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Characterization of novel forward osmosis hollow fiber membranes

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ABSTRACT

Forward osmosis (FO) has received intensive studies recently for a range of potential applications such as wastewater treatment, water purification and seawater desalination. One of the major challenges to be overcome is the lack of an optimized FO membrane that can produce a high water flux comparable to commercial RO membranes. Two types of thin-film composite FO hollow fibers with an ultra-thin polyamide-based RO-like skin layer (300–600 nm) on either the outer surface (#A-FO) or inner surface (#B-FO) of a porous hollow fiber substrate have been successfully fabricated. These novel composite FO hollow fibers have been characterized by a series of standard protocols and benchmarked against commercially available FO flat sheet membranes and reported NF hollow fibers used for the FO process.

The characterization reveals that the FO hollow fiber membranes possess a large lumen. The substrates are highly porous with a narrow pore size distribution. The active layers present excellent intrinsic separation properties with a hydrophilic rejection layer and good mechanical strength. The #B-FO hollow fiber membrane can achieve a high FO water flux of 32.2 L/m^2 h using a 0.5 M NaCl draw solution in the active rejection layer facing draw solution (AL-facing-DS) configuration at 23 °C. The corresponding salt flux is only 3.7 g/m^2 h. To the best of our knowledge, the performance of the #B-FO hollow fiber is superior to all FO membranes reported in the open literature. The current study suggests that the optimal FO membrane structure would possess a very small portion of sponge-like layer in a thin and highly porous substrate, which suggests a way for further improvement.

1. Introduction

Forward osmosis (FO) is a concentration-driven membrane process, which utilizes the osmotic pressure difference across a selectively permeable membrane as the driving force for the transport of water through the membrane. Compared with pressure-driven membrane processes, the FO process exhibits unparalleled advantages of nearly no hydraulic pressure operation, nearly complete rejection of many contaminants, and potentially low membrane fouling tendency [1]. As a result, FO has received intensive studies recently for a range of potential applications, which include wastewater treatment [2,3], water purification [4], seawater desalination [5], as well as power generation [6].

However, there exist a number of technical barriers that impede FOs industrial applications. One of the major challenges to be overcome is the lack of an optimized membrane that can produce a high flux comparable to commercial reverse osmosis (RO) membranes. Most existing membranes used in the FO process are dense semipermeable membranes that were originally designed for pressure driven RO process [1]. These RO membranes have an asymmetric structure, typically consisting of a thin selective active layer supported by thick layers of porous polymer and fabric [7]. There are only two companies—Osmotek Inc. which is now known as Hydration Technologies Inc. (HTI) [8] and Catalyx Inc. (Anaheim, California) [9], producing commercial FO membranes. The HTIs proprietary cartridge-type FO membrane is made of cellulose triacetate supported by an embedded polyester screen mesh and has been widely used in FO studies, while the Catalyx FO membrane was newly developed in 2009 and its specifications have not been reported yet. In addition, polybenzimidazole (PBI) nanofiltration (NF) hollow fibre membranes were developed recently for FO applications [10–12], but the draw solutions used were limited to divalent salts to ensure reasonable salt rejections, and PBI material tends to be brittle.

Prior studies on FO reported that experimental FO flux tends to be significantly lower than the theoretical values predicted from the classical solution-diffusion theory [13–15]. The lower-than-expected flux is attributed to the presence of internal and external concentration polarization (ICP and ECP) during the mass transport process, which significantly reduces the available osmotic

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driving force. The concentration polarization phenomena are associated with solute physical properties, fluid dynamics and, most significantly, the membrane structure. The ECP can be controlled hydrodynamically but the ICP occurs in the porous support layer of the membrane, making it difficult to handle. Thus, the key challenge is to produce a membrane that can minimize the ICP—the main cause of the substantial flux decline [6,13,14].

According to the literature [6,14], the desired characteristics of membranes used for FO would be a dense ultra thin active layer with high water permeability and low solute permeability, which is supported by a relatively thin and highly porous substrate for low ICP. In addition, the membrane needs to be hydrophilic to help reduce membrane fouling [16], and possesses high mechanical strength to sustain long-term operation. Furthermore, it has been suggested that tubular/hollow fiber membranes may be most suitable for FO than flat sheet membranes because they are self-supported and possess a flow pattern necessary for FO process [6,17]. Additionally, it is much simpler to fabricate hollow fiber module with a high packing density.

Two types of thin-film composite FO hollow fibres with an ultra-thin RO-like skin layer on either the inner surface or outer surface of a porous hollow fiber substrate have been successfully fabricated in our lab by a two-step preparation. This study aims to examine these novel composite FO hollow fibers by a series of standard protocols for characterization, and benchmark against commercially available FO flat sheet membranes and reported NF hollow fiber membranes used for the FO process. The characterization includes the measurements of the characteristics of the hollow fiber substrate and membrane morphology observation. The resultant FO membrane transport parameters will be determined through filtration experiments using a lab-scale hydraulically pressurized RO cross-flow filtration setup. A lab-scale forward osmosis cross-flow setup will be used to evaluate the FO performance of the membranes. It is expected that the characterization can reveal important features of the FO hollow fiber membranes and further provide guidance on the fabrication and optimization of FO hollow fiber membranes.

