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**Highly efficient forward osmosis based on porous membranes -
applications and implications**

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ABSTRACT

For the first time, forward osmosis (FO) was performed using a porous membrane with an ultrafiltration (UF)-like rejection layer and its feasibility for high performance FO filtration was demonstrated. Compared to traditional FO membranes with dense rejection layers, the UF-like FO membrane was two orders of magnitude more permeable. This gave rise to respectable FO water flux even at ultra-low osmotic driving force, e.g., 7.6 L/m².h at an osmotic pressure of merely 0.11 bar (achieved by using a 0.1% poly(sodium 4-styrene-sulfonate) draw solution). The membrane was applied to oil/water separation, and a highly stable FO water flux was achieved. The adoption of porous FO membranes opens a door to many new opportunities, with potential applications ranging from wastewater treatment, valuable product recovery, and biomedical applications. The potential applications and implications of porous FO membranes are addressed in this paper.

INTRODUCTION

Forward osmosis (FO) has received increasing attention from both research and industry communities¹⁻⁶ for their potential use in desalination⁷, wastewater treatment^{8,9}, food processing⁴, and energy production^{10,11}. In FO, the trans-membrane osmotic pressure difference drives water across an FO membrane from a feed solution (FS) to a draw solution (DS) that has higher osmotic pressure. Compared to pressure-driven membrane processes (e.g., reverse osmosis (RO) and nanofiltration (NF)), FO enjoys several key advantages including low or negligible hydraulic pressure, reduced fouling tendency, and potentially reduced energy consumption and operational cost.^{1,2,12}

Based on the existing literature^{1,2}, semi-permeable dense membranes with non-porous rejection layers are required for FO filtration. Depending on the separation properties of the dense rejection layer, FO membranes can be divided into RO-like and NF-like membranes. RO-like FO membranes has good rejection to NaCl in addition to a wide range of many other solutes.^{8,13-15} Examples of this type of FO membranes include thin film composite (TFC) polyamide membranes¹⁶⁻²³ as well as the commercially available cellulose triacetate (CTA) membranes from Hydration Technology Inv. (HTI).^{5,24} On the other hand, NF-like FO membranes can be formed by layer-by-layer (LbL) assembly²⁵⁻²⁷, chemical crosslinking²⁸, direct phase inversion²⁹, and interfacial polymerization³⁰. These membranes are able to adequately reject multivalent ions but have low rejection against monovalent ions.^{25-27,29,31} Despite that they are not suitable for desalination applications where NaCl rejection is critical³⁰, NF-like FO membranes have potential applications in wastewater treatment, food

processing, and biomedical uses.

To the best knowledge of the authors, the use of porous membranes (e.g., with a porous rejection layer resembling that of an ultrafiltration (UF) or microfiltration (MF)) for FO processes has not been reported in the literature. Conceptually, one could use a combination of a porous membrane and draw solutes that can be adequately rejected by the membrane to achieve the desired trans-membrane osmotic pressure difference (Fig. 1). For example, a UF-like FO membrane can be potentially used together with DSs made of macromolecules, polyelectrolytes or nanoparticles, where water from FS permeates through the porous membrane while contaminants (or valuable products for the case of product/resource recovery) in FS are retained by the membrane. Since typical UF membranes are orders of magnitude more permeable than NF and RO membranes, we envisage that that UF-like FO membranes can achieve excellent water fluxes at ultra-low osmotic pressure driving force (say, $\ll 1$ bar). Low osmotic pressure of the DS also means low energy requirement for DS regeneration (e.g., DS reconcentration via low pressure UF filtration). Such UF-like FO membranes can be used in many potential applications including sludge dewatering, wastewater treatment, microalgae harvesting, protein concentration, oil-water separation, and food processing.

Figure 1. Conceptual diagram of a porous membrane based FO process. With a UF-like rejection skin, the membrane can be potentially used for valuable products concentration (e.g., protein and polysaccharides), resource recovery (e.g., oil/water separation), and wastewater treatment (e.g., biomass retention). Draw solutions (DS) can be prepared using macromolecules or nanoparticles, and DS regeneration can be achieved using a low pressure UF system.

