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Relating thin film composite membrane performance to support membrane morphology fabricated using lignin additive

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ABSTRACT

In this study, three nonwoven fabrics were used as supports to form thin film composite membranes for forward osmosis (FO) applications. Lignin additive was added to the polysulfone layer in two different concentrations to increase the porosity of the substructure. The fabrics were characterized in terms of their Frazier permeability, tortuosity, porosity, thickness, structural parameter and capillary pressure. It was found that the fabric tortuosity and thickness had strong negative correlations with FO water flux, while fabric porosity had a strong positive correlation. The fabric capillary pressure was found to be indicative of how well the polysulfone layer adhered to the fabric layer. The membrane structural parameter of the fabric, unsupported and supported polysulfone layers were measured and compared using a "resistance-in-series" model. Although seepage of the casting solution into the fabric layer was physically observed, the addition of the individual structural parameters of the layers offered a good approximation of the composite membrane structural parameter. Membrane structural parameters calculated for fabric supported composite membranes using reverse osmosis (RO) permeability parameters and FO/RO established transport equations were much larger than structural parameters obtained from physical measurements. The difference may be due to compaction of composite membranes in reverse osmosis experiments, casting solution seepage partially plugging the upper layers of the support fabric and other non-idealities not captured in the established FO/RO transport equations.

1. Introduction

Forward osmosis is a membrane process that involves the spontaneous movement of water from a region of high concentration to a region of low concentration through a semi-permeable membrane. This process has promising applications in desalting water, concentration of fruit juices, membrane bio reactors, clean water reclamation and industrial water treatment [1–6]. In order for the FO process to be effectively used in desalination, there is a dire need for a membrane with properties similar to those of existing RO commercial membranes with respect to high salt rejection and high water permeability, and a draw solution with high osmotic pressure, which can be effectively regenerated in an energy efficient method [7–9].

Different materials and types of membranes are currently explored for FO applications, including integrally skinned cellulose triacetate (CTA) and thin film composite (TFC) polyamide membranes. Cellulosic membranes have a limited pH and thermal stability range while TFC membranes are limited in performance in FO due to internal concentration polarization [10,11]. Recent research, however, have shown that the performance of TFC membranes can be improved by optimizing each layer individually [12,13]. In order to increase the porosity of the membrane support layer, different additives have been used in the casting process, including polyvinyl pyrrolidone (PVP), polyethylene glycol (PEG), glycerol and maleic acid [14–16]. Lignin derivatives have also been used as additives in membrane synthesis because they are readily available and are a by-product in pulp industries. Zhang et al. incorporated lignosulfonate in polysulfone membranes to induce electrolyte transference [17]. They reported that higher concentrations of lignosulfonates induced larger surface pores and caused a decrease in macrovoid formation. Recently, Nevarez et al. used propionated lignin to fabricate cellulose triacetate membrane for water purification [18]. Propionating the lignin was found to improve its interaction with cellulose triacetate.

While extensive research has focused on improving the properties of membranes by altering the membrane substructure, such as including additives, little attention has been given on using

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different types of fabric supports in membrane fabrication and its effects on membrane performance. Woven fabrics are being used by Hydration Technology Innovations, LLC (HTI, Albany, OR) to fabricate CTA membranes while nonwoven fabrics are typically used in the production of TFC membranes [19,20]. The extent to which a fabric support affects membrane performance largely depends on its properties. Sairam et al. discovered that when preparing membranes using nylon woven fabrics, a casting blade height of 200 μm formed membranes with no osmotic permeation, while a height of 100 μm produced membranes with pin hole defects [21]. They concluded that the penetration of the dope solution into the fabric formed defective, low permeability membranes. To prevent this, the fabric was pasted on a glass plate using polyvinyl pyrrolidone solution. Another way to prevent the dope solution from seeping into the support material is to pre-wet it with the solvent used to dissolve the polymer as demonstrated in a study by Tiraferri et al.[22]. Increasing the polymer concentration also prevents the polymer solution from seeping into the fabric, but will increase resistance to permeation, thereby lowering the water flux since the effective surface porosity and mean pore size have been reported to be inversely proportional to the polymer concentration [23]. However, for large scale applications, some of these methods of preventing the polymer solution from penetrating the fabric support would not be feasible or economical.

