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Synthesis and characterization of flat-sheet thin film composite forward osmosis membranes

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ABSTRACT

Forward osmosis (FO) technology has become increasingly attractive in the past decades for water related applications and will likely continue to develop rapidly in the future. This calls for the development of high performance FO membranes. Thin film composite (TFC) polyamide FO membranes with tailored support structure were prepared in the current study. The porous polysulfone substrates with finger-like pore structures were prepared via phase inversion, and the polyamide rejection layers were synthesized by interfacial polymerization. The resulting TFC FO membranes had small structural parameters ($s = 0.67–0.71$ mm) due to the thin cross-section, low tortuosity, and high porosity of the membrane substrates. Meanwhile, their rejection layers exhibited superior separation properties (higher water permeability and better selectivity) over commercial FO membranes. When the rejection layer is oriented towards the draw solution, FO water flux as high as 54 L/m^2 h can be achieved with a 2 M NaCl draw solution while maintaining relatively low solute reverse diffusion. Comparison of the synthesized TFC FO membranes with commercial FO and RO membranes reveals the critical importance of the substrate structure, with straight finger-like pore structure preferred over spongy pore structure to minimize internal concentration polarization. In addition, membranes with high water permeability and excellent selectivity are preferred to achieve both high FO water flux and low solute flux.

1. Introduction

Forward osmosis (FO) is an osmotically driven membrane process in which water diffuses through a semi-permeable membrane under an osmotic pressure difference across the membrane. In the FO process, both concentration and dilution of a given stream can be performed by applying a more-concentrated or less-concentrated solution on the other side of the membrane [1,2]. Compared to conventional pressure-driven membrane separation processes such as reverse osmosis (RO) and nanofiltration (NF), FO can operate at nearly zero hydraulic pressure [1,3]. Where a high-osmotic-pressure draw solution (DS) is naturally available or can be easily regenerated, the FO energy consumption can be potentially significantly lower than that of pressure-driven processes [1,4]. FO is also believed to have reduced risk of membrane fouling [5–7], though further research is still required to understand the mechanisms involved [2,8–11]. In recent years, FO technology has become increasingly attractive, with potential applications for wastewater treatment [5–7,12], biomass concentration [2], and seawater desalination [13–16]. In addition, FO is also ideal for some sensitive applications where high pressure and high temperature needs to be avoided (e.g., food processing [17,18], pharmaceutical applications [19,20], etc.).

Despite the many interesting potential applications of the FO technology, there are some technological barriers that have yet to be overcome. One of the major problems in FO process is concentration polarization. Like pressure-driven membrane processes, FO experiences concentration polarization at the solution–membrane interface (external concentration polarization or ECP), which can be controlled by increasing cross flow or using spacers [8]. In addition, concentration polarization can occur inside the porous support layer of an FO membrane, which is known as internal concentration polarization (ICP) [11,21,22]. ICP, a unique problem in FO processes, arises as the water flux in FO has an opposite direction to the solute flux. This can lead to either (1) a concentrative ICP for the active-layer-facing-the-draw-solution (AL-DS) orientation, where the solutes from the feed solution (FS) accumulate in the porous support layer as a result of their retention by the active rejection layer, or (2) a dilutive ICP for the active-layer-facing-the-feed-solution (AL-FS) orientation caused by the dilution of the draw solution inside the support layer [11,22]. In addition, ICP can be contributed by the solutes that diffuse from the high concentration DS

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Table 1
Synthesis conditions for TFC FO membranes.

Membrane ID	Substrate via phase inversion					Rejection layer via interfacial polymerization[a]			
	PSf (wt.%)	NMP (wt.%)	PVP (wt.%)	LiCl (wt.%)	Thickness of casting solution (μm)	MPD (wt.%)	SDS (wt.%)	Water (wt.%)	TMC in n-hexane (w/v, %)
TFC-1	17.5	82.0	0.5	–	175	1.0	–	99.0	0.05
TFC-2	15.5	81.0	0.5	3.0	150	1.5	0.1	98.4	0.1

Notes:
[a] Compositions of monomer solutions (MPD dissolved in water and TMC dissolved in n-hexane) are listed.

to the low concentration FS for a low-rejection membrane [2,11,12]. In either case, the effective driving force (i.e., the osmotic pressure difference across the active layer) can be dramatically reduced, causing a severe reduction in the available water flux [11,22].

Up to present, the synthesis of high-performance FO membrane is still in the early stage of its development. An ideal FO membrane shall possess high water flux and low solute flux in addition to good chemical stability [23]. Although many researchers have investigated the mechanisms of ICP [11,12,21–26], there have only been a handful of studies focusing on FO membrane fabrication [23,27–38]. In parallel, commercial FO membranes are still limited in terms of both manufacturers and choice of membrane chemistries – the only FO membranes available commercially are the cellulose triacetate asymmetric membranes from Hydration Technologies Inc. (HTI, Albany, OR) [8,11,22]. The HTI membranes have been highly optimized in terms of the support structure to allow these membranes to achieve decent FO water flux [11,22]. On the other hand, the rejection layers of these membranes tends to have low water permeability and limited solute retention [2,11,12], which means that there are still significant opportunities to further improve the FO performance.