2. Experimental

2.1. Membrane material and chemicals

2.1.1. Commercial FO membranes

Pouch-type and cartridge-type FO flat sheet membranes were kindly provided by Hydration Technologies Inc. (HTI).

2.1.2. Chemicals for preparing and characterizing hollow fiber FO substrate

Commercial polymer polyethersulfone (PES) was used for substrate preparation. N-Methyl-2-pyrrolidone (NMP, >99.5%, CAS#872-50-4, Merck Chemicals, Singapore) was used as a solvent. Isopropyl alcohol (IPA, CAS#67-63-0 VWR company, analytical reagent) was used as wetting solvent. Some dextran $(C_6H_{10}O_5)_n$ samples with different molecular weights (molecular weight from 1500 to 400,000 Da, CAS# 9004-54-0, Sigma) were used to characterize the molecular weight cut-off (MWCO) of hollow fiber membranes.

2.1.3. Chemicals for preparing and characterizing hollow fiber FO rejection layer

m-Phenylenediamine (MPD, >=99%, CAS#108-45-2, Sigma), ε-Caprolactam (>=99%, CAS#203-313-2, Merck Chemicals, Singapore), sodium dodecyl sulphate (SDS, >95%, CAS#151-21-3), trimesoyl chloride (TMC, >99%, CAS#4422-95-1, Sinopharm Chemical Reagent), hexane (>99.9%, CAS#110-54-3, FisherChemicals) were used to perform interfacial polymerization. Draw solutions with various concentrations were prepared using sodium chloride (VWR). All the reagents were used as received.

2.2. Fabrication of PES hollow fiber substrates and post-treatment

Both substrates were made based on the same PES polymer material but with different additives and different spinning conditions. Substrate #A-PES used tap water as the external coagulant and a mixture of water and NMP as the bore fluid; while #B-PES used water as the internal and external coagulants.

To prepare dope solutions for spinning, a desired amount of pre-dried PES polymer powder with pore formers was dissolved into NMP using jacket flasks. The dope solution was then subjected to heating at 70 °C and continuous stirring for 3 days. Prior to spinning, the dope prepared was statically degassed under vacuum at ambient temperature overnight.

PES hollow fiber membranes were fabricated by a dry–jet wet spinning process. Similar methods have been reported elsewhere [18,19]. The dope was dispensed through a spinneret at a controlled volume rate by a Zenith gear pump, and went through a certain air gap before immersing into a coagulation bath. The nascent hollow fiber was taken up by a roller at a free falling velocity and stored in a water bath to remove residual solvent for at least 2 days.

A post-treatment was performed to alleviate the membrane shrinkage and pores collapse during drying process at ambient condition. The membrane was immersed into a water/glycerol mixture for 24 h. This process allowed the glycerol to replace water gradually in the membrane pores. The membranes were subsequently dried at room temperature prior to the characterization tests and further application. The glycerol inside the membrane pores can act as the pore supporter to alleviate the collapse of pores during membrane drying process.

2.3. Fabrication of FO thin film composite hollow fibers by interfacial polymerization

The formation of a RO-like skin layer on the outer or inner surface of the PES hollow fiber substrate was made based on interfacial polymerization [20]. Basically, an MPD aqueous solution with a desired concentration was brought into contact with the surface of the hollow fiber substrate followed by the interaction with a TMC hexane solution, and then the fibers went through a post treatment. Between the contact of the fibers with MPD and TMC solutions, a drier was used to provide a sweeping air in order to remove the droplets on the surface of the fibers. The produced membranes were stored in water before module fabrication.

2.4. Measurements of hollow fiber substrate's pure water flux, MWCO, pore size, pore size distribution and porosity

Ten pieces of PES hollow fibers were potted into a glass tube to form a lab-scale module. The effective length of the fibers in the glass module was 25 cm. Milli-Q ultrapure water was circulated through the shell side of the membrane module under 1 atm pressure to get the pure water flux. The specific flux of the membranes was calculated using the formula:

$$J = \frac{Q}{\Delta P \times A_m} = \frac{Q}{n\pi D_{HF} l_{eff} \Delta P} \quad (1)$$

where J is the specific pure water flux of the hollow fiber membrane (L/m^2 h atm); Q the water flux reading (L/h); ΔP the pressure difference between the feed side and the permeation side of the membrane (atm); A_m the effective membrane surface area (m^2); n the number of fibers in the module; D_{HF} the outer diameter of hollow fiber (m) and l_{eff} represents the effective length of hollow fibers (m).