Although penetration of the polymer solution into the backing of the fabric support is not desired, lack of proper adhesion between the polymer and fabric layers, on the other hand, can lead to the polymer delamination, and formation of blisters in-between the two layers [24]. Fabrics used in membranes for high pressure driven applications should have high porosity in order to provide low resistance to permeation. Goettmann found that there is insufficient polymer solution penetration into dense non-woven fabrics [24].The use of dense fabrics in membrane formation can cause delamination of the polymer layer, and the formation of pinhole defects due to the presence of residual bubbles (lack of sufficient debubbling during manufacturing of the fabric) [24]. Less-dense fabrics, on the other hand, can result in over penetration of the polymer into the back side of the support, resulting in a limited amount of polymer to form a film on the surface of the membrane [24]. Smooth fabric surfaces prevent surface imperfections, while fabric non-uniformities will cause uneven distribution of polymer during the casting process, creating pinholes, buildup of polymer, which will project itself as uneven flux distribution in operation [25]. As a result, the polymer, its concentration, the fabric support properties, and the interplay between these properties must be taken into consideration in the membrane formation process [25,26].

A limited number of published studies have considered the effect of non-woven fabrics in the formation of membranes. Loeb et al. conducted a study on the influence of the fabric on commercial asymmetric membranes, and found that the support fabric decreases permeation flux significantly as it increases the resistivity of the membrane [9]. McCutcheon and Elimelech also studied the effect of using a fabric support during membrane fabrication and reported that membranes without the fabric had a steady flux over time compared to membranes with a fabric which showed a decline in flux that was attributed to the fabric preventing full wetting of the TFC membrane [27]. Lohokare et al. monitored the change in performance of a polyacrylonitrile ultrafiltration (UF) membrane using woven and nonwoven fabrics [28]. They found that woven fabrics gave higher flux, reduced protein rejection and higher compaction resistance under hydraulic pressure.

Herein, we report on the influence of different nonwoven fabrics on the performance of TFC membranes tested in both RO and FO modes. Various non-woven fabrics have previously been incorporated into different membranes but to the best of our knowledge no dedicated study has reported on the effect of using different types of nonwoven fabrics on both RO and FO membranes. Yip et al. and Tiraferri et al. used a commercial polyester nonwoven fabric obtained from Ahlstrom Co. whereas, other researchers used nylon fabric in the formation of their membranes [21,22,29]. Herein, we investigate the change in membrane performance as a result of using different fabrics during membrane fabrication for both RO and FO processes.

Beginning with the introduction of the asymmetric Loeb–Sourirajan osmotic membrane and work by Lee et al. and Loeb et al. parameters K and S have been introduced to help characterize and design FO membranes [9,30].The resistance to solute diffusion by the porous support, K, describes the hindered transport diffusion of solutes into and out of the support layer of the membrane. The membrane structural parameter, S, describes the average distance a molecule must travel from the bulk solution through the support layer, to reach the active layer of the membrane, which was derived to be proportional to the thickness, tortuosity and inversely proportional to the porosity of the support [31]. However, the membrane structural parameter is experimentally determined using water and salt permeability coefficients determined by RO experiments. It is expected that the permeability coefficients under RO conditions (hydraulic pressures of over 400 psi) do not accurately reflect the permeability coefficients of the much thinner and structurally weaker FO membranes that operate under low pressure (FO, PRO) conditions. This issue has been recently addressed by Tiraferri et al. in which water and salt permeability coefficients along with the structural parameters are determined solely by a series of FO experiments [32]. In addition to the effects of using different non-woven fabrics on FO performance, the accuracy of using the membrane structural parameter in designing FO membranes will be investigated in this study.

2. Experimental

2.1. Materials

To prepare the polymer casting solution, polysulfone (PSf) beads (22 kDa), lignin alkali and *N*,*N*-Dimethyl formamide (DMF) (Sigma Aldrich, St. Louis, MO), and *N*-Methylpyrrolidone (NMP, Merck Millipore, Darmstadt, Germany), were used as received. Polymer solutions were cast onto three different fabric materials: Fabric A, made of polyester (Ahlstrom Co., USA), and Fabric TH and HS made of polyester and polyphenylenesulphide (PPS), respectively (Hirose Co., Japan).The chemicals used in interfacial polymerization were hexane (anhydrous, $>95\%$), 1,3-benzene diamine (MPD), 1,3,5-benzenetricarbonyl trichloride (TMC), sodium hypochlorite (NaOCl) and sodium bisulfite ($NaHSO_3$) (Sigma Aldrich). Sodium Chloride (NaCl, Sigma Aldrich) was used to prepare the draw solution while deionized (DI) water was used as the feed solution in testing the membranes.

2.2. Fabrication of UF support membranes

Lignin alkali was dissolved in a mixture of NMP and DMF solvents at 50 °C (below the flash point of the solvent mixture). After complete dissolution of lignin, small amounts of polysulfone beads (26 kDa) were added, while stirring, to the cooled lignin solution in amounts as shown in Table 1. The solution was then mixed for at least 8 h and allowed to settle overnight. The solutions were cast on three different nonwoven fabrics (labeled Fabric A, TH and HS), which were attached onto a clean glass plate