WATER RESEARCH 47 (2013) 1867–1874

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Organic fouling of thin-film composite polyamide and cellulose triacetate forward osmosis membranes by oppositely charged macromolecules

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ARTICLE INFO

Article history:
Received 30 July 2012
Received in revised form
3 January 2013
Accepted 5 January 2013
Available online 22 January 2013

Keywords:
Forward osmosis (FO)
Organic fouling
Thin film composite polyamide
Cellulose triacetate
Macromolecules

ABSTRACT

Fouling of cellulose triacetate (CTA) and thin-film composite (TFC) forward osmosis (FO) membranes by organic macromolecules were studied using oppositely charged lysozyme (LYS) and alginate (ALG) as model foulants. Flux performance and foulant deposition on membranes were systematically investigated for a submerged membrane system. When an initial flux of 25 L/m^{2}h was applied, both flux reduction and foulant mass deposition were severe for feed water containing the mixture of LYS and ALG (e.g., 50% LYS and 50% ALG at a total foulant concentration of 100 mg/L). In comparison, fouling was much milder for feed water containing either LYS or ALG alone. Compared to the CTA FO membrane, the TFC FO membrane showed greater fouling propensity under mild FO fouling conditions due to its much rougher surface. Nevertheless, under severe FO fouling conditions, fouling was dominated by foulant-deposited-foulant interaction and membrane surface properties played a less important role. Furthermore, when the feed water contained both LYS and ALG in sufficient amount, the deposited cake layer foulant composition (i.e., the LYS/ALG mass ratio) was not strongly affected by membrane types (CTA versus TFC) nor testing modes (pressure-driven NF mode versus osmosis-driven FO mode). In contrast, solution chemistry such as pH and calcium concentration had remarkable effect on the cake layer composition due to their effects on foulant–foulant interaction.

1. Introduction

Forward osmosis (FO) is a membrane separation process in which water flows from a low-osmotic-pressure feed solution (FS) to a high-osmotic-pressure draw solution (DS) across a semi-permeable membrane (Cath et al., 2006; Zhao et al., 2012). Compared to conventional pressure-driven separation processes such as reverse osmosis (RO) and nanofiltration (NF), FO shows advantage of lower energy input when concentrated DS is available or can be easily regenerated. In recent years, FO has been considered for various potential applications, such as water and wastewater treatment (Holloway et al., 2007; Cornelissen et al., 2008), seawater desalination (McCutcheon et al., 2006) and power generation via pressure retarded osmosis process (Achilli et al., 2009; Chou et al., 2012; She et al., 2012b; Sivertsen et al., 2012).

Fouling can severely deteriorate membrane performance during water/wastewater treatment (Jarusutthirak and Amy,

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0043-1354/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.watres.2013.01.008

2006; Lay et al., 2011; Tang et al., 2011). Existing FO fouling studies have focused on the effects of permeate flux level (Mi and Elimelech, 2008; Tang et al., 2010; Zou et al., 2011; She et al., 2012a), membrane orientation (Tang et al., 2010; Wang et al., 2010b; Zhao et al., 2011), and DS type (Zou et al., 2011; She et al., 2012a). Investigations on FO fouling mechanisms often involve single type of model foulant (Mi and Elimelech, 2008; Tang et al., 2010; Zhao et al., 2011; She et al., 2012a). On the other hand, literature on FO fouling by mixed foulants is still lacking (Liu and Mi, 2012). Systematic study is still required to understand the role of the interactions between the different foulant species on FO fouling behavior in mixed foulants systems.

The effect of FO membrane materials on fouling is also of great interest. Due to the dominance of cellulose triacetate (CTA) FO membranes in the commercial market (Wei et al., 2011), most existing FO fouling studies were performed with CTA membranes (Mi and Elimelech, 2008; Tang et al., 2010; Wang et al., 2010b; Zhao et al., 2011; She et al., 2012a). On the other hand, recent developments in thin film composite (TFC) polyamide FO membranes show these membranes can have significantly higher water flux and better solute rejection compared to CTA FO membranes (Wang et al., 2010a; Yip et al., 2010; Wei et al., 2011). In addition, TFC membranes are also superior to CTA membranes in terms of their better pH stability and resistance to hydrolysis and biological degradation (Vos et al., 1966; Mulder, 1996; Geise et al., 2010). Despite the great potential of TFC membranes for FO applications, their fouling behavior is rarely reported in the literature. Thus, there is a critical need to assess fouling performance of TFC FO membranes and to compare it with that of CTA FO membranes.

