Emerging investigator series: Post-Synthesis Modification of Reverse Osmosis Membranes for the Enhanced Separation of Small Neutral Molecules

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Current reverse osmosis membranes are poor at removing small neutral molecules from water. This work has resulted in a notable improvement in a commercial reverse osmosis membrane rejection of small neutral molecules by using carbodiimide chemistry to activate the membrane surface for amine coupling and heat treatment. The membrane urea and boric acid removal was improved from 20% to 60%.

Emerging investigator series: Post-Synthesis Modification of Reverse Osmosis Membranes for the Enhanced Separation of Small Neutral Molecules

Shahriar Habib†, Madison A. Wilkins†, and Steven T. Weinman*

Department of Chemical and Biological Engineering, The University of Alabama, Tuscaloosa, AL 35487, USA

*Corresponding author: Tel: +1 (205)-348-8516, Fax: +1 (205)-348-7558. Email address: stweinman@eng.ua.edu

†These authors contributed equally to this work.

Abstract

Reverse osmosis (RO) membranes are used ubiquitously for seawater desalination. Ideally, the interfacial polymerization (IP) reaction used to synthesize RO membranes would form a uniform pore or free volume element structure within the polyamide layer. In reality, the self-limiting and chaotic nature of IP prevents the saturation of the RO active layer with the aqueous reactant. Unexploited attachment sites on the organic reactant are negatively charged in an aqueous solution, facilitating the desalination apt of RO membranes. However, these unreacted sites leave the pore structure with sizeable free-volume holes which permit small, neutral molecules (SNMs) to permeate through the membrane. The goal of this research is to decrease free volume space on the surface of the polyamide layer to improve the size exclusion properties of RO membranes and SNM rejection. We hypothesize that conjugating diamines or a branched polyamine to the synthesized polyamide layer will increase cross-linking to facilitate this improvement. To test this hypothesis, the polyamide layer of a commercial RO membrane is activated using carbodiimide chemistry and subsequently modified with an amine. Then, the modified membranes are heat treated in a microwave or hot water bath. The effects of various amines including 1,6-diaminohexane, 1,8-diaminooctane, m-phenylenediamine, and polyethyleneimine (10,000 MW) are evaluated. The results show that combining the application of amine conjugation and heat treatment significantly improves SNM rejection. Specifically, urea rejection was increased from 21% to 61%, and boron rejection was increased from 23% to 59%.

Keywords: Thin-film composite membrane; Fully aromatic polyamide; Carbodiimide chemistry; Urea; Boron

1. Introduction

Beginning in the late 1950's, reverse osmosis (RO) membranes have been studied as tools to combat the scarcity of potable, clean water.[1, 2] Since then, RO membranes have been used ubiquitously for seawater desalination.[3] The desalination performance of RO membranes stems from the interfacial polymerization (IP) reaction used to synthesize them. During this process, the polyamide layer is formed at the interface of two immiscible phases: aqueous m-phenylene diamine (MPD) and organic trimesoyl chloride (TMC). Due to its slight solubility in the organic phase, MPD diffuses from the aqueous to the organic phase.[4, 5] This diffusion allows MPD to react with TMC at the interface to generate the polyamide layer of RO membranes.[6] Ideally, IP would generate a uniform pore free volume element structure (known as network pores) within the polyamide layer. However, in reality, this reaction is rapid, uncontrolled, and semi self-limiting.[7, 8] Due to this, the pore structure contains not fully reacted TMC (and likely some MPD) molecules leading to larger free volume space (known as aggregate pores).[9]

Conveniently, incomplete IP contributes to the excellent charge-exclusion properties of RO membranes. When TMC molecules encounter the aqueous phase, acid chloride groups which do not form amide bonds with MPD hydrolyze to generate carboxylic acid groups. These acid groups are negatively charged in an aqueous solution at a pH > 4.0.[10] Due to charge repulsion, these increased negative charges on the surface of the RO membrane make the membrane able to repel anions, such as chloride.[11] By more effectively rejecting anions, the membrane also effectively rejects salt counter ions, like sodium, per the principles of membrane equilibria.[12] Therefore, the not fully reacted TMC molecules contribute to the impressive desalination ability of RO membranes.