The current study aimed to demonstrate the technical feasibility of a novel FO process based on porous membranes. For the first time, a porous UF-like FO membrane was developed and its FO water flux performance was systematically investigated. Results from the current study may open many new opportunities for FO applications.

EXPERIMENTAL DETAILS

Chemicals and Reagents

Unless stated otherwise, all solutions and reagents were prepared with analytical grade chemicals and deionized (DI) water (Millipore Integral 10 water purification system, Singapore). Polyacrylonitrile (PAN, average weight molecular weight (M_w) ~ 150 KDa, Sigma-Aldrich), lithium chloride (LiCl, Sinopharm) and N,N-dimethylformamide (DMF, $\geq$ 99.8 %, Sigma-Aldrich) were used as polymer, additives and solvent, respectively. Sodium hydroxide (NaOH, Sigma-Aldrich) was used for membrane post-treatment. DI water was used as feed solution. Draw solution was prepared by poly(sodium 4-styrene-sulfonate) (PSS) (M_w ~ 70 KDa, 30 wt.% in H_2O , Sigma-Aldrich). Sodium dodecyl sulfate (SDS, Sigma-Aldrich) was used as the surfactant for preparing oil/water emulsion. Soya bean oil was purchased from a local supermarket for preparing oil emulsion.

Membranes

RO-like and NF-like FO membranes

Two RO-like FO membranes were evaluated for comparison purpose (Table 1). The cellulose triacetate (CTA) FO membrane was obtained from HTI (Albany, OR), and the TFC polyamide FO membrane was prepared in-house using interfacial polymerization procedures following our prior studies.^{19,32} In addition, an NF-like FO membrane, prepared using LbL assembly following Qi et al.^{25,31}, was also included in this study.

Porous UF-like FO membrane

A porous UF-like FO membrane was prepared by the phase inversion method using a PAN polymer solution (18 wt.% PAN, 2 wt.% lithium chloride in DMF). Briefly, a casting knife (Elcometer Pte Ltd, Asia) was set a gate height of 150 μm to spread the polymer solution onto a clean glass plate. Upon immersing the plate into a coagulant bath (tap water at room temperature 23 ± 1 $^{\circ}\text{C}$), a PAN membrane was immediately formed. The nascent PAN membrane was then annealed in DI water at 55 $^{\circ}\text{C}$ for 2 mins to tighten the membrane pore structure. Finally, the membrane was alkaline treated (soaking in 1.5 M NaOH at 45 $^{\circ}\text{C}$ for 1.5 h) to make the surface more hydrophilic by partial hydrolysis.²⁵

Table 1. Intrinsic separation properties of RO-like, NF-like and UF-like FO membranes.

Membrane type	A^a L/m ² h bar	Rej_{NaCl}^b %	Rej_{PSS}^c %
CTA (RO-like)	1.19 ± 0.19^d	78.5^d	$\sim 100^e$
TFC (RO-like)	1.7 ± 0.3	97 ± 1	$\sim 100^e$
LbL (NF-like)	3.4 ± 0.4	60 ± 3	$\sim 100^e$
UF-like	78.8 ± 7.2	0	97.5 ± 1.0

Notes:

^a DI water used as feed solution and compacted under 5 bars for at least 2 hours.

^b 10 mM NaCl used as feed solution and compacted under 5 bar for at least 2 hours.

^c 0.05 % PSS (70 KDa) used as feed solution and compacted under 1 bar for at least 2 hours.

^d Data obtained from Ref. 19.

^e PSS not detectable in the permeate solution.

Membrane Characterization

The morphologies of membrane surface and cross-section were characterized by field emission scanning electron microscopy (FESEM, Carl Zeiss, Germany). Cross-sections were prepared by fracturing membrane samples in liquid nitrogen. All the samples were sputtered with a uniform gold coating (Emitech SC7620 Sputter Coater) before FESEM examination. The surface roughness was measured using an atomic force microscopy (AFM, Park system,

Korea) following similar procedures by Qi et al.²⁷ Molecular weight cutoff (MWCO) of the membrane was determined according to Wang et al.¹⁶ Membrane contact angle was measured by an OCA Contact Angle System (DataPhysics Instruments GmbH, Germany).