The objectives of the current study were 1) to understand the effect of foulant composition and feed solution chemistry on FO fouling by binary mixture of organic macromolecules, and 2) to compare CTA FO membrane and TFC FO membrane in terms of flux performance and foulant mass deposition during FO fouling. To the best knowledge of the authors, this is the first study comparing fouling behavior of CTA FO and TFC FO membranes.

2. Materials and methods

2.1. *Membranes*

Two membranes were used in the current study, including a commercially available CTA FO membrane supplied by Hydration Technology Inc. (HTI, Albany, OR) and a polyamide TFC FO membrane synthesized in-house according to Wei et al. (2011). The properties of these membranes are summarized in Table 1. The TFC membrane was formed by interfacial polymerization of m-phenylenediamine and trimesoyl chloride on a polysulfone substrate with straight finger-like pores to minimize its mass transfer resistance (Wei et al., 2011). Compared to the CTA membrane, the TFC membrane has a higher water permeability and a lower salt permeability (i.e., better salt rejection). The TFC membrane rejection layer is also more hydrophilic (contact angle ~45°) and more negatively charged (zeta potential ~−10 mV at pH 7) compared to the CTA membrane (contact angle ~77° and zeta potential ~−2 mV). The surface roughness of the TFC membrane (~105 nm) is significantly higher than that of CTA membrane (~30 nm) based on the root-mean-square roughness measurements by atomic force microscopy (AFM) (see Supporting Info S1).

2.2. *Foulants*

Lysozyme (LYS, Fluka 62971) and sodium alginate (ALG, Sigma A2158) were chosen as model foulants in the current study to represent proteins and polysaccharides with opposite charge. The molecular weights of LYS and ALG are 14.3 kDa and 12–80 kDa, respectively (Palecek and Zydney, 1994; Wang and Tang, 2011a). Within the test pH range (pH 5–8), LYS is positively charged and ALG is negatively charged (Wang and Tang, 2011a, b). Both foulants were received in powder form with purity above 98%. They were freshly dissolved in ultrapure water (resistivity of 18.2 MΩ cm, Millipore Integral 10 Water Purification System) prior to fouling tests.

2.3. *FO submerged setup and fouling test*

The FO setup is shown in Supporting Information S2. The membrane cell with effective membrane area of 80 cm^2 was fully submerged into a 6-L feed solution (FS) tank. Air bubbles were introduced into the FS by an air diffuser for FS mixing and fouling control. A diamond-shaped spacer was placed in the draw solution (DS) channel (width of 5 cm and depth of 2 mm), and a peristaltic pump was used to recirculate the DS at a crossflow velocity of 16.7 cm/s. The weight of the DS tank (3 L) was measured by a digital balance that is connected to a computer data acquisition system.

For each FO experiment, a new membrane coupon was used with its active layer facing the FS (i.e., the AL-FS

Table 1 – FO membrane properties.

Membrane	Water permeability, *A* (10^{-12} m/s Pa)	Salt permeability, *B* (10^{-8} m/s)	NaCl rejection (%)	Contact angle (°)[d]	Zeta potential at pH 6 (mV)[d]	RMS surface roughness[d] (nm)
CTA	2.8 ± 0.1[a]	17.5 ± 0.5[a]	89.5[a]	77 ± 1[b]	−2.1 ± 0.3[b]	30 ± 6
TFC	5.0 ± 0.7[c]	9.4 ± 1.9[c]	93.4[c]	45 ± 4[c]	−10 ± 5	105 ± 11

a *A*, *B* values, NaCl rejection of CTA membrane are obtained from She et al. (2012b).
b Contact angle and zeta potential of CTA membrane are obtained from Jin et al. (2012).
c Characterization of TFC membrane are obtained from Wei et al. (2011).
d Measured for active layer of both membranes.