While the self-limiting and chaotic nature of IP may contribute to charge-exclusion, it hinders the size-exclusion properties of RO membranes. TMC molecules that are not fully reacted break the expected chain of uniform network pores within the polyamide layer, resulting in larger aggregate free volume holes.[9] Small, neutral molecules (SNMs) which do not respond to Donnan exclusion mechanisms can slip through this free volume space.[13] In this way, not fully reacted TMC molecules resulting from the incomplete IP between MPD and TMC squander the potential of RO membranes for use as a tool for SNM rejection.[14]

It is desired to improve the ability of RO membranes to effectively reject SNMs. SNMs of particular interest are urea and boric acid. Urea is used worldwide as a cheap source of nitrogen fertilizer, and its use has increased more than 100-fold in the last four decades.[15] Additionally, urea is used extensively in animal feeds and manufacturing processes.[15] The industrial shift towards using urea as an abundant and cheap source of nitrogen for these purposes parallels the increasing demand for food to feed the growing global population.[15]

Urea used for agriculture and livestock care is retained in soil, and overland transport allows urea to travel to both coastal and estuarine waters, elevating the total dissolved organic nitrogen amount to an environmentally unsafe level.[15] Elevated levels of dissolved organic nitrogen in coastal waters fuel harmful algal bloom species. Over time, harmful algal blooms can irreversibly damage marine ecosystems. Harmful algal blooms not only affect marine life, but they can also result in seafood which is toxic to human health.[16] As a result of the increase in urea usage in the recent years, these adverse environmental effects of urea contaminated wastewater have become of particular concern.

Another relevant application of urea-rejecting RO membranes is the miniature, peritoneal dialysis artificial kidney. In these miniature dialysis devices, RO membranes may be used to eliminate the need for large quantities of dialyzing solutions.[17] A standard hemodialysis machine weighs 195 lbs and reaches 33.5 in height.[18] Continuously recycling the dialysis solution using hyperfiltration by reverse osmosis membranes allows a standard hemodialysis machine to become small enough to be both portable and wearable. Improving the ability of the RO membrane to reject urea could allow these devices to become even more compact.

In addition to urea, boron is another SNM that is of interest for separation. Primarily, boron is produced by the natural weathering of clay-rich sedimentary rocks.[19] While boron is an important element in humans' diet, long-term consumption of water or food with increased boron concentrations can negatively impact the cardiovascular, coronary, nervous, and reproductive systems.[20-22] The concentration of boron in the sea is as high as 4 to 5 mg/L.[19] The guideline value for boron concentration in drinking water established by the World Health Organization is 2.4 mg/L. As a result, in order to use RO membranes to generate potable water from seawater to combat the shortage of freshwater resources, both desalination and boron separation must occur.[23]

Many methods have been studied for the separation of aqueous urea and boron. Current methods used to remove urea from aqueous solutions include hydrolysis, decomposition, adsorption, and electro-chemical oxidation.[24] However, these methods are either energy-intensive, or they require complex biological processes.[25] Additionally, decomposition processes produce additional waste, making the treatment process more expensive and complex.[26] Presently, there is no simple and economic technology which can be used to effectively remove boron from aqueous mediums.[20] Methods that have been studied for boron separation include thermal desalination and sorption on solids.[11] Although effective in removing dissolved boron to nearly-zero concentration, thermal desalination has lost popularity as a tool for boron separation due to its high energy intensity.[27, 28] Removal of boron from aqueous solutions via sorption on solids requires a large sorbent to boron ratio, does not allow for regeneration of the sorbent, and is limited by surface-active agents.[11]

Membrane technologies, such as RO, offer a simple to use, cost-effective, stable, and predictable method for the separation of small molecules.[29] Additionally, membranes are capable of simultaneously removing other solutes.[29] However, unaltered RO membranes are unable to effectively separate aqueous SNM's due to the aggregate free volume holes within the polyamide layer. Unaltered RO membranes are only able to produce urea rejections anywhere from 20-60% and boron rejections anywhere from 20-90%, depending on pH.[13, 30] Reducing this aggregate free volume space would allow the advantages of membrane technologies to be utilized for the treatment of SNM contaminated water.

