



Solute and water transport in forward osmosis using polydopamine modified thin film composite membranes



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HIGHLIGHTS

- Reverse osmosis membrane support layers were modified with polydopamine.
- The modified membranes were tested under forward osmosis conditions.
- An ammonia–carbon dioxide draw solution was used for the testing.
- Sodium ion rejection was found to be low, while chloride ion rejection was high.
- Differing ion rejection is an evidence of ion exchange between the feed and draw.

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ABSTRACT

Forward osmosis is a rapidly emerging technology that has potential to enable low cost water treatment and desalination. Previous investigations have found that reverse osmosis (RO) membranes were unsuitable for forward osmosis in part due to their hydrophobic support layers, which inhibit wetting. Poor wetting hinders water and solute transport in the support layer, dramatically increasing the severity of internal concentration polarization. In this study, RO membrane support layers were modified with polydopamine (PDA) to increase their hydrophilicity and promote wetting. The results indicate that the modified RO membranes exhibited a four to six fold increase in forward osmosis (FO) water flux under test conditions relative to unmodified membranes. Additional tests were performed under model desalination conditions using an ammonia–carbon dioxide draw solution with a sodium chloride feed. The sodium and chloride rejections were measured independently and in some instances substantial differences were observed. Additionally sodium and chloride rejections were lower than anticipated with a peak rejection of 90%. The substantial difference between sodium and chloride rejections was attributed to a cationic exchange effect between the draw and feed solutions.

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1. Introduction

Forward osmosis (FO) is an emerging process being considered for the desalination, purification, and treatment of water [1–6]. A functional FO process requires an easily recoverable draw solution capable of generating high osmotic pressures as well as a highly productive and selective membrane [1,4,7]. Various draw solutes exist, but only the ammonia–carbon dioxide ($\text{NH}_3\text{--CO}_2$) draw solution has been demonstrated as both an effective and recyclable solute that may enable osmotically driven desalination [1,4,7–10]. Amongst the most commonly studied membrane for forward osmosis is the asymmetric cellulose acetate (CA) manufactured by Hydration Technology Innovations™ (HTI) [1,4,9–12,16]. This membrane's morphology has been optimized for use in osmotically driven membrane

processes [12]. The CA membrane while offering acceptable permselectivity and desirable hydrophilicity has inherent chemical compatibility drawbacks, notably hydrolysis in alkaline conditions [13–15]. Hydrolysis reduces salt rejection, which in FO translates to higher draw solute cross-over and a lower osmotic pressure difference across the membrane [14,15]. The $\text{NH}_3\text{--CO}_2$ draw solution will hydrolyze CA as this draw solution can be expected to have pHs above 7.7 [16,17].

This leads to the consideration of alternative membrane chemistries for use with the $\text{NH}_3\text{--CO}_2$ draw solution. The commercial alternative to the CA membranes is the thin film composite (TFC) membrane platform. These membranes, typically used in reverse osmosis, comprise an ultra-thin aromatic polyamide layer supported by a polysulfone (PSu) or polyethersulfone (PES) layer that has been cast onto a polyester (PET) nonwoven [18]. Each of these layers is capable of withstanding a broad range of pH and temperature conditions making them suitable for use with the $\text{NH}_3\text{--CO}_2$ draw solution. Despite these desirable characteristics for use FO processes early studies which attempted to use TFC

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membranes in FO found the performance of TFC RO membranes to be inferior to that of HTI's CA FO membrane [1,2]. In later work, the lack of TFC support layer wetting was demonstrated as a hindrance to osmotic flux due to a reduced effective porosity and enhanced internal concentration polarization (ICP) [19,22]. To address this problem the use of TFC membranes with an intrinsically hydrophilic support would be desirable. This would require a retuning of the delicate interfacial polymerization process, which can be impacted by the support layer properties [21,22]. Furthermore, hydrophilic supports may plasticize in the presence of water and cause damage to the fragile selective layer. Ideally, one could start with a TFC membrane made from a non-swelling hydrophobic support that also exhibits good permselectivity; then modify that membrane's support layer to increase its hydrophilicity. Recently commercial TFC FO membranes have just begun to enter the market with limited availability, with only HTI providing theirs for sale at the time of writing [6,11,23,24].

A recently developed technique to impart a hydrophilic character onto microfiltration, ultrafiltration, and reverse osmosis membrane selective layers for enhanced fouling resistance to oil/water emulsions and protein mixtures was reported by McCloskey and co-workers using polydopamine (PDA) [25–28]. PDA is a polymer with a chemistry similar to the adhesive secretions of mussels [29–31]. It is formed from the spontaneous polymerization of dopamine in an alkaline aqueous solution. A subsequent study by Arena examined the first use of PDA modified membranes for osmotically driven membrane process. This was done through the application of PDA to TFC membrane support layer(s). Significant improvements in the water flux of PDA modified TFC RO membranes were observed in the pressure retarded osmosis (PRO) orientation [32]. Others, such as Han, adopted this technique prior to synthesis of the membrane [33].

