flux after the addition of humic acid did not result any decline until the end of the experiment. Tang et al. (2010) reported that at low initial flux levels, the FO flux in the presence of humic acid foulant was nearly identical to the baseline flux, indicating little flux decline due to fouling. However, significant flux decline has been observed at very high initial flux (>40 LMH). Moreover, instead of decrease in flux, a slight increase was observed during the humic acid fouling. This might be due to humic acid adsorption affected certain properties of the membrane as what have been studied by Mänttari et al. (2000). Humic acid was adsorbed on the membrane surface and that the negatively charged functional groups of humic acid dominate the membrane surface charge. The slight enhancement in flux during the presence of humic acid may be due to the change in hydrophilicity of the membrane. Since the membrane was covered by humic acid, foulant-fouled membrane interaction took place. As a result, the membrane would become more hydrophilic and negatively charged.



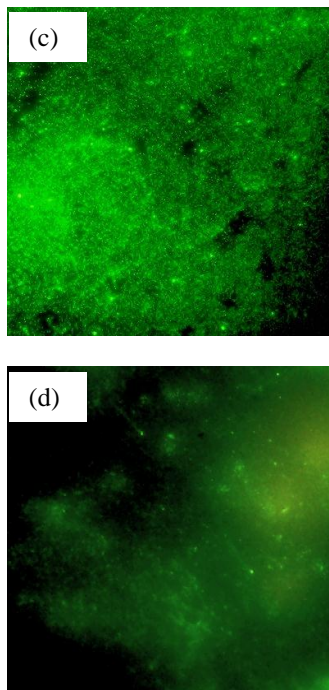


Figure 2: Normalized flux at different fouling conditions (a) DI feed and (b) 10 mM feed; Microscopic images of CML particles attached on the membrane during (c) colloidal fouling only and (d) combined colloidal and humic acid fouling at 6 h

Colloidal fouling experiment, unlike humic acid, showed flux decline for both feed solution conditions. Around 15% and 20% decline in flux were obtained for the DI and 10 mM feed solution respectively within 6 h. For salt rejecting membranes just like the TFC polyamide used in this study, cake-enhanced osmotic pressure (CEOP) is the major contributor in overall flux decline in colloidal fouling wherein the deposited colloid layer hinders the back diffusion of salt into the bulk solution (Lee et al., 2010). Under CEOP condition, the salts accumulated near the membrane surface need to diffuse through the tortuous paths within the colloid layer but were unable to be exposed to the shear by tangential flow, therefore, the significant decrease in the effective back diffusion will greatly enhance the concentration polarization and the osmotic pressure of salt near the membrane surface (Guo et al., 2012). The elevated osmotic pressure near the membrane surface leads to a substantial drop in the net driving force, and thus, results in a significant decline in permeate flux (Boo et al., 2012). The higher ionic strength of the 10 mM feed shows difference in flux behavior as compared to the DI water as feed. Increased ionic strength caused the electric double layer of the membrane and particles to shrink which becomes more susceptible to adhesion. On the otherhand, one factor could be that the colloid size could help in the lower back transport rate of the particles to the bulk solution (Boo et al., 2012).

Combined organic and colloidal fouling showed same results were with that of humic acid fouling alone, wherein there was no significant flux decline even the ionic strength was increased to 10 mM. Two possible mechanisms were stated for the synergistic effects of combined fouling: adsorption of humic acid to the colloidal surface as well as to the membrane surface and hindered colloidal attachment. Figures 2c and 2d demonstrate the CML particles attached on the membrane with and without the presence of humic acid. Flux decline is more significant during colloidal fouling alone due to the greater CML particles attached on the membrane causing much severe CEOP. CML attachment on the membrane is lesser in the presence of the humic acid resulting to negligible flux difference.

B. Reverse flux selectivity

Table 1 shows the reverse flux selectivity which is the ratio of the water flux to the reverse solute flux. Based on the modeling study of Phillip et al. (2010), it can be regarded as the volume of water produced per moles of draw solute lost. It is said to be independent of the membrane structural parameter and bulk draw solution concentration. Reverse flux selectivity is higher for DI water as compared to 10 mM NaCl feed solution. Nonetheless, it does not vary much in the case of 10 mM NaCl feed solution. For DI water as feed solution, reverse flux selectivity is highest during humic acid filtration. This might be attributed to the change in membrane properties by the adsorbed humic acid. Moreover, the rate of water flux per reverse solute flux is least during colloidal fouling by CML particles on both types of feed solution. We can formulate that, since colloidal fouling is significant in this study due to CEOP, the diffusion of salt to the bulk feed solution was hindered by the CML particles attached on the membrane.

Table 1 : Average reverse flux selectivity of different fouling conditions

Foulant Type	J_w/J_s	
	DI	10 mM NaCl
No foulant	0.15296	0.04436
HA	0.22119	0.04378
CML	0.13896	0.03421
HA + CML	0.15805	0.04430

v. Conclusions

Organic fouling by humic acid and colloidal fouling in the presence of humic acid did not show any significant flux decline due to the changed properties of the membrane.

However, colloidal fouling still governed the fouling mechanism of TFC polyamide membrane in forward osmosis. CEOP played a major role by hindering the passage of salt to the bulk solution. Moreover, the number of particles or cells attached on the membrane is directly proportional to the flux decline. Therefore, in this study, colloidal fouling control is extremely important in FO process.

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