Membrane intrinsic separation properties (pure water permeability (A) and solute rejection (R)) were evaluated using a pressurized cross flow filtration setup²⁵. Briefly, A was determined based on weighting permeate water samples by using DI water as feed water. NaCl rejection (Rej_{NaCl}) was calculated by measuring conductivity (Ultrameter II, Myron L Company, Carlsbad, CA) of feed and permeate water using a 10 mM NaCl feed solution.²⁵ PSS rejection (Rej_{PSS}) was calculated based on total organic carbon measurements (TOC-Vcsh, Shimadzu) of feed and permeate water using a 0.05 % PSS feed solution.

FO Performance Evaluation

FO performance was evaluated using a cross flow FO setup as described elsewhere.^{25,27} All the FO tests were performed at a cross flow velocity of 18.75 cm/s (for both feed and draw solutions) at room temperature. For each test, a new FO membrane coupon (active filtration area $\sim 42 \text{ cm}^2$) was used. Polyelectrolyte solutions containing 0-1 wt.% PSS were used as DS. Unless specified otherwise, all FO tests were performed using the active layer facing feed solution (AL-FS) orientation, since this orientation is preferred for FO operation due to its lower fouling tendency.³³ FO water flux (J_V) was determined by measuring the weight changes of the FS at predetermined time intervals.

Oil-water separation tests were also performed to demonstrate the applicability of porous FO based process. The oil emulsion was prepared in accordance to existing literature^{34,35}, where a mixture of 5 ml oil and 1.5 L DI water (O/W mixture) or 5 ml oil and 1.5 L DI water with 0.1 g SDS (O/W/S mixture) was ultrasonicated (Fisher Scientific FB15068) for 1 hour until the mixture changed to a milky color. The size of oil droplets ranges from 10-50 μm in O/W and 5-30 μm in O/W/S (Supporting Information S1). For FO tests, a clean membrane was equilibrated under FO testing condition for 30 minutes (DI water as FS and 0.1 % PSS as DS), after which the FS was replaced with the O/W mixture or O/W/S mixture for evaluating oil-water separation performance.

RESULTS AND DISCUSSION

Intrinsic Membrane Separation Properties

The separation properties of various FO membranes are presented in Table 1. In general, the water permeability (A) had the following order: CTA < TFC < LbL << UF-like FO membranes. The UF-like FO membrane ($A = 78.8 \pm 7.2 \text{ L/m}^2\cdot\text{h}\cdot\text{bar}$) was nearly two orders of magnitude more permeable compared to typical RO- and NF-like FO membranes due to its lack of dense rejection layer. This also indicates that the porous UF-like FO membrane can potentially achieve much better FO water flux compared to their nonporous counterparts (refer to the section on *FO Performance*). Although the UF-like FO membrane did not show any rejection of NaCl, its rejection of PSS (70 kDa) was as high as 97.5%, suggesting that PSS solutions can be potentially used in couple with this membrane for FO operation. MWCO analysis shows that the membrane had an MWCO of 45 kDa. Figure 2 shows the

FESEM micrographs of the UF-FO membrane. It had finger-like pores that are designed to enhance the mass transfer inside the membrane and thus to minimize ICP.²⁵ The membrane surface was relative smooth with an RMS roughness ~ 11 nm (based AFM measurement).

Figure 2. FESEM images of (a) cross section and (b) surface of UF-FO membrane.

FO Performance

Comparison of UF-like FO with RO-like and NF-like FO membranes

Fig. 3 compares the FO water flux (J_V) for various membranes. The experimental FO water flux was obtained using 0-1 % PSS as DS (osmotic pressure ranging from 0 – 1.06 bar, see Table 2) in the AL-FS orientation. In addition, ideal FO water flux is defined by $A\Delta\pi$ without considering internal concentration polarization (ICP) and external concentration polarization (ECP), where A is the water permeability and $\Delta\pi$ is the osmotic pressure difference across the membrane. Overall, both experimental and ideal water flux increased at higher PSS concentration as a result of increasing the apparent driving force. For the RO-like and NF-like FO membranes, the experimental results agreed well with the ideal results. For these membranes, water fluxes were very low ($\sim$ or < 3 L/m².h) due to the combination with their relatively low water permeability (≤ 3.4 L/m².h.bar) and the low osmotic pressure of the draw solution (≤ 1.06 bar). Previous studies^{1,2} have shown an exponential dependence of

concentration polarization on water flux. At the low water flux levels under the current experimental conditions, it is not surprising that both ICP and ECP were negligible for the RO-like and NF-like membranes and that the available FO water flux was largely governed by the frictional resistance of the membrane rejection layers.³⁰