With the improved performance of these membranes in the PRO mode, we hypothesized that a similar improvement would be possible in the FO mode as well. The excellent selectivity of these membranes as well as tolerance to the often used ammonia–carbon dioxide draw solution make such a platform appealing. Membranes were tested for desalination performance using this draw solution in hopes of demonstrating the promise of these modified membranes; however, it was found that rejection, especially for cations, was far lower than anticipated. This was attributed to an ion exchange phenomenon occurring through the polyamide selective layer.

2. Materials and methods

2.1. Selected membranes and chemicals

The membranes selected for this investigation are the Dow Water & Process Solutions™ BW30 and SW30-XLE. Both membranes' support layers are made of PSu supported by a PET nonwoven [34]. These membranes were chosen for their high permselectivity, use in earlier studies, and reported properties [46]. Sodium chloride, tris–hydrochloride, sodium hydroxide, ammonium bicarbonate, and ammonium hydroxide were purchased from Fisher Scientific (Pittsburgh, PA). Dopamine–hydrochloride was purchased from Sigma-Aldrich (St. Louis, MO). Isopropanol, sodium tetraphenyl boron, potassium chromate, calcium nitrate, and silver nitrate were purchased from Acros Organics (Geel, Belgium). Water used in this study was ultrapure Milli-Q water produce by a Millipore Integral 10 water system (Millipore Corporation, Billerica, MA).

2.2. PDA modification of TFC membranes

The PDA modification followed the procedure set forth in previous work [32]. Since the PDA formation only occurs in the aqueous phase, it was necessary to prewet the support in isopropanol (IPA) prior to PDA modification. The support was soaked IPA for 1 hr and then washed

in a series of three deionized water baths for 45 min each. Following the IPA wetting and DI water rinsing, the membranes were stored in DI water at 4 °C before being modified with PDA. The dopamine polymerization took place within a custom built coating container where the membrane separates two reservoirs. This container ensures that nearly all of the PDA polymerizes within the PSu layer and not the selective layer (which would negatively impact permeability [26–28]). Both sides of the membrane were placed in contact with a pH 8.8 Tris buffer solution. Dopamine-HCl was added to the solution in contact with membranes' PSu support layers to bring the support layer coating solution to a concentration of 2 g · L⁻¹ dopamine. Polymerization occurs at room temperature with non-agitated solutions exposed to the air. The PDA polymerization can be observed upon the addition of dopamine where the formation of PDA is indicated by the change in color of the polymerizing dopamine solution from clear to orange and finally to brown.

2.3. Mercury intrusion porosimetry

A mercury intrusion porosimeter (MIP) (AutoPoreIV, Micrometrics) was used to characterize the membranes for pore diameter and total pore volume. The Washburn equation was used to calculate the pore diameters from the intrusion pressure.

$$d = \frac{-4\gamma \cdot \cos(\theta)}{P} \quad (1)$$

In Eq. (1), P is the intrusion pressure (MPa), d is the pore diameter (μm), γ is the surface tension of mercury ($485 \text{ dyn} \cdot \text{cm}^{-1}$) and θ is the contact angle of mercury (a value of 130° was assumed) with the sample. The sample was tested in the pressure range of 1–720 bar. It is to be noted that Eq. (1) assumes that measured pore diameters are cylindrical. While this assumption is idealized for the membrane supports tested in this study, the resulting values for d calculated in Eq. (1) represent the equivalent cylindrical pore diameters of the support. It is also to be noted that the intrusion technique can detect both through and blind pores but not closed pores [38].

2.4. Fourier transform infrared spectroscopy

The modified TFC RO membranes were tested in Fourier transform infrared (FTIR) spectroscopy to examine the surface functional groups of the membranes' selective layers. Membranes were tested, after drying, in a Thermo Scientific (Waltham, MA) Nicolet iS10 FTIR spectrophotometer with Smart iTR attachment was used to perform these measurements on a dried membrane. Measurements were taken on the selective layer using 64 scans with a resolution of 4 cm^{-1} .

2.5. Osmotic flux testing of modified membranes

2.5.1. Sodium chloride as the draw solute

Both neat and modified TFC RO membranes were tested under osmotic flux conditions with the membrane oriented in the FO mode (with the support layer facing the draw solution) [35]. Both membranes were tested in each of the four following varieties neat (used as-received), no PET (where the PET backing has been removed from the membrane), one hour PDA modified, and forty-two hour PDA modified membranes (both modified using the method reported above). Membranes not modified with PDA were tested following storage in DI water. Prior to testing no wetting technique was implemented. The membrane area exposed to the feed and draw solutions were approximately 19 cm^2 (3 in.^2). Sodium chloride (NaCl) was used as the draw solute at concentrations of 0.05, 0.1, 0.5, 1.0, and 1.5 M. The osmotic flux testing procedure has been described previously [11,22,32,37,39]. Temperature was maintained at $23 \pm 1^\circ \text{C}$. Flux was measured gravimetrically using a balance (Denver Instruments

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