Poly(vinyl) alcohol coating of the support layer of reverse osmosis membranes to enhance performance in forward osmosis

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HIGHLIGHTS

• Poly(vinyl alcohol) coating of of reverse osmosis membranes enhances their use in forward osmosis
• Amount and type of Poly(vinyl alcohol) crosslinking agent impacts FO membrane performance
• Hydrophilicity and fractional free volume of PVA influence FO membrane performance

ARTICLE INFO

ABSTRACT

Membrane hydrophilicity influences the transport of water through the membrane in osmotically driven separations such as forward osmosis. In this paper, we coated the polysulfone support layer of two types of commercially available reverse osmosis membranes (brackish water and seawater) with hydrophilic polyvinyl alcohol (PVA). The aim of this was to increase the support layer hydrophilicity and, correspondingly, the rate of water transport through the membrane. Previous work with polydopamine coatings of the polysulfone support of reverse osmosis membranes has yielded promising results. In this work, we explore more readily available materials. Specifically, we studied the effects of two different PVA crosslinking agents – maleic acid and glutaraldehyde – on the resultant membrane properties and osmotic performance. For seawater membranes we found that PVA crosslinked to a limited degree with maleic acid creates a significant improvement in water flux in RO and FO systems, as compared to membranes with PVA crosslinked by glutaraldehyde. However, brackish water membranes did not have comparably significant changes in membrane performance. We conclude that the smaller pores of the brackish water membrane become clogged, and this effect is magnified by the lack of fractional free volume available within PVA that is highly crosslinked with glutaraldehyde.

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1. Introduction

Meeting the growing demand for clean water requires improved technologies to reclaim or purify saline, waste, and impaired water sources. Osmotic processes such as reverse osmosis (RO) and forward osmosis (FO) are proven methodologies for water reclamation [1]. Additionally, pressure retarded osmosis (PRO) is a membrane process capable of producing energy from salinity gradients [2]. While thin film composite (TFC) membranes have been somewhat optimized for the applied pressure driven RO processes [3], highly effective membranes for FO and PRO processes have yet to be developed [4,5].

Traditional polyamide-based TFC RO membranes consist of a three-tiered structure. The base of the TFC RO membrane is a dual-layered membrane that provides mechanical support to the thin polyamide film. This dual-layered support membrane consists of a 50–100 μm thick non-woven polyester fabric (polyethylene terephthalate, PET),

on which an approximately 50 μm thick phase-inversion polysulfone layer is cast. A polyamide thin film (~30–100 nm thick) is deposited onto the polysulfone surface of the support, providing the main selective layer of the asymmetrically structured RO membrane [6].

Internal concentration polarization (ICP) is a well known problem in FO processes and limits widespread implementation [5,7]. During ICP, solute accumulates within the membrane support structure, lowering the effective osmotic pressure difference across the membrane (the driving force for separation), and hence, lowering the flux [8]. Asymmetrically structured RO membranes suffer from severe internal concentration polarization when used in FO, as solute is easily entrapped within the tri-layer structure [9]. In recent work on asymmetrically structured membranes, Arena et al. coated the polysulfone support of RO TFC membranes with the hydrophilic polymer polydopamine, attempting to minimize ICP. This coating improved water and salt fluxes of asymmetrically structured RO membranes when used in FO processes [10].

Additionally, increasing the hydrophilicity of the support layer also enables more thorough wetting of the support layer to expel entrapped air and facilitates water flow through the membrane during

forward osmosis [11]. Hydrophilic polymers such as cellulose acetate, polybenzimidazole, polydopamine, and sulfonated polysulfone have been integrated into the support layer of asymmetrically structured membranes to improve wetting [12–14]. In this work we study the effects of PVA on the support membrane of asymmetrically structured membranes. Previously, researchers have coated PVA onto the polyamide selective layer of RO TFC membranes to increase hydrophilicity and reduce fouling [15–18]. Here, we coated PVA on the polysulfone support of TFC membranes to see its impact on membrane hydrophilicity and flux performance.

PVA is inexpensive and readily available but lacks mechanical strength and swells in water [10,19]. Crosslinking agents bind with the hydroxyl groups of the PVA, increasing its mechanical strength and reducing swelling in water [15]. In this study, we investigated the effect of varying concentrations of two PVA crosslinking agents – maleic acid and glutaraldehyde – on membrane hydrophilicity and separation performance in osmotic processes.

2. Materials and methods

2.1. Materials

Two types of commercially available reverse osmosis membranes were used: seawater SW 30-XLE and brackish water BW 30 (DOW Water Process Solutions; Edina, MN). Both are thin film composite membranes composed of a thin polyamide layer coated onto a support membrane made up of a polysulfone layer and the polyethylene terephthalate (PET) fabric described in Section 1. We removed the polyethylene terephthalate (PET) support from the membrane to expose the polysulfone layer. To modify the polysulfone surface, we used polyvinyl alcohol (PVA 6-98; Sigma Aldrich) with an average molecular weight of 47,000 g/mol, 98.0–98.8% hydrolyzed. We explored the effectiveness of two different PVA crosslinking agents: maleic acid, molecular formula $C_4H_4O_4$ (MA >99%, Sigma Aldrich), and glutaraldehyde, molecular formula $C_5H_8O_2$ (25% aqueous solution, Sigma Aldrich) [18,20]. Sodium chloride (NaCl, Sigma Aldrich) was used in RO rejection measurements and in FO performance tests. All aqueous synthesis solutions and test solutions were made with ultrapure water produced by a Millipore Integral 10 water system (Millipore Corporation Billerica, MA). Isopropyl alcohol (IPA, >98%, Sigma Aldrich) was used to facilitate wetting of the support membrane pore structures.