The goal of this study was to improve the ability of RO membranes to separate aqueous SNMs by reducing the aggregate free-volume space on the surface of the polyamide layer. We tested the hypothesis that exploiting not fully reacted TMC molecules via carbodiimide activation and subsequent reaction with an amine would reduce the free volume space on the surface of RO membranes and improve SNM rejection. Additionally, based on previous our work,[31] we tested the hypothesis that combining diamine or a branched polyamine coupling with thermal treatment would further improve the size-exclusion properties of the modified membranes. In this work, we modified the surface of the Dupont XLE RO membrane with various diamines and one branched polyamine, and we studied how this modification impacted membrane performance. The modified membranes were tested for pure water permeance (PWP), NaCl rejection, urea rejection, and boron rejection using a dead-end stirred testing cell. The membrane surface chemistry, hydrophilicity, and zeta potential were also analyzed.

2. Materials and methods

2.1 *Materials*

Commercially produced polyamide thin-film composite (TFC) extra low energy (XLE) RO membranes were kindly provided by Dupont Water Solutions. These membranes are made up of a polyester fabric backing, a polysulfone support layer, a thin-film polyamide selective layer. We chose the XLE membrane because it does not have a coating that could potentially alter the carbodiimide chemistry modification pathway described in *Section 2.2*. Deionized water was obtained from a Millipore Synergy ultraviolet water purification system. 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC, ≥98%), β-(N-morpholino)-ethanesulfonic acid buffer (MES, anhydrous, ≥99%), 1,6-diaminohexane (DAH, ≥98%), and crystallized urea (ACS grade, ≥99%) were used as received from VWR. N-hydroxysuccinimide (NHS, ≥98%), and 1,8-diaminooctane (DAO, ≥98%) were used as received from TCI chemicals. 4-(2-hydroxyethyl)piperazine-1-ethanesulfonic acid buffer (HEPES, ≥99.5%), sodium chloride

(NaCl, ≥99%), boric acid (ACS grade, ≥99.5%), and m-phenylenediamine (MPD, 99%) were used as received from Sigma Aldrich (Millipore-Sigma). Polyethyleneimine, branched, M.W. 10,000 (PEI, 99%) was used as received from Thermo Fisher Scientific Inc.

2.2. *Membrane Modification*

Figure 1 depicts a schematic of the membrane modification process. A small section of dry XLE membrane was cut from the flat sheet roll. This membrane piece was immersed in DI water on a VWR Standard Analog Shaker to wash the pore filler out of the membrane pores. The membrane was kept in the DI water on the shaker plate for at least 30 min. Prior to activation, the membrane was cut into a coupon with an area of 19 cm^2 using a precut stencil. The stencil was sized to fit the bottom of a 250 mL beaker.

