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Fabrication of a robust high-performance FO membrane by optimizing substrate structure and incorporating aquaporin into selective layer

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ABSTRACT

In present study, we explored the fabrication of a high performance thin-film composite (TFC) forward osmosis (FO) membrane by minimizing the structural parameter of hollow fiber substrates and enhancing the water permeability of selective layer. A theoretical analysis specified that a minimized structural parameter of substrate combined with an enhanced water permeability of selective layer could generate a significantly high water flux in FO process. The experimental results showed that the addition of LiCl into polyetherimide (PEI) polymer dope made the membrane less tortuous and thereby significantly reduced the structural parameter. The elevated take-up speed reduced the substrate thickness but also made the substrate more tortuous. Further study showed that a robust hollow fiber with low structural parameter can be obtained by reducing the substrate wall thickness and dimension simultaneously. After optimization, the structural parameter of the substrate declined from 308 μm to 172 μm. After interfacial polymerization, the thin-film composite membrane constructed on the optimized substrate showed an improved water permeability (from 2.85 L m^{-2} h^{-1} bar^{-1} to 3.66 L m^{-2} h^{-1} bar^{-1}) and a comparably low salt permeability (0.36 L m^{-2} h^{-1} versus 0.31 L m^{-2} h$^{-1)}$. The low structural parameter, in combination with the high water permeability and low salt permeability, contributed to significantly increased water flux (J_v) from 25.4 L m^{-2} h^{-1} to 38.5 L m^{-2} h^{-1} when 1 M NaCl was used as draw and deionised water as feed in a configuration of active layer facing feed solution (AL-FS). Furthermore, aquaporins were incorporated into the polyamide selective layer to enhance the water permeability, which remarkably reached up to 7.6 L m^{-2} h^{-1} bar^{-1}. The aquaporin-incorporated FO membrane demonstrated a J_v of 49.1 L m^{-2} h^{-1} and a J_s/J_v (J_s indicates the salt flux) of 0.10 g/L with 1 M NaCl as draw and deionised water as feed in the AL-FS configuration, which is favourable to mitigate membrane fouling in practical application. The AQP-FO membrane reported in this study outperforms most of other reported FO membranes.

1. Introduction

Forward osmosis (FO) has drawn increasing attention as an emerging membrane technology in the past decade [1,2]. In a FO process, a draw solution with high-osmolarity withdraws water from a feed solution with low-osmolarity through a permeable and selective membrane. The feed can be concentrated if dewatering is the purpose of the process, or if water is the final product, the withdrawn water is then separated from the draw solutes by applying other technologies such as thermal process, nanofiltration, and membrane distillation. Distinct from the hydraulic pressure-driven membrane process (e.g. reverse osmosis (RO)), FO is an osmotic pressure-driven process in which the osmotic pressure difference across the membrane is the only driving force. Therefore, it requires less energy consumption and has less fouling propensity in the operation mode of active layer facing feed, as compared to conventional RO membrane technology. In addition, FO process in combination with other processes offers more flexibility and applicability when it is applied for beverage processing, wastewater treatment and high salinity water desalination [3]. For example, the coupling of FO with membrane distillation is promising to treat a variety of wastewaters that are usually challenging for membrane distillation because of severe fouling issues [4].

However, one primary hurdle for FO development is the lack of a highly permeable and selective FO membrane [2,5]. Although some

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newly-designed FO membranes such as inorganic support composite membrane [6], nanofiber composite membrane [7] and organic-inorganic composite membrane [8] are promising to deliver decent water flux, their vulnerable mechanical strength, high reverse salt diffusion or poor scalability remains challenging for practical applications. Meanwhile, FO process usually uses a highly concentrated draw solution to achieve a sufficiently high osmotic pressure for a desirable water flux, especially when treating high-salinity feed. Therefore, the selectivity of FO membranes is very critical for reducing the back diffusion of draw solutes through membranes [9]. Of all reported FO membranes, conventional thin-film composite (TFC) is the most extensively fabricated and studied [5]. A TFC membrane is generally comprised of a thin polyamide layer integrated on a porous support. The unique composite structure of TFC membrane allows the polyamide layer and the support to be tailored separately to optimize FO performance.

An effective optimization of TFC FO membranes relies on a thorough understanding of the relationship between FO performance and membrane structure. A well-defined flux model is used to describe the water flux behavior in FO mode as follows [10]:

$$J_v = \frac{D_D}{S} ln \frac{B + A\pi_{D,b}}{B + J_v + A\pi_{F,m}} \qquad (1)$$