2.2. Membrane preparation

In the first step of membrane preparation, we removed the nonwoven PET backing from the TFC membranes. We then soaked the remaining layers (polysulfone coated with polyamide) in a 98% isopropyl alcohol (IPA) solution for 1 h (based on the method of Arena et al. [10]). This soaking step facilitated later wetting of the polysulfone pores with aqueous solutions. After soaking in IPA, the membranes were rinsed with deionized (DI) water and stored in a DI water bath.

Next, we coated the polysulfone support with a PVA solution. The PVA was prepared based on the method of Peng et al. [18]. We added 0.1 wt.% PVA powder to boiling deionized water with continuous stirring. After the PVA was completely dissolved into the boiling water, the solution was allowed to cool to room temperature. After the solution cooled to ~25 °C, we added 1 mL of 2 M hydrochloric acid (crosslinking catalyst) and either maleic acid or glutaraldehyde to achieve the desired theoretical crosslinking agent concentration (X_{cl}) of either 10% or 50%. The theoretical crosslinking agent concentration of the subsequent PVA solution was estimated through Eq. (1), in terms of the molar ratio of crosslinking agent to PVA [18].

$$X_{cl} = \frac{W_{cl} \cdot M_{PVA} \cdot 2}{W_{PVA} \cdot M_{cl}} \times 100 \tag{1}$$

The theoretical crosslinking agent concentration (X_{cl}) is a function of the total weight in grams of crosslinking agent used (W_{cl}), the molecular weight of a single PVA chain (M_{PVA}), the total weight in grams of PVA used (W_{PVA}), and the molecular weight of the crosslinking agent (M_{cl}).

The PVA solution with the added crosslinking agent was stirred continuously for an additional 30 min. During this time, the RO membrane was removed from the deionized water storage, placed on a glass plate, and held in place by a rubber frame with the polysulfone layer facing up. Immediately after stirring, the PVA solution was poured into the frame and allowed to contact the wetted-polysulfone surface of the RO membrane for 10 min. After this time, the PVA solution was poured out of the frame, and the membrane was allowed to dry overnight at room temperature. After drying, the membrane was cured at 100 °C for 10 min in a convection oven (Heratherm Oven Thermo Scientific OGS; Waltham, MA, USA) and then stored in deionized water until testing. This method prevents the PVA from contacting and coating the polyamide selective layer.

2.3. Membrane characterization

2.3.1. Membrane surface characterization

We measured the sessile drop deionized water contact angles of the membrane surfaces with a goniometer (Kruss Easy Drop DSA-20, Palo Alto, CA, USA) using 2 μL drops. Measurements were repeated a minimum of six times per sample on triplicate samples.

We used a scanning electron microscope (SEM) (FEI/Philips, XL30 ESEM-FEG Hillsboro, Oregon, USA) to image the surface and cross-sections of the unmodified and PVA-coated support membranes. We then analyzed the SEM cross-sectional images with ImageJ software (National Institutes of Health) to estimate the porosity of unmodified SW 30-XLE and BW 30 RO membranes [26].

With the ImageJ program, we used the technique of image thresholding to determine the membrane porosity from SEM images. Thresholding is a simple method of image segmentation that allowed us to detect dark colored pores of the membrane image. It involves finding an appropriate darkness value (the "threshold") below which all the pixels corresponding to black pores take the value zero and the remaining pixels take the value of one, simplifying the information in the image. The porosity is estimated from the percentage of black pixels in the image.

2.3.2. Hydraulically driven membrane performance

We used a stirred cell (Sterlitech HP4750 Kent, WA, USA) to test the hydraulically driven (RO) performance of the three types of membranes: (1) the unmodified membranes, (2) the membranes with the PET removed, and (3) the membranes with PVA coating and the PET reinserted behind the coated polysulfone support. Membranes with PVA coating of 10% and 50% maleic acid or glutaraldehyde were tested for permeability. In case (3), the removed polyester was reinserted for additional mechanical strength in RO testing. This addition did not cause any significant change in observed membrane fluxes. Previous work by Arena et al. also indicated that removal of the polyester nonwoven backing from the TFC membrane does not result in loss of permeability or selectivity [10]. We measured pure water flux and NaCl rejection (2000 ppm) of all of the types of membranes in the stirred cell as a function of pressure (from 2.5 to 73.8 bar). NaCl rejection was calculated from the measured conductivity values of the permeate and feed solution.

The water flow through the membrane was calculated using Eq. (2) [21].

$$J_w = \frac{V}{A_m t} \tag{2}$$

In Eq. (2), J_w [L m^{-2} h^{-1}] is the water flux, V [L] is the volume of permeate collected during a time period t [h], and A_m [m^2] is the area of the