Prototype aquaporin-based forward osmosis membrane: Filtration properties and fouling resistance

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ABSTRACT

The trade-off between water permeability and selectivity is considered as the biggest challenge during membrane fabrication for water purification. The aquaporin (AQP)-based biomimetic membrane has been proven to have both enhanced water permeability and improved selectivity due to the unique features of the AQP protein water channel that permits water molecules and rejects all other components. In this study, a prototype forward osmosis (FO) Aquaporin Inside™ membrane (AIM) was evaluated in terms of intrinsic filtration properties, membrane surface chemistry and fouling behaviour, and compared with a commercial FO membrane. The surface of the prototype AIM appeared to be a modified semi-aromatic polyamide layer instead of fully-aromatic as in other conventional FO products. As a result, compared to the commercial FO membrane, the prototype AIM shows higher water flux and comparable reverse salt flux (RSF) when tested under identical conditions. Due to the lower RSF, the AIM had less organic fouling by a sodium alginate solution when calcium chloride ($CaCl_2$) was used as the draw solution (DS). The membrane integrity of the prototype AIM was maintained after repeated cycles of fouling by high concentration of gypsum and physical cleaning tests. This demonstrates the possibility of using the AIM membrane for treating harsh feed solutions.

1. Introduction

Although forward osmosis (FO) has been extensively studied over the past decade, it has been a challenge to achieve acceptable water flux, salt rejection and membrane integrity at the same time [1]. Aquaporin (AQP)-based membranes (ABM) appear to be promising candidates to tackle the challenges associated with current water purification processes such as low productivity, membrane fouling and high costs [2]. Recently, ABMs have received considerable attention because AQP water channels avoid the water permeability and selectivity trade-off of traditional polymers. Therefore, they can offer enhanced water flux (high water permeability, A) and solute rejection (low solute permeability, B) when incorporated into membranes [3]. AQPs are protein channels that permit water transport across the cell membranes and reject all types of solutes such as salts, ions, bacteria and other impurities [4]. Although their mechanical stability could make their commercial viability questionable due to the non-

compatibility of AQPs to porous support materials, this has been overcome by fabricating via AQP vesicle incorporation in the interfacial polymerisation process [2]. In this way, AQP proteins can be hosted by a thin-film coating which ensures that the natural activities are encapsulated during water treatment processes. It has been shown that defect-free ABMs were successfully produced via interfacial polymerisation process [5–12]. Thus, the AQP-enabled membrane has multiple vesicles with high A/B embedded in a polymer matrix of conventional A/B; the resultant membrane can have enhanced A with unchanged, or smaller, B. Therefore, appropriate selection of membrane support, deposition method and lipid characteristics are crucial for practical applications ABMs.

Some of the commercially available thin-film composite (TFC)-FO membranes are listed in Table 1 and their filtration properties are compared with a commercial FO Aquaporin Inside™ membrane (AIM; Aquaporin A/S, Denmark). In spite of the fact that the overall performance of the FO membrane has been advanced, the permeability-

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Table 1
Filtration property of commercial polyamide (PA) based thin-film composite (TFC)-FO membranes.

Membranes	Pure water permeability, A (L/m²·h (LMH)/bar)	Salt permeability, B (LMH)	Structural parameter, S (μm)	B/A (bar)	Water flux, J_w (LMH)	Reverse salt flux, J_s (g/m²·h (gMH))	Reference
HTI[*]	1.78	1.23	533	0.69	22.9	6.4	[14]
Toray chemical	5.36	0.95	266	0.49	37.8	–	[13]
Porifera	2.22	0.49	269	0.22	24.9	–	[18]
AIM[**]	0.52	0.09	569	0.17	8.7	4.0	[15]

[*] Hydration Technology Inc. (HTI), USA.
[**] Aquaporin Inside™ membrane (AIM) by Aquaporin A/S, Denmark.

selectivity trade-off was still observed and has yet to be overcome. For instance, Toray Chemical (Korea) reported the highest water permeability coefficient, yet the salt permeability was the second highest of the listed membranes. In fact, the reverse salt flux (RSF) value of the FO membrane from Toray Chemical was higher [13] than that of HTI TFC-FO membrane [14] at the identical draw solution (DS) concentration. On the other hand, despite having superior selectivity, the first generation AIM exhibited the lowest water permeability coefficient which resulted in substantially lower pure water flux (J_w) than other commercially available FO membranes. In addition, the structural parameter value of the AIM was shown to be higher than other membranes. The higher structural parameter can be optimised but it is likely at the expense of the loss of mechanical strength [15]. However, the structural parameter should be considered as an important element in order to surmount the limiting factors of the FO process such as the internal concentration polarisation (ICP) effect and low water flux [16]. It has been suggested that modest water permeability, high selectivity, inert surface chemistry, and a low structural parameter would be ideal for the best-performing TFC FO membrane [17].

