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Developing high throughput thin film composite polyamide membranes for forward osmosis treatment of SAGD produced water

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ABSTRACT

Application of thin film composite (TFC) membranes for forward osmosis (FO) separation processes has attracted growing attention due to their outstanding permeation properties as compared to conventional asymmetric membranes. The aim of the present study is to fabricate high-performance TFC membranes by an innovative adjustment of interfacial polymerization (IP) reaction between m-phenylenediamine (MPD) and trimesoyl chloride (TMC) at the surface of a polyethersulfone (PES) microporous support. It was found that reducing the temperature of the organic solution down to −20 °C effectively reduced the thickness of the PA selective layer and thus, significantly enhanced water permeation through the membranes. The water flux increased more than double from 17.6 LMH for membranes prepared at 25 °C to 38.5 LMH at −20 °C, when 3 M NaCl solution and de-ionized water were used as draw and feed solutions, respectively. In addition, all the lab-made membranes showed significantly lower specific solute flux than the commercial membrane. The performance of lab-synthesized TFC membranes was also evaluated for the treatment of boiler feed water (BFW) of steam assisted gravity drainage (SAGD) process. The results showed superior permeation properties of lab-made membranes to commercially available TFC-FO membranes. This was attributed to the thinner PA selective layer and lower structural parameter (451 ± 13) of the lab-made membranes compared to the commercial membrane (1770 μm) which alleviated the effect of internal concentration polarization (ICP) remarkably. This study provides valuable guidelines for an effective tuning of the organic solution temperature during the IP reaction to develop high-throughput TFC FO membranes.

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1. Introduction

Forward osmosis (FO) has attracted increasing interest in the past decade as an alternative to conventional pressure-driven membrane processes for various applications including seawater desalination [1], wastewater treatment [2], food processing [3] and clean energy generation [4]. The mechanism of transport in a FO membrane is based on the osmotic pressure gradient between a low-concentration solution, known as “feed”, and a high concentration solution which is referred to as “draw”. Applying a semi-permeable membrane between the draw and the feed solutions provides pathways for water molecules while restricting the passage of solutes from one side of the membrane to the other side.

An ideal FO membrane exhibits high water permeability and solute rejection, low concentration polarization and fouling propensity as well as high chemical and mechanical stability [5,6]. The majority of the recent advances in the FO process is devoted to membrane materials development with the aim of fabricating high-performance FO membranes [7]. Commonly used commercial FO membranes are made from asymmetric cellulose triacetate (CTA) [8–10] which became popular due to its hydrophilic nature and relatively low-cost [11]. However, the major drawbacks of the CTA membranes are their low-permselectivity and poor stability in harsh acidic and basic environment [12]. These limitations have diverted attention from single layer cellulose based membranes toward thin film composite (TFC) polyamide (PA) based membranes.

A typical TFC membrane comprises a top skin layer (~100 to 300 nm thick, mostly made from PA) formed by an interfacial polymerization (IP) reaction at the surface of a microporous substrate [13,14]. The support substrate usually consists of polysulfone

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(PSf) or polyethersulfone (PES) cast over a polyester fabric, typically polyethylene terephthalate (PET), using a phase inversion technique [15,16]. The composite structure of the TFC membranes provides beneficial flexibility in their design, as both the top active and the bottom support layers can be tailored separately to optimize the final performance [11]. Although the TFC membranes are very popular in pressure-driven separation processes like reverse osmosis (RO) and nanofiltration (NF), their application in FO is at the early stage [17]. TFC-RO and TFC-NF membranes typically have a dense active layer to provide high selectivity and a thick support layer to offer mechanical stability when external hydraulic pressure is applied. But these membranes exhibit low permeation flux when tested for the FO process, as in the absence of hydraulic pressure, the dense active layer hinders the permeation flux through the membrane [3,8,10]. Additionally, the thick and dense support layer provides a large resistance against the diffusion of the draw solute to the back side of the active layer, contributing to internal concentration polarization (ICP) phenomenon, thereby adversely affecting the water permeation of the membranes [18]. The ICP generally occurs inside the pores of the porous support layer and depends mainly upon the thickness, porosity and tortuosity of the support layer rather than the hydrodynamics of the flow [18]. Ideally, the support layer should be thin, highly porous with low tortuosity [18,19]. To date, numerous efforts have been made on modification of TFC membranes in terms of the physico-chemical characteristics of both the active and support layers to make them efficient for the FO process. Much of these efforts were dedicated to improve the support layer characteristics by the following strategies:

(1) Modifying the support layer morphology [10,17,20–23]
(2) Increasing the hydrophilicity of the common support materials (i.e. PES or PSf), either by blending them with more hydrophilic materials such as sulfonated polysulfone (SPSf) [5], polyphenylsulfone (PPSU) [21], carboxylated polysulfone (CPSf) [24], Montmorillonite (MMT)-sulfonated polyethersulfone (SPES) [25] or by coating them with hydrophilic polymers like polydopamine [8] or sodium dodecyl sulfate (SDS) [26]
(3) Using alternative hydrophilic support materials like cellulose acetate (CA) [27], cellulose acetate propionate (CAP) [28], polyacrylonitrile (PAN) [29], polyketone (PK) [30], sulfonated poly(ether ketone) (SPEK) [31], and sulfonated polyphenylenesulfone (sPPSU) [32]
(4) Incorporating nanofillers like TiO_2 and layered double hydroxide (LDH) nanoparticles into the support polymer matrix [33,34]
(5) Using a highly porous electrospun nanofiber matrix of polyvinylidene fluoride (PVDF), PES and PAN as support layer [35–39]

According to our search of the literature, there are only a few studies focused on modifying the characteristics of the active thin layer of the TFC membranes for FO application [40], and these are mainly focused on incorporating nanoparticles like Zeolite, SiO_2, graphene oxide (GO), and multi-walled carbon nanotube (MWCNT) into the active layer of the TFC membrane [41–45]. However, the addition of nanoparticles in a thin film with the aim of fabricating a thin film nanocomposite (TFN) membrane is more complicated than it appears, due to (i) severe aggregation of the nanoparticles in the organic solvent during the IP reaction, and (ii) weak compatibility of the nanoparticles with the synthesized polymer matrix. It is well known that non-uniform dispersion of nanoparticles forms non-selective voids at the interface of the polymer and the nanoparticles, which significantly reduces the rejection percentage [46,47]. The uncertainties related to the formation of an integrally-skinned and defect-free thin film due to the presence of nanoparticles limit further development of the TFN membranes.

In the present work, we present an easily-implemented approach for fabrication of high throughput TFC-FO membranes by synthesizing an ultra-thin PA film over a PES microporous support. The PA film is prepared via an IP reaction between m-phenylenediamine (MPD) and trimesoyl chloride (TMC) at the surface of a polyethersulfone (PES) substrate. The key innovative adjustment in this approach was reducing the temperature of the TMC-heptane solution to −20 °C. Three TFC membranes were prepared with TMC-heptane solutions at 25 °C, 1 °C and −20 °C, and their surface physico-chemical and morphological characteristics were analyzed using field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), and attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), and contact angle measurements. The permeation performance and structural properties of the lab-made TFC membranes were evaluated by both RO and FO tests and compared with a commercially available TFC-FO membrane (called TFC-HTI here). Additionally, in order to evaluate the separation performance of the synthesized TFC membranes for treatment of industrial water with different types of contaminants, FO tests were carried out using boiler feed water (BFW) of steam assisted gravity drainage (SAGD) process.

SAGD is a thermally enhanced heavy oil recovery method which is widely practiced for bitumen extraction from oil sands in Alberta, Canada. In this process, steam is injected through a horizontal well into the bitumen-containing formation to decrease the viscosity of the bitumen and effect its extraction. An emulsion of steam condensate and heated bitumen flows down along the periphery of the steam chamber to the production well which is located below the injection well. This emulsion is then pumped to the surface where the bitumen and water are separated and the water is treated for reuse as BFW. In a conventional SAGD plant, the re-used produced water is de-oiled and treated by lime softening and ion exchange to reduce inorganic scalants, and then used as BFW for a robust style of steam generator known as a once through steam generator (OTSG), which can tolerate relatively high amounts of TDS, but is limited to low-quality steam (70–85%). In this study, the feasibility of FO process to be used as a polishing step after the conventional lime softening/ion exchange treatment processes was evaluated to yield high-quality desalinated BFW suitable for higher efficiency drum boilers, while consuming less energy than if desalination evaporators were used.

2. Materials and methods

2.1. Chemicals and reagents

A microporous polyethersulfone (PES, 0.2 μm) membrane was provided by Sterlitech Co. (WA, USA) and used as the support for the TFC membranes fabricated in this research. MPD (≥99%), TMC (98%) and camphorsulfonic acid (CSA) were obtained from Sigma-Aldrich. Heptane (≥99%), triethylamine (TEA) and sodium dodecyl sulfate (SDS) were purchased from Fisher Scientific. All materials were used as they were received from the suppliers. Commercial PA TFC-FO membranes with embedded polyester fabric support were purchased from Hydration Technology Innovation (HTI, Albany, USA). The industrial process water used for measuring the membranes permeation performance and fouling characteristics was conventionally-treated SAGD BFW obtained from an in-situ water treatment plant located in the Athabasca oil sands region of Alberta, Canada. The pH of this water, as received was 10, and was not adjusted during the filtration experiments.

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