Figure 3. Comparison of FO water flux performance for RO-like, NF-like and UF-like FO membranes. The ideal J_v was calculated based on membrane water permeability by ignoring both internal and external concentration polarizations. The experimental J_v values were measured using 0.05, 0.1, 0.5 and 1 % of PSS as DS (corresponding to osmotic pressure values of 0.053, 0.11, 0.53, and 1.06 bar, respectively) and DI water as FS in AL-FS orientation at 23 ± 1 °C. Results were obtained based on at least 3 membrane coupon tests. Error bars were smaller than the size of the symbols.

Compared to its RO-like and NF-like counterparts, the UF-like membrane had FO water flux one order of magnitude higher. This is consistent with its much higher water permeability in comparison to the conventional FO membranes with dense rejection layers (Table 1). Despite of the very low osmotic driving force, decent water fluxes were achieved. In particular, an FO water flux of ~ 7.6 L/m².h was obtained at a transmembrane osmotic pressure difference of as

low as 0.11 bar. At low osmotic pressures (i.e., ≤ 0.11 bar), the water flux of the UF-like membrane was well approximated by the ideal flux line (whose slope indicates the water permeability of the membrane, $A = 78.8 \text{ L/m}^2\text{.h.bar}$). Under these testing conditions (water flux $\sim$ or $< 7.6 \text{ L/m}^2\text{.h}$), concentration polarization was likely mild and the FO water flux was solely determined by the membrane water permeability.³³ At increased osmotic pressure (0.53 and 1.06 bar), the experimental water flux became much lower than the ideal water flux, which can be attributed to the dilutive ICP of DS inside the membrane in addition of ECP at the increased water flux levels.^{33,36} Indeed, doubling the osmotic pressure from 0.53 to 1.06 bar only marginally increased the FO water flux from 19.8 to 23.5 $\text{L/m}^2\text{.h}$, indicating that this region was largely dominated by the concentration polarization effect that counter-acts the increased osmotic driving force at higher DS concentration.

Table 2. Viscosity and osmotic pressure of PSS solutions with different concentration

Concentration of PSS (%)	Viscosity (Pa.s)	Osmotic pressure (Bar)
0.05	0.000985	0.053
0.1	0.00107	0.11
0.5	0.00124	0.53
1	0.00119	1.06

Porous FO membrane for oil/water separation

Fig. 3 demonstrates that respectable FO water flux can be achieved for the porous FO membrane at ultra-low osmotic driving force (e.g., $7.6 \text{ L/m}^2\text{.h}$ at 0.11 bar). With such low osmotic pressure, the DS can be easily regenerated using a low pressure UF regeneration system (Fig. 1). This may open a wide range of potential applications. In the current section, the porous UF-like FO membrane is applied to oil/water separation.

Fig. 4 shows the normalized FO water flux (normalized against the initial water flux) during 1-hr oil/water separation tests. Baseline tests were performed without adding oil/water emulsion in the FS under otherwise identical experimental conditions. The slight decrease in the baseline flux is due to the dilution of DS (thus reduced osmotic driving force) over time.³³ The flux curves for oil/water separation (O/W or O/W/S) were comparable to the baseline values, suggesting negligible effect of membrane fouling. Microscopic inspection of the membrane after oil/water separation experiments did not show any discernible changes of the membrane surface (Supporting Information S2). The superior flux stability can be attributed to the relatively hydrophilic membrane surface (contact angle $\sim 20.9 \pm 10.2^\circ$, see insert of Fig. 4).^{34,35}

Figure 4. Normalized FO water flux during oil/water separation. Initial flux was 7.6 ± 0.9 L/m².h. The feed emulsion was prepared by dispersing 5 ml of soya bean oil in 1.5 L of water. A 0.1 % PSS solution (osmotic pressure = 0.11 bar) was used as DS. All FO tests were performed in the AL-FS orientation at 23 ± 1 °C.

