Journal of Membrane Science 394–395 (2012) 140–150

Contents lists available at SciVerse ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Composite forward osmosis hollow fiber membranes: Integration of RO- and NF-like selective layers to enhance membrane properties of anti-scaling and anti-internal concentration polarization

Wangxi Fang[a,b], Rong Wang[a,b,*], Shuren Chou[a,b], Lauren Setiawan[a,b], Anthony Gordon Fane[a,b]

[a] Singapore Membrane Technology Centre, Nanyang Technological University, 639798 Singapore, Singapore
[b] School of Civil and Environmental Engineering, Nanyang Technological University, 639798 Singapore, Singapore

ARTICLE INFO

Article history:
Received 4 September 2011
Received in revised form
26 November 2011
Accepted 23 December 2011
Available online 31 December 2011

Keywords:
Forward osmosis
Double skinned hollow fiber
Composite membrane
Internal concentration polarization (ICP)
Membrane scaling

ABSTRACT

One of the major barriers that hinder the application of forward osmosis (FO) processes is the lack of optimized membranes that possess high water flux, low salt leakage and good anti-internal concentration polarization (ICP) and anti-fouling/anti-scaling properties during practical FO operations. In this study, novel composite FO hollow fiber membranes with an RO-like selective skin and an NF-like secondary selective skin were successfully developed for the first time. The fabrication procedures involved making ultrafiltration hollow fiber substrate using poly(amide–imide) (PAI) polymer material via phase inversion method, followed by interfacial polymerization (IP) and chemical modification to yield a polyamide RO-like inner skin and a positively charged NF-like outer skin, respectively.

It was found that the sequence of conducting IP on the substrate inner surface prior to the chemical modification of the outer skin was preferred in order to achieve better performance for the resultant double-skinned hollow fibers. The newly developed FO hollow fibers exhibited high water permeability of 2.05 L/m^2 h bar and 85% rejection to NaCl at 1 bar pressure as well as superior FO water flux of 41.3 L/m^2 h and low ratio of salt flux over water flux of 0.126 g/L when using DI water and 2.0 M NaCl as feed and draw solutions, respectively, in the active layer facing draw solution (AL-DS) orientation. Furthermore, the experimental results showed that the composite FO hollow fiber membrane was able to outperform single-skinned membrane when the feed contains divalent ions or the feed exhibits high scaling tendency to membrane. This suggested that the integration of RO- and NF-like two selective skins in FO membrane is an effective way to minimize the ICP effect, mitigate the membrane scaling and thus enhance the feasibility of FO processes for practical applications.

1. Introduction

Forward osmosis (FO) process has attracted much attention in recent years. Unlike pressure-driven reverse osmosis (RO) membrane process, the driving force for water transfer in FO arises from the osmotic pressure difference due to the concentration gradient between draw and feed solutions separated by a semi-permeable membrane. As a result, the energy consumption in FO can be reduced significantly in comparison with RO. FO process has potential for many emerging applications such as seawater desalination [1–3], wastewater treatment [4–6], feed solution dewatering [7,8], food processing [9,10], and power generation [11–13].

However, one of the major barriers that hinder the application of FO processes is the lack of optimized membranes that possess high water flux, low salt leakage and good anti-fouling/anti-scaling property during FO operations. From the perspective of mass transfer through the membrane, a desired FO membrane should have an asymmetric structure consisting of an ultra-thin dense active layer for salt rejection and a very thin and porous substrate that not only provides mechanical support, but also mitigates internal concentration polarization (ICP) [14]. The ICP phenomenon describes the dilution of draw solution inside the substrate (dilutive ICP) when the active layer is placed against the feed solution (AL-FS orientation), or the concentration of feed solution (concentrative ICP) inside the substrate due to the salt leakage when the active layer is facing the draw solution (AL-DS orientation) [15–17]. The ICP occurred in the thick and relatively dense RO substrate has been identified to be the main factor responsible for extremely low water flux of RO membranes when used in FO process [14].

* Corresponding author at: School of Civil and Environmental Engineering, Nanyang Technological University, 639798 Singapore, Singapore.
Tel.: +65 6790 5327; fax: +65 6791 0676.
E-mail address: rwang@ntu.edu.sg (R. Wang).

0376-7388/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.memsci.2011.12.034

Extensive efforts have been made to develop high performance FO membranes, which include commercial FO flat sheet membranes developed by Hydration Technologies Inc. (HTI) [5,6], thin film composite (TFC) FO hollow fiber membranes [18–20], TFC FO flat sheet membranes [21,22], FO hollow fibers and flat sheet membrane with a NF-like skin layer [23,24], and dual-layer hollow fibers for FO applications [25].

Nevertheless, these efforts are far from sufficient for bringing the FO technology to practical applications. Similar to many other membrane processes, a great challenge that has to be tackled for FO application is membrane fouling/scaling. Normally, in the AL-DS orientation, the membrane possesses a high fouling/scaling propensity if the feed solution contains organic macromolecules or inorganic scalants that can penetrate into the porous support layer easily. Due to the internal fouling and/or pore clogging, the substrate structure was altered, leading to enhanced ICP effect and mass transfer resistance, consequently, a sharp decreased water flux in the AL-DS orientation [26]. In contrast, though the AL-FS orientation experiences more severe reduction of effective driving force due to dilutive ICP [18,19], the AL-FS orientation offers the advantage of anti-internal fouling/scaling, as the dense active layer prevents the penetration of foulants/scalants into the support layer.

