Protein fouling of nanofiltration, reverse osmosis, and ultrafiltration membranes—The role of hydrodynamic conditions, solution chemistry, and membrane properties

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ABSTRACT

The effect of hydrodynamic conditions, membrane properties, and feed solution chemistry on membrane fouling by bovine serum albumin (BSA) was systematically investigated under crossflow conditions over a 4-day fouling period. The initial flux behavior was highly dependent on membrane properties, where membranes with smoother and more hydrophilic surface and those with favorable electrostatic repulsion experienced less initial fouling. Interestingly, the flux at the end of the 4-day tests (J_{96h}) showed little dependence on membrane properties, with reverse osmosis, nanofiltration, and ultrafiltration membrane fluxes all converged into a nearly identical value. This suggests that the long-term flux was primarily controlled by the foulant–fouled-membrane surface interaction. Membranes tested at different initial fluxes had a strong tendency to approach to a surface-interaction-limited value, although slightly lower J_{96h} was observed at increased applied pressure, likely due to foulant layer compaction. BSA fouling was more severe at pHs close to its isoelectric point (IEP), at high ionic strength and in the presence of Ca^{2+} and Mg^{2+} as a result of reduced electrostatic repulsion or the promotion of specific ion interactions under these conditions. A linear correlation was observed between J_{96h} and the square of zeta potential of BSA (ζ^2), suggesting that ζ^2 can be potentially a good indicator for predicting the long term fouling behavior.

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1. Introduction

Reverse osmosis (RO) and nanofiltration (NF) have stimulated wide interest in water and wastewater treatment in the recent decades due to the growing demand for high quality water, improved membrane separation properties, and reduced treatment cost. However, membrane fouling remains as a major challenge. One of the important membrane foulants is protein, which is known to cause significant loss of membrane permeability [1,2]. Many investigations on protein fouling have been performed for microfiltration (MF) and ultrafiltration (UF) membranes. Existing studies on these porous membranes have demonstrated that protein fouling are affected by hydrodynamic conditions (permeate flux and crossflow velocity) [3,4], feed water characteristics (solution pH, ionic compositions, and foulant concentration) [4–7], and membrane properties (hydrophobicity, roughness, and charge density, etc.) [8,9]. In general, severe protein fouling is observed at the iso-

electric point (IEP) of a protein where the electrostatic repulsive force among protein molecules is at the minimum [4,5]. In addition, increased applied pressure (and permeate flux) and reduced crossflow velocity can result in faster flux reduction [3].

In spite of the vast literature on MF and UF protein fouling, there have been only a handful number of systematic studies on the fouling of RO membranes by proteins [10–13], and even less attention has been paid to protein fouling of NF membranes. It is worthwhile to note that the fouling behavior of RO and NF membranes are likely to be very different from that of MF and UF membranes – pore blocking has been reported as an important fouling mechanism for porous MF and UF membranes but is unlikely to be important for non-porous RO and NF membranes [10,14]. In addition, most existing protein fouling studies for RO membranes were performed for relatively short durations (on the order of 1 day or less). It has been observed that the rate of protein fouling was highly dependent on membrane properties such as surface roughness and hydrophobicity [12]. On the other hand, prior fouling studies on humic acid revealed that the long term flux behavior was independent of membrane properties [15,16]. Presumably, the initial stage of membrane fouling is controlled by the interaction of hydrodynamic forces and foulant–clean-membrane interaction, while the foulant-deposited–foulant interaction become dominant once the

Table 1
Properties of membranes used in the current study.

Membrane	Chemistry	Water permeability (L/m² h psi)[c]	NaCl rejection (%)[c]	MWCO (Da)	Contact angle (°)[c]	Membrane zeta potential at pH 7 (mV)	Root mean square roughness (nm)
XLE (RO)[a]	TFC, fully aromatic polyamide	0.396	96.5	<200	71.0 ± 1.0	−26[c]	129.5 ± 23.4[e]
NF90 (NF)[a]	TFC, fully aromatic polyamide	0.398	84.9	200	65.6 ± 1.9	−10[c]	142.8 ± 9.6[e]
NF270 (NF)[a]	TFC, poly(piperazinamide)	0.870	35.0	200–300	29.1 ± 1.1	−35[c]	9.0 ± 4.2[e]
GM (UF)[b]	TFC Polyamide	1.088	20.2	8000[d]	39.3 ± 1.3	−17[d]	10.7[f]

[a] Supplied by Dow FilmTec.
[b] Supplied by GE Osmonics.
[c] From current study.
[d] From Ref. [1].
[e] From Ref. [20].
[f] From Ref. [21].

membrane properties are masked by those of the foulant cake layer upon the formation of a foulant layer [15,17]. Thus, it is important to contrast fouling behavior at the initial stage to the longer term flux behavior. It is further interesting to compare the fouling of NF and RO membranes to that of UF membranes to better understand the role of membrane properties during protein fouling.