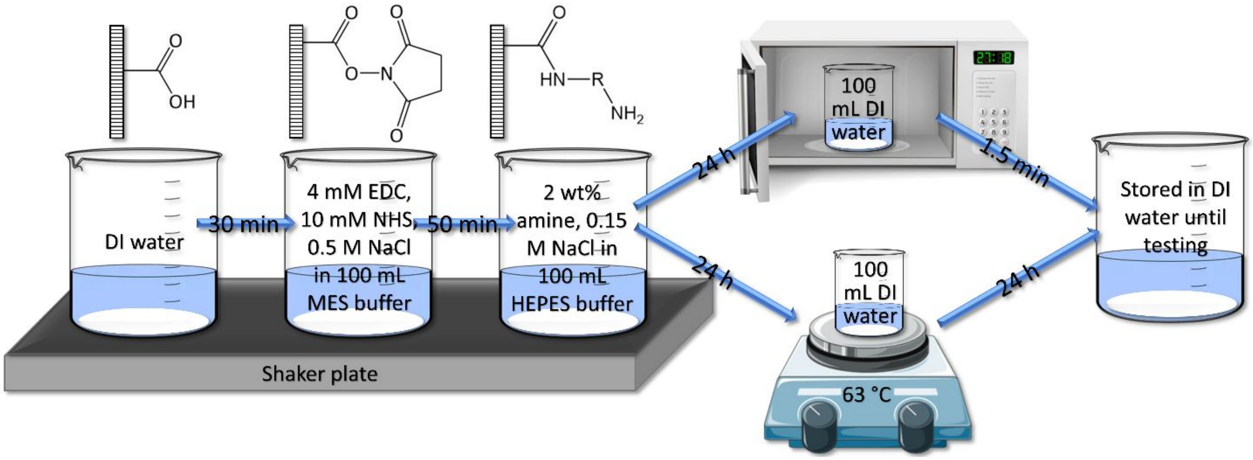

Figure 1. Modification of polyamide layer reaction schematic. EDC/NHS is used to activate the carboxylic acid groups of the polyamide layer to allow for amine coupling which is followed by heat treatment.

An activation solution consisting of 0.078 g EDC, 0.115 g NHS, 2.922 g NaCl, and 97 g of 10 mM aqueous MES buffer (pH 5.2), weighed using a ME403E precision balance (Mettler Toledo), was mixed in a 250 mL beaker and stirred for 10 min until the solution was homogeneous. Solution pHs were measured using an HACH HQ411d pH/mV meter. The rinsed membrane was immersed in the homogeneous activation solution. The beaker was covered with Parafilm and aluminum foil to protect the membrane from light, and it was left on the shaker plate for 50 min. EDC was used to activate free carboxylic acid groups on the surface of the polyamide layer formed by hydrolysis of acid chlorides at unreacted TMC sites.[32] Because the resulting O-acylisourea intermediate is not water stable, NHS was used.[32] After the carboxylic acid group is activated with EDC, NHS immediately replaces EDC, forming a water-stable NHS-ester intermediate.[32] This intermediate is now activated for diamine coupling.

While the rinsed membrane reacted in the activation solution, the amine solution for the cross-linking step of the modification was prepared. The amine solution consists of 2 g amine (MPD – pH 7.1, DAH – pH 12.0, DAO – pH 12.0, or PEI – pH 10.8), 0.876 g NaCl, and 97 g of 10 mM aqueous HEPES buffer. The amine solution was mixed in a 250 mL beaker and stirred to homogeneity. Following the 50 min activation step, the membrane coupon was immersed in the amine solution. The cross-linking solution was covered with Parafilm and aluminum foil, and it was left on the shaker plate for 24 h. During this step, the NHS-ester intermediate reacts with the amine to form a new amide bond.

After 24 h, the amine had conjugated to active sites on the surface of the membrane. The membrane was then thoroughly rinsed with DI water to remove any unreacted amine from the surface of the membrane. Following rinsing, membranes which did not undergo heat treatment were stored in DI water, covered with Parafilm, and kept in a dark place until testing. When applicable, a heating step was performed. Half of the heat-treated membranes were treated using a standard kitchen BLACK+DECKER (Model No. – EM925AZE-P) microwave oven. For this process, the cross-linked membrane was placed in 100 mL DI water in a 250 mL beaker and microwaved on high, uncovered for 1.5 min. We used the microwave to reduce the processing time of the heating step from 24 h in our previous work to 1.5 min.[31] During this procedure, the water in the beaker begins to visibly boil after ~45 s. Immediately following the microwave treatment, the membrane was carefully removed from the hot water using tweezers, and it was transferred to another beaker containing clean, room-temperature DI water. This beaker was covered in Parafilm and stored in a dark place until testing.

The other half of the heat-treated membranes were treated using a VWR professional hot plate stirrer (7 x 7 Cer Hot/Stir 120V ADV) as a comparison to our previous work.[31] For this process, a 250 mL beaker was filled with 100 mL DI water and placed on the hot plate which was set to a temperature of 80 °C. The DI water was heated until its temperature equilibrated at 63 °C. Then, the rinsed cross-linked membrane was immersed in the hot water. The beaker was then topped with a glass Petri dish and wrapped with aluminum foil to insulate the solution. After 24 h, the solution was removed from the hot plate, the membrane was removed from the hot water using tweezers, and the membrane was immersed in clean, room-temperature DI water and stored in a dark place until testing. The membranes will be discussed with the acronyms provided in **Table 1**. It should be noted that the EDC/NHS activated membranes were not tested as a control because the hydrolysis of the NHS ester can happen in a matter of minutes to hours, depending on the solution pH.[33]

Table 1. Acronyms for the XLE membranes.