where J_v (m/s) is the water flux in FO tests and A (L m^{-2} h^{-1} bar^{-1}) is the water permeability, indicating the water transport ability of the selective layer constructed on the substrate. B (L m^{-2} h^{-1}) is the salt permeability coefficient, D_D (m^2/s) is the diffusivity of draw solute, $\pi_{D,b}$ and $\pi_{F,m}$ (bar) are the osmotic pressures of the bulk draw solution and the feed solution proximate to membrane interface, respectively. The structural parameter, S (m), is a key parameter to determine the water flux as it indicates how severely the membrane would suffer from internal concentration polarization [11]. If the membrane is tested using 1 M NaCl as draw and water as feed, we may assume that $\pi_{F,m}$ is close to zero and B is also negligible for a high salt rejection membrane as compared to J_v and $A\pi_{D,b}$. Eq. (1) can be simplified and thus give rise to a contour plot which describes the correlation between J_v and A, given a specified S. The unit of J_v (m/s) is converted to a generally used unit (L m^{-2} h^{-1}) in FO studies. The plotted curves in Fig. 1 demonstrate that increasing A leads to a higher J_v, but the benefit tends to be levelled off when S remains unchanged. Apparently, it is not a practical way to pursue a higher water flux by only relying on continuously increasing A. Instead, the decrease in S can significantly amplify the J_v enhancement from increasing A. For instance, for a typical TFC membrane with A of 2 L m^{-2} h^{-1} bar^{-1} and S of 400 μm, tripling A from 2 to 6 L m^{-2} h^{-1} bar^{-1} can have a 45.7% increment of J_v, as indicated in Fig. 1. However, the increment can expand to 55.3% if the tripling of A is applied on a membrane with S of 200 μm. Based on the analysis, it is clear that increasing water permeability of the selective layer and reducing structural parameter of the substrate have a strong synergistic effect to enhance water flux of resultant membranes.

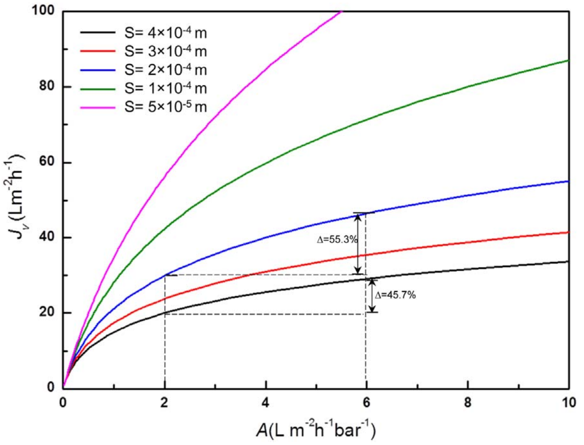

Fig. 1. Contour plot of structural parameters (S) required to achieve a specified water flux (J_v) as a function of water permeability (A). It is assumed that 1 M NaCl is used as draw solution and DI water as feed solution and the FO process is operated at the AL-FS orientation. The salt diffusivity (D_D) is 1.4e-9 m^2 s^{-1} and osmotic pressure ($\pi_{D,b}$) of draw solution is 4.9 MPa for calculation.

In present study, first of all, our attempt is to develop a robust hollow fiber substrate with a low structural parameter by optimizing fabrication conditions. In comparison with flat sheet membranes, the fabrication process of hollow fiber membranes allows a more precise manipulation of membrane structure by adjusting the spinning conditions such as bore fluid flow rate, dope flow rate, take-up speed and bore fluid coagulant, etc. Most of work on reducing structural parameter of hollow fiber has been focused on introduction of novel fabrication materials [12] or adoption of new spinning technique [13]. However, there were limited studies on the effects of dope formula and fabrication conditions on the structural parameter of hollow fiber membrane. For example, despite that pore former additives have been widely used in preparation of FO membrane substrates, their influences on the structure of FO membrane substrates have scarcely studied [14]. Herein we investigated the effect of one of commonly used pore forming additives, LiCl, on the structure of PEI hollow fiber substrate and its impact on FO performance, as it has been well-known in creating a porous membrane structure even with a small amount [14,15]. In addition, low concentration of polymer dope is favourable to fabricate a loose and porous substrate while it also risks having a viscosity too low to form a membrane. The introduction of LiCl can significantly increase the viscosity of polymer dope because of its strong interactions with polymer and solvent [14,15].

Some fundamental understandings on this field will be presented in this work. Thereafter, the water channel molecule, aquaporin (AQP), is employed to enhance the water permeability of the selective layer of TFC membrane. Extensive studies have revealed that AQP is responsible for the fast and exclusive water transport across the biological membrane due to its unique channel structure [16–20]. Aquaporin Z, expressed and purified from *Escherichia coli*, has superior water permeability [21] and in-vitro stability [22]. It has been employed to make biomimetic membranes to enhance the water permeability [22–27], and to break the permeability/selectivity trade-off of TFC membranes [28]. Our previous works [26,27] have verified that incorporation of AQPs into polyamide layer could efficiently enhance water permeability while there was no compromise on salt rejection, which is highly desirable for fabricating highly permeable and selective membranes. The ultimate goal of this study is to fabricate a robust high-performance FO membrane by optimizing the substrate structure and incorporating AQPs into the selective layer, so as to promote FO as a competitive membrane technology for practical applications.

2. Materials and methods

2.1. Materials

Polyetherimide (PEI, *ULTEM 1100, Sabic*) was used for fabricating hollow fiber substrates and N-Methyl-2-pyrrolidone (NMP, *Merck Chemicals*) was used as the solvent to prepare the polymer dope. *E. coli* total lipid extract was purchased from Avanti Polar Lipids (*Alabaster, US*). All other chemicals in the present study were purchased from Sigma-Aldrich (*Singapore*) and used as received unless otherwise stated. Deionised (DI) water with a resistivity of 18.2 MΩ cm was supplied with a Millipore integral water purification system.

2.2. AQP reconstitution into lipid vesicles

The detailed procedures for the expression and purification of