To solve or mitigate the potential problem of internal fouling/scaling without sacrificing much the higher water flux of AL-DS orientation compared to the AL-FS orientation, the concept of double-skinned FO membranes has been developed. In addition to the dense ultra-thin active layer, a secondary skin layer was proposed on the substrate to face the feed solution so as to prevent possible foulant/scalant penetration into the support layer. A mathematical model has been derived to analyze the mass transfer in the double-skinned FO membranes, which provides guidance for the membrane structure design [27]. However, a handful of study was conducted to make double-skinned FO membranes, which includes double-skinned or double dense-layer integral asymmetric FO flat-sheet membranes reported by Wang et al. [28] and Zhang et al. [29].

The current works aim to develop composite FO hollow fiber membranes by integrating RO- and NF-like two selective skins on each side of an ultrafiltration (UF) hollow fiber substrate, and its FO performance under some application scenarios have been evaluated. This double-skinned FO hollow fiber is expected to present better anti-scaling property when the feed solution exhibits high scaling tendency to membrane, or better anti-ICP effect if the feed solution contains divalent salts. To the best of our knowledge, no composite FO hollow fiber membranes with a RO-like and a NF-like skin layers have yet been reported.

2. Theory

Different from a single-skinned FO membrane, the two skin layers of a double-skinned FO hollow fiber membranes contribute to the overall water and salt permeability coefficients (A and B values, respectively) by following the principle of the resistance-in-series model. Since the surface areas of the inner and outer skins are different, the water and salt permeability coefficients for the NF-like outer skin need to be normalized as the current study is based on the RO-like inner skin:

$$A'_{out} = \frac{D_o}{D_i} A_{out} \tag{1}$$

$$B'_{out} = \frac{D_o}{D_i} B_{out} \tag{2}$$

where A'_{out} and B'_{out} are the normalized water and salt permeability coefficients for the NF-like outer skin, while D_o and D_i are outer and inner diameters of the hollow fiber. Assuming the resistance of the porous support layer is negligible, the formula for the calculation of overall A and B is derived as

$$\frac{1}{A} = \frac{1}{A_{in}} + \frac{1}{A'_{out}} = \frac{1}{A_{in}} + \frac{1}{(D_o/D_i)A_{out}} \tag{3}$$

$$\frac{1}{B} = \frac{1}{B_{in}} + \frac{1}{B'_{out}} = \frac{1}{B_{in}} + \frac{1}{(D_o/D_i)B_{out}} \tag{4}$$

where A and B are the overall water and salt permeability coefficients for the double-skinned hollow fibers, whereas A_{in} and B_{in}, A_{out} and B_{out} are the water and salt permeability coefficients for the RO-like inner skin and NF-like outer skin, respectively. It should be pointed out that this calculation is also based on the assumption that no concentration polarization takes place inside the substrate structure between the two skins.

The theoretical calculation of NaCl rejection was based on the solution-diffusion model using the A and B computed from Eqs. (3) and (4). As a result, this value indicated the expected overall NaCl rejection throughout the two skin layers in series if no concentration polarization occurred inside porous support layer sandwiched by the two layers.

3. Materials and methods

3.1. Membrane materials and chemicals

Torlon® 4000T (copolymer of amide and imide) (PAI), supplied by Solvay Advanced Polymers (Alpharetta, GA), was used for UF hollow fiber substrate preparation. N-Methyl-2-pyrrolidone (NMP, >99.5%, CAS#872-50-4, Merck Chemicals, Singapore) and lithium chloride (LiCl, anhydrous, CAS#7447-41-8, MP Biomed) were used as a solvent and pore former, respectively.

M-Phenylenediamine (MPD, ≥99%, CAS#108-45-2, Sigma–Aldrich), ε-Caprolactam (≥99%, CAS#203-313-2, Merck), trimesoyl chloride (TMC, >99%, CAS#4422-95-1, Sinopharm Chemical Reagent), hexane (>99.9%, CAS#110-82-7, Merck Chemicals, Singapore) were used for interfacial polymerization. Polyethyleneimine (PEI) ethylenediamine end-capped (Sigma–Aldrich) was used for chemical modification of the hollow fiber substrate.

Sodium chloride (NaCl, ≥99%, Merck) were used to prepare draw solutions with a concentration ranging from 0.5 M to 2.0 M, while 5.0 M NaCl solution was prepared to simulate a brine solution for the dosing system. In addition to NaCl, magnesium chloride ($MgCl_2$, hexahydrate), calcium chloride ($CaCl_2$, dihydrate), and dipotassium hydrogen phosphate (K_2HPO_4, anhydrous) purchased from Merck were involved during the feed solution preparation. Deionized water (Milli-Q, 18 MΩ cm) was used for the preparation of solutions. All chemicals were used as received.

3.2. Preparation of double-skinned composite FO hollow fiber membranes

3.2.1. Fabrication of PAI hollow fiber substrates

The polymer dope of PAI/LiCl/NMP (14/4/82 wt.%) was prepared by dissolving the Torlon® 4000T into NMP solvent. The detailed preparation procedure of polymer dope solution was described by Setiawan et al. [23]. Two types of PAI hollow fiber substrates, denoted as PAI#1 and PAI#2, were fabricated by the dry-jet wet spinning method using the same dope composition but different spinning conditions, which are listed in Table 1. The details of fabrication method were reported elsewhere [30,31]. The fabricated hollow fibers were soaked in tap water followed by 50% glycerol aqueous solution for 48 h, respectively. The membranes were then dried in the air and stored at room temperature for characterization and further use.