Although ABMs have shown promising results in the previous literature, only a handful of practical applications have been reported. Li and co-workers used commercially available ABM in the FO application for a long-term operation [19]. They tested the AIM supplied by Aquaporin A/S (Denmark) in terms of filtration performance and chemical stability. The results showed that the AIM had superior performance compared to a commercial TFC-FO membrane. The AIM was also shown to be robust with resistance against chemical cleaning agents including ethylenediaminetetraacetic acid (EDTA), sodium hypochlorite (NaOCl), sodium dodecyl sulphate (SDS) and Alconox over a wide range of pH from 1.4 to 11.7. In addition to this, high salt rejection (> 98%) was maintained after testing with the above-mentioned cleaning agents. More recently, Luo et al. [20] successfully incorporated a flat-sheet FO membrane supplied by Aquaporin Asia (Singapore) into an osmotic membrane bioreactor (OMBR). The AQP FO membrane used in this study showed remarkably lower salt permeability compared to conventional cellulose tri-acetate (CTA) and TFC-FO membranes without compromising water permeability. The membranes exhibited stable trace organic contaminants (TrOC) removal of over 85% during the OMBR operation.

In this study, a prototype flat-sheet AIM has been tested and compared with a conventional FO membrane for filtration performance, membrane characteristics and fouling resistance. Membrane integrity while treating harsh inorganic scalants and repeated cleaning was also tested as this is often considered as a major drawback of ABMs in practical applications.

2. Materials and methods

2.1. Membranes

The new generation prototype AIM samples were supplied by Aquaporin Asia (Singapore). These membranes are AQP based polyamide (PA) TFC-FO membranes, produced roll-to-roll on a pilot production line via interfacial polymerisation and then post-treated using NaOCl to further improve the membrane water permeability. The difference between the first and new generation of AIM is that a nonwoven backing material is used in the support layer of the new generation AIM and the active layer is re-optimised with this new support. Another PA TFC-FO membrane was used (Hydration Technology Inc. (HTI), USA) as a comparison because it is a popular benchmark [13,15]. Membrane samples were stored in MilliQ water (Millipore™) at 4 °C at least 24 h before use.

2.2. Feed and draw solutions

Flux and fouling behaviours were examined using synthetic organic and inorganic foulants. MilliQ water was spiked with organic and inorganic model foulants, namely, 200 mg/L sodium alginate (alginic acid; SA), 200 mg/L Bovine serum albumin (BSA) and gypsum (GS; CaSO$_4$·2H$_2$O; 35 mM calcium chloride (CaCl$_2$), 20 mM sodium sulphate (Na$_2$SO$_4$) and 19 mM sodium chloride (NaCl), corresponding to a GS saturation index (SI) of 1.3). All the chemicals were obtained from Sigma Aldrich. NaCl and CaCl$_2$ were used as draw solutes.

2.3. FO system configuration

A custom-made bench-scale FO system was employed with a minor modification from a previous study [21] to investigate the filtration performance and fouling and cleaning behaviours. The system included a cross-flow membrane cell with two symmetric flow channels, 88 mm long, 42 mm wide and 2 mm deep. Diamond shaped spacers (Toray Chemical, Republic of Korea) were used on both sides of the membrane cell. The feed and draw solutions were pumped in counter-current directions at the flow rates of 1000 mL/min (cross-flow velocity of 9.5 cm/s) in each channel on both sides of the membrane using gear pumps (WT3000-1JB, Longer Pump, China). The feed solution tank was placed on a balance (KERN FKB, Germany) to determine water flux by measuring weight variations during the experiments. Conductivity in the feed tank was also measured using a conductivity meter (Orion Star A212, Thermo Scientific, USA). All filtration experiments were performed in FO mode (the active layer facing the feed solution (AL-FS)).

2.4. Transport and structural parameters

A single FO experimental method was used to determine transport and structural parameters of the osmotic membranes. The experimental method for this membrane characterisation can be found elsewhere [22]. In this study, the single-stage method which is optimised from the aforementioned reference was performed with a single initial solute concentration in the DS. In the single batch FO test, the initial DS concentration was set at 3 M and the volume was set as low as 0.5 L. Feed solution was MilliQ water and the volume was 1.5 L. During a single batch operation, the test duration was set as long as 4 h which is long enough to dilute the DS and account for the impact of concentration and dilution. During the test, sufficient data span of water flux and RSF were generated. Feed solute concentration and weight data were recorded over time as described in Section 2.3. J_w and J_s were calculated by virtually dividing the testing duration into multiple