Potential Applications and Implications

For the first time, porous membrane based FO filtration is reported. Since their A values are generally orders of magnitude higher compared to those of conventional RO-like and NF-like FO membranes, porous FO membranes can potentially achieve much higher FO water flux when compatible draw solutes are used. The advantage of higher water permeability is more outstanding at lower osmotic driving forces, under which conditions concentration polarization is less prominent and the water flux is largely determined by the membrane frictional resistance. In the current study, we demonstrated a flux of $7.6 \text{ L/m}^2\cdot\text{h}$ in the AL-FS orientation using a porous UF-like FO membrane and 0.1 wt.% PSS DS (osmotic pressure = 0.11 bar). It is reasonable to project that even higher water fluxes can be potentially achievable by using more permeable loose UF or even MF membranes, provided that suitable draw solutes (that can be adequately retained by the membranes) are selected.

A major bottleneck of traditional FO processes is DS regeneration. Although FO itself consumes little pumping energy, the high energy demand for reconcentrating the diluted DS can be overwhelming^{1,2}. The possibility to use ultra-low-osmotic-pressure DS for porous FO based processes means that its regeneration can be realized at very low energy cost. For the case of macromolecules, nanoparticles, or polyelectrolytes, a low-pressure UF is sufficient for regeneration purpose.

The adoption of porous FO membranes opens a door to many new opportunities (Fig. 1). By properly tuning their rejection properties, such membranes may be used to retain biomass (for

sludge dewatering and membrane bioreactor applications), oil droplets (for oil/water separation), microalgae (for algae harvesting for subsequent biodiesel production), proteins (protein concentration), blood cells (biomedical applications), just to name a few. Indeed, porous FO membranes can be applied to many cases where pressure-driven UF and MF membranes are currently employed. Meanwhile, the low fouling feature of FO^{1,12} could potentially translate into significant cost savings of porous FO based processes over their pressure-driven UF and MF counterparts (see a comparison of FO and UF fouling in Supporting Information S3).

Up to date, the material and fabrication choices for synthesizing dense FO membranes are limited.^{1,2} With porous FO membranes, however, a much wider range of materials, synthesis methods, and surface modification options are available. The greater freedom in tuning membrane chemistry, pore structure, morphology, surface charge, and hydrophilicity offers a great tool box for designing highly selective and anti-fouling membranes. In the current study, it is demonstrated that highly stable FO water flux can be maintained during an oil/water separation process as a result of the highly hydrophilic membrane surface.

Despite the many potential advantages of porous FO membranes, it is important to also recognize their limitations. Their porous nature means that such membranes are usually not applicable where salt retention is required (e.g., seawater desalination). It is always important to match the membrane selectivity properties with the draw solutes and feed solutes for a particular application. On the other hand, the lack of salt retention can be also a potential

advantage in some applications. When an RO-like FO membrane is used in an osmotic membrane bioreactor for concentrating municipal wastewater to allow its anaerobic treatment and energy recovery in the form of methane³⁷, its high salt retention can result in severe salt accumulation and subsequent loss of osmotic driving force (or even inhibition of the biological process).^{37,38} In contrast, salt accumulation is no longer an issue if a porous FO membrane were to be used for such applications. Since a porous membrane does not retain dissolved salts in the feed solution, the concentration of these feed solutes are equal on both sides of the membrane. That is, the dissolved salts in the feed solution does not contribute to the osmotic difference across the membrane such that the porous FO membrane can still be driven by a low osmotic pressure draw solution. In this case, it is the high selectivity of organic matter and draw solutes (high retention) over dissolved salts (low/no retention) makes the porous FO membrane a better candidate. Thus, the pore structure of an ideal porous FO membrane shall be tailored to achieve high selectivity towards target contaminants while allows high water permeability and solute mass transfer.

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Supporting Information

S1. Optical micrograph of oil/water emulsion; S2. Micrographs of the porous UF-like FO membrane; S3 comparison of UF and porous-FO fouling behavior. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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