Membranes	EDC/NHS	Heat Treatment	Amine
Control XLE (XLE-RT)	Not used	None	None
XLE-HP	Not used	Hot plate at 63 °C	None

XLE-MW	Not used	Microwave	None
XLE-DAH	Used	None	DAH
XLE-DAH-HP	Used	Hot plate at 63 °C	DAH
XLE-DAH-MW	Used	Microwave	DAH
XLE-DAO	Used	None	DAO
XLE-DAO-HP	Used	Hot plate at 63 °C	DAO
XLE-DAO-MW	Used	Microwave	DAO
XLE-MPD	Used	None	MPD
XLE-MPD-HP	Used	Hot plate at 63 °C	MPD
XLE-MPD-MW	Used	Microwave	MPD
XLE-PEI	Used	None	PEI
XLE-PEI-HP	Used	Hot plate at 63 °C	PEI
XLE-PEI-MW	Used	Microwave	PEI

2.3. *Membrane testing*

The control and modified XLE membranes were tested using a Sterlitech HP4750 dead-end filtration cell (Sterlitech, USA). The dead-end cell has a cell volume of 270 mL, and it has an effective filtration area of 14.6 cm^2. Prior to testing, the membranes were cut into circles with an area of ~17.4 cm^2 to fit the test cell. The cell was pressurized to 150 psig using either compressed nitrogen gas or air (AirGas). The membranes were challenged with DI water, 2,000 ppm aqueous NaCl (pH 6.0), 500 ppm aqueous urea (pH 6.3), and 40 ppm aqueous boric acid (pH 6.1). Each solution was allowed to permeate through the membrane for at least 30 min to achieve steady state before collection of permeate began. Approximately 10 mL of permeate was collected for each test. The time required to obtain the permeate was recorded to calculate the membrane permeance. Then, the mass of permeate obtained in that time was measured. At least three of each membrane were tested for statistical relevance. The water permeance (A) of each membrane when challenged with DI water was calculated using **Equation 1**.

$$A = \frac{Flux}{Pressure} = \frac{m}{a * t * P} \qquad (1)$$

where m is the mass of the permeate, a is the testable membrane area (14.6 cm^2), t is the permeate collection time, and P is the gauge pressure (150 psi). The units of A are in L/m^2/h/bar or LMH/bar.

The conductivities of the feed and permeate NaCl solutions were measured using a VWR Traceable Bench/Portable Conductivity Meter. A calibration curve was made as a function of salt concentration to ensure measurements were taken in the linear range of the conductivity meter. See **Figure S1A** in the Supporting Information for the NaCl calibration curve. The salt rejection was calculated using **Equation 2**.

$$NaCl\ Rejection = \left(1 - \frac{C_p}{C_f}\right) * 100\% \qquad (2)$$

where C_p and C_f are the permeate and feed conductivities, respectively.

The urea feed and permeate were each diluted two times using DI water, and the absorbances of the diluted solutions were determined using a HACH DR6000 UV-Vis Laboratory Spectrophotometer at a wavelength of 195 nm using quartz cuvettes (VWR), similar to Cheah and coworkers.[34] A calibration curve was made as a function of urea concentration to ensure measurements were taken in the linear range of the UV-Vis spectrophotometer. See **Figure S1B** in the Supporting Information for the urea calibration curve. The urea rejection was calculated using **Equation 3**.

$$Urea\ Rejection = \left(1 - \frac{Abs_p}{Abs_f}\right) * 100\% \tag{3}$$

where Abs_p and Abs_f are the permeate and feed absorbances obtained from the UV-Vis spectrophotometer, respectively.

The boron feed and permeate concentrations were determined using an Agilent 5800 Inductively Coupled Plasma Optical Emission spectroscopy (ICP-OES) instrument. The boron rejection was calculated using **Equation 4**.

$$Boron\ Rejection = \left(1 - \frac{B_p}{B_f}\right) * 100\% \tag{4}$$

where B_p and B_f are the permeate and feed concentrations, respectively.