The objective of current study was to investigate the effect of hydrodynamic conditions, solution chemistry, and membrane properties on protein fouling of NF, RO, and UF membranes. Crossflow fouling experiments were performed under constant pressure using bovine serum albumin (BSA) as a model foulant. This study may provide important insights of the role of hydrodynamic force, foulant–clean-membrane interaction, and foulant-deposited–foulant interaction during protein fouling.

2. Materials and methods

2.1. Chemicals

Unless otherwise specified, all reagents and chemicals were of analytical grade with purity over 99%. Ultrapure water was supplied by an ELGA water purification system (UK) with a resistivity of 18.2 MΩ cm. The ionic compositions of the feed solution were adjusted by using reagent grade sodium chloride, calcium chloride, and magnesium chloride, and the solution pH was adjusted by hydrochloric acid and sodium hydroxide. Bovine serum albumin (BSA) was used as a model protein foulant. BSA was received

in powder form (98% purity, A7906, Sigma–Aldrich) and was stored at 4 °C in the dark. It has a molecular weight of ∼67 kDa [5,10]. BSA molecules are ellipsoidal (9.5 nm × 5 nm × 5 nm), and have an IEP at pH 4.7 [5]. BSA working solutions were freshly prepared prior to each fouling experiment.

2.2. Membranes

Four commercial membranes were used in this study: an RO membrane XLE, two NF membranes NF90 and NF270, and an UF membrane GM. XLE, NF90, and NF270 were obtained from Dow FilmTec©, while GM was provided by GE Osmonics©. All the membranes were received as dry flat sheet coupons. The properties of these membranes are summarized in Table 1. Membranes XLE and NF90 are fully aromatic polyamide membranes formed by m-phenylene-diamine and tri-mesoyl chloride [18–20]. According to Tang et al. [17,18,20], these membranes have relatively rough membrane surfaces (root mean square roughness R_{RMS} on the order of 100 nm) as a result of their peak-and-valley structures. In contrast, the semi-aromatic piperazine based membrane NF270 has a much smoother membrane surface ($R_{RMS} \sim 9$ nm) [17,19,20]. Compared to XLE and NF90, the semi-aromatic NF270 has significantly higher water permeability and lower salt rejection (Table 1). It also has a more hydrophilic and more negatively charged membrane surface. Membrane GM is a polyamide based UF membrane with a molecular weight cutoff (MWCO) of ∼8 kDa [21]. It has a
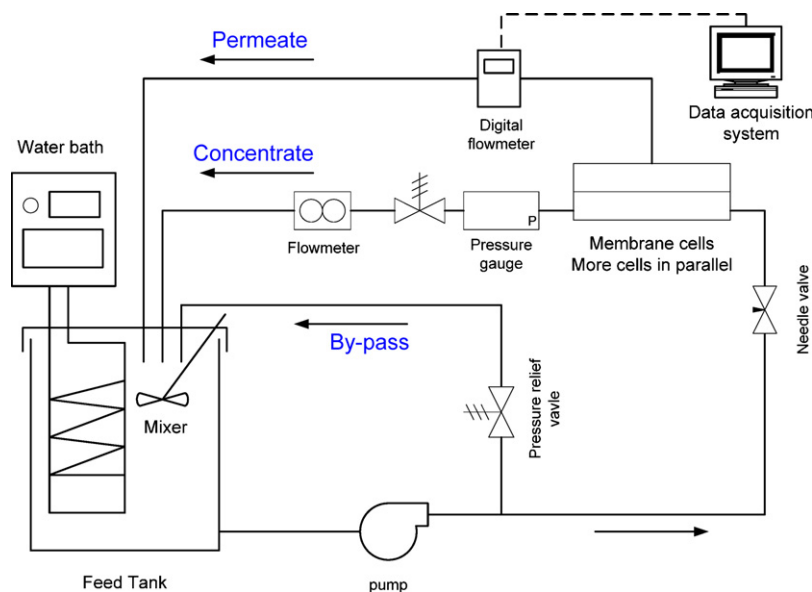

Fig. 1. Schematic diagram of the crossflow membrane testing setup.