The objective of the current study was to determine the effect of the substrate and rejection layer properties on the FO performance. In this study, thin film composite (TFC) polyamide membranes with tailored support structures were developed. Morphologies and physical characteristics of the resultant FO membranes were investigated and compared to commercial FO as well as RO membranes to illustrate the importance of both the support layer structure and the active rejection layer separation properties.

2. Materials and methods

2.1. Chemicals and membrane materials

Unless otherwise specified, all chemicals were of analytical grade with purity over 99% and were used as received. Ultrapure water was supplied from a Milli-Q ultrapure water system (Millipore Singapore Pte Ltd) with a resistivity of 18.2 MΩ cm.

Polysulfone beads (PSf, molecular weight 75,000–81,000 Da, Solvay Advanced Polymers, LLC, GA) were used for preparing the membrane substrates. N-methyl-2-pyrrolidone (NMP, Merck Schuchardt OHG, Hohenbrunn) was used as the solvent for the casting solution. Polyvinyl pyrrolidone (PVP, average molecular weight 1,300,000 Da, Alfa Aesar, MA) and lithium chloride (LiCl, Sinopharm Chemical Reagent Co. Ltd, China) were used as additives in the casting solution. Chemicals used for interfacial polymerization included m-phenylenediamine (MPD, Sigma–Aldrich Pte. Ltd, Singapore), trimesoyl chloride (TMC, Sinopharm Chemical Reagent Co. Ltd, China), and n-hexane (Fisher Scientific, NJ).

Three commercial FO membranes obtained from HTI (Albany, OR) and one commercial RO membrane obtained from Dow FilmTec (Minneapolis, MN) were used for comparison purpose. The HTI FO membranes are all based on cellulose triacetate (CTA). One of the FO membranes was cut from a Hydrowell® module (denoted as CTA-HW). This membrane has been well studied in the literature [1,2,8]. It is formed by casting cellulose triacetate onto a polyester woven fabric [8]. The other two membranes were received as flat coupons, either supported by a polyester woven fabric (denoted as CTA-W) or a non-woven fabric (denoted as CTA-NW). The RO membrane BW30 was a thin film composite (TFC) polyamide membrane supported by a non-woven fabric [39,40]. In some experiments, the non-woven fabric of BW30 was carefully removed before characterizing and evaluating the membrane (denoted as BW30-o in this study).

2.2. Synthesis of flat-sheet TFC FO membranes

2.2.1. Preparation of FO substrate

The TFC FO membranes were prepared via two steps: (1) a phase inversion step to form the membrane substrate (this section), and (2) an interfacial polymerization step to form the active rejection layer (Section 2.2.2). To prepare a casting solution for FO substrate, certain amount of PSf, PVP and LiCl (Table 1) was dissolved in NMP and stirred by magnetic stirrers at 70 °C until the solution became homogeneous and transparent. After cooling down to the room temperature (23 °C), the polymer solution was filtered with a stainless steel filter connected to compressed nitrogen gas cylinder. The filtered dope was then degassed in air-tight bottles for 24 h before use. To prepare the polysulfone support, the casting solution was spread onto a clean glass plate to form a uniform film using an Elcometer 4340 Motorised Film Applicator (Elcometer Asia Pte Ltd). The film was then quickly and smoothly immersed with the glass plate into a coagulant bath where 23 °C tap water was used as coagulant. The nascent substrate was kept in flowing water bath to remove residual solvent and stored in ultrapure water before use.

2.2.2. Preparation of polyamide rejection layer

The active rejection layer of TFC FO membrane was prepared by interfacial polymerization on the surface of a pre-casted PSf substrate. The preparation was carried out at room temperature (23 °C) unless otherwise specified. The substrate was heated in 70 °C ultrapure water for 2 min before cooling down to room temperature. It was then soaked in an aqueous solution of MPD for 2 min, and the excessive MPD solution on the substrate surface was removed with compressed air. Subsequently, an n-hexane solution of TMC was gently poured onto the MPD-soaked substrate and was allowed to react with the residual MPD for 1 min to form the polyamide rejection layer. The resultant TFC composite membrane was rinsed with tap water to remove the residual monomers and was stored in ultrapure water before characterization. Two types of TFC FO membranes were synthesized (denoted as TFC-1 and TFC-2), and their preparation conditions are summarized in Table 1.

2.3. Membrane characterization

2.3.1. Characterization of membrane morphology, porosity, and contact angle

The morphologies of the membranes were observed with a scanning electron microscope (SEM) according to Ref. [11]. Membrane samples were dried in vacuum at room temperature for 24 h. Samples were then fractured in liquid nitrogen and coated with a