2.4. *Membrane characterization*

2.4.1. *ATR-FTIR*

Attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR) was used to characterize the surface chemistry of the control and modified XLE membranes. The measurements were obtained using a Perkin Elmer Spectrum 2 ATR-FTIR spectrometer equipped with a diamond ATR crystal in the range of 400-4000 cm^{-1}. The data were processed using Spectrum 10 software. Each spectrum was collected for 32 scans at a resolution of 4 cm^{-1}. Each spectrum was baseline and ATR corrected with the Spectrum 10 software. All spectra were normalized to the peak at ~1490 cm^{-1}. A background of the ATR crystal was taken before testing each set of samples to ensure the crystal was clean.

2.4.2. *Static contact angle goniometry*

Static water contact angles were measured on the control and modified XLE membrane samples to evaluate changes in the hydrophilicity of the membrane surface. Changes in hydrophilicity can provide information about changes in surface chemistry. A contact angle goniometer (Attention Theta Lite, Biolin Scientific, Uusimaa, Finland) was used to measure all static water contact angles. A liquid drop of deionized water (~10 µL) was carefully placed on the sample surface. For consistency, all measurements were taken 20 s after the water droplet was placed on the surface. Measurements were done at a minimum of three locations on each sample to get a statistically relevant average contact angle.

2.4.3. *Streaming potential analysis*

The zeta potential of the surfaces of the control and modified XLE membranes were determined using an electrokinetic analyzer (SurPASS 3, Anton-Paar). Two membrane coupons were fixed to the sample holders of an adjustable gap cell with a gap size of 100 µm (sample size is 20 mm × 10 mm). In the experiment, an aqueous 0.01 M KCl solution was used as the measuring solution. For the pH adjustment, 0.05 M HCl and 0.05 M NaOH were used. The zeta potential was measured sequentially at pH 6, 9, and 3. The zeta potential was computed using the SurPASS 3 software using the Helmholtz-Smoluchowski equation. Measurements were done a minimum of three times to get a statistically relevant zeta potential value.

3. **Results and Discussion**

3.1. *Membrane Performance*

The control and modified XLE membranes were tested for pure water permeance, salt rejection, urea rejection, and boron rejection. The water permeance test results for membranes modified without heat treatment, as well as membranes heat treated using a hot water bath or a microwave are shown in **Figure 2A**. Through statistical analysis (see **Table S1** in the supporting information), it was found that amine-modified XLE membranes that did not undergo heat treatment and those which underwent heat treatment via the hot plate had statistically lower pure water permeance than the XLE-RT and XLE-HP membranes. The statistical decrease in pure water permeance between the control and amine modified XLE membranes (modified without heat treatment and using the hot plate) may be explained by increased cross-linking and a likely decrease in the free volume hole size within the polyamide layer. This improved cross-linking was likely brought about via amine coupling and/or thermal rearrangement. In the case of amine-modified membranes treated using the microwave, except for the XLE-DAO-MW membranes, the water permeance was not significantly different from the XLE-MW membrane.

The differences in water permeance between the different amine modified membranes could be attributed to a couple of factors. Firstly, it may be due to a difference in the extent of attachment of the different amines to available sites on the polyamide layer. Another possible cause of these differences could be the varying hydrophilicities of the different amines used during modification. The octanol-water partition coefficient of amines can give us an estimate regarding the hydrophobicity of the amines (see **Table S6** in the supporting information). The higher the octanol-water partition coefficient value, the higher the hydrophobicity of the molecule. It was found that DAO had the highest octanol-water partition coefficient by far, which helps explain why DAO modified membranes exhibited the lowest water permeance.

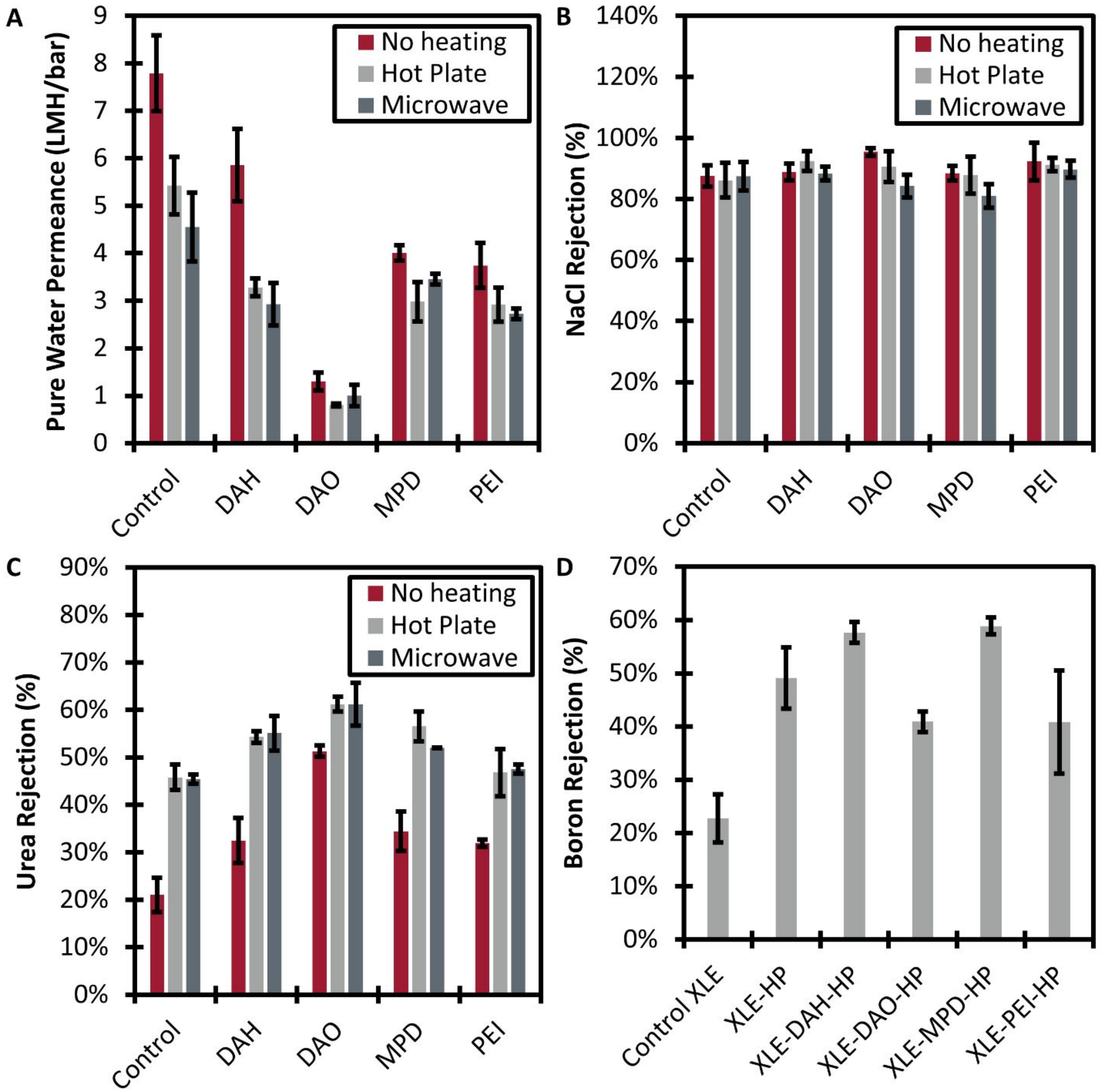

Figure 2. Membrane performance graphs depicting (A) pure water permeance, (B) NaCl rejection, (C) urea rejection, and (D) boron rejection for the control and modified XLE membranes. The error bars represent one standard deviation among three tests.

The ability of the control and modified XLE membranes to reject NaCl is displayed in **Figure 2B**. The average NaCl rejection of the control XLE membrane was found to be 86.5%. This value was lower than the expected value of 97% provided by the manufacturer. This difference in NaCl rejection can likely be explained by the concentration polarization associated with dead-end filtration, in contrast to less sensitive cross-flow filtration.[35] It was found that salt rejection exhibited by all but one of the modified membranes were not statistically different (see **Table S2** in the supporting information) from the salt rejection exhibited by the unaltered, control XLE membrane. Only the XLE-DAO-RT membrane showed a statistically significant increase in NaCl rejection from the control XLE membrane. These results indicate that the modification of the membranes does not significantly impair the salt rejecting properties of the XLE membranes.

In **Figure 2C**, the urea rejection is shown for both the control and modified XLE membranes. According to statistical analysis, the urea rejection of the membranes modified with amines at room temperature increased significantly (see **Table S3** in the supporting information) from the control XLE membranes, suggesting that amine coupling alone improves the ability of the membrane to reject urea. Thermal treatment alone also improved the ability of the membrane to reject urea, as demonstrated by the statistical increase in urea rejection for the XLE-HP and XLE-MW membranes compared to the control membranes.[31]

While amine coupling and thermal treatment alone was effective, the combination of both modifications provided the greatest improvement in urea rejection as demonstrated by the fact that each of the modified membranes treated with the hot plate and microwave had a higher average urea rejection than their counterparts which did not undergo heat treatment, except for the PEI-modified membranes. We believe the PEI was not attached to a large extent to XLE membranes, which was indicated in ATR-FTIR spectra (see **Figure 3**). Also, it was found that the membranes modified using the hot plate had a comparable urea rejection to their counterparts modified using the microwave. Among all the membranes, the membranes modified with DAO and heat treatment exhibited the greatest average urea rejection of ~61%.

In addition to the urea rejection performance of the modified membranes, the boron rejection performance of the membranes was also evaluated. The boron rejection for the control and modified XLE membranes is shown in **Figure 2D**. The hot plate treated amine-modified membranes were chosen for the boron rejection testing due to their superior performance in urea separation. According to statistical analysis, the boron rejection of the membranes modified with amines using the hot plate increased significantly (see **Table S4** in the supporting information) from the control XLE membranes. Among all of the membranes, the XLE-MPD-HP modified membrane exhibited the greatest average boron rejection. Surprisingly, the DAO-modified membranes showed significantly lower boron rejection compared to the DAH-modified membranes and MPD-modified membranes.

Although boric acid and urea are both small molecules, their chemical properties and interactions with the DAO-modified membranes may be different. It is possible that the difference in the octanol-water partition coefficient of boric acid (-0.509) and urea (-1.364) may be the cause behind the difference in the urea rejection and boron rejection performance of DAO-modified membranes. The higher octanol-water partition coefficient value of boric acid molecules makes them more hydrophobic compared to urea molecules. DAO has a higher octanol-water partition coefficient compared to DAH, MPD, and PEI (see **Table S6** in the supporting information), which made the modified membrane surface slightly more hydrophobic compared to other modified membranes. Huang et al. showed that the hydrophobic membrane tends to reject a lower percentage of hydrophobic solutes compared to hydrophilic solutes which may happen due to their hydrophobic adsorption followed by diffusion and/or convection through the polyamide surface.[36]

This could be a reason why the DAO-modified membranes exhibited a lower boron rejection compared to the urea rejection.

The modification of the XLE membranes with linear diamines showed comparable or in some cases better SNM rejection compared to the aromatic amine. It appears that the flexibility of the linear diamine better facilitates the linking mechanism between amines and unreacted carboxylic groups of the polyamide surface as compared to the aromatic diamine.[37] Considering the high pK_a values of the linear amines compared to the aromatic amine (see **Table S6** in the supporting information), besides having stable amide linkage, there is a possibility that the unreacted end of the linear diamines formed ion pairs with the remaining free carboxylic acid groups (pK_a ~4-5) at intermediate pHs, which may play a role in reducing the free volume.[37]

3.2. *Membrane Characterization*

3.2.1. *ATR-FTIR*

Membrane surface activation was done using carbodiimide chemistry to activate the carboxylic acid groups on the surface of the polyamide layer. In this work, commercial membranes were modified using DAH, DAO, MPD, and PEI. By combining carboxylic acid groups with amines, a new amide bond was formed. The ATR-FTIR spectra (2800 cm^{-1} - 3800 cm^{-1} range) of the control and modified XLE membranes modified at room temperature and using a hot plate or microwave are shown in **Figure 3A**, **Figure 3B**, and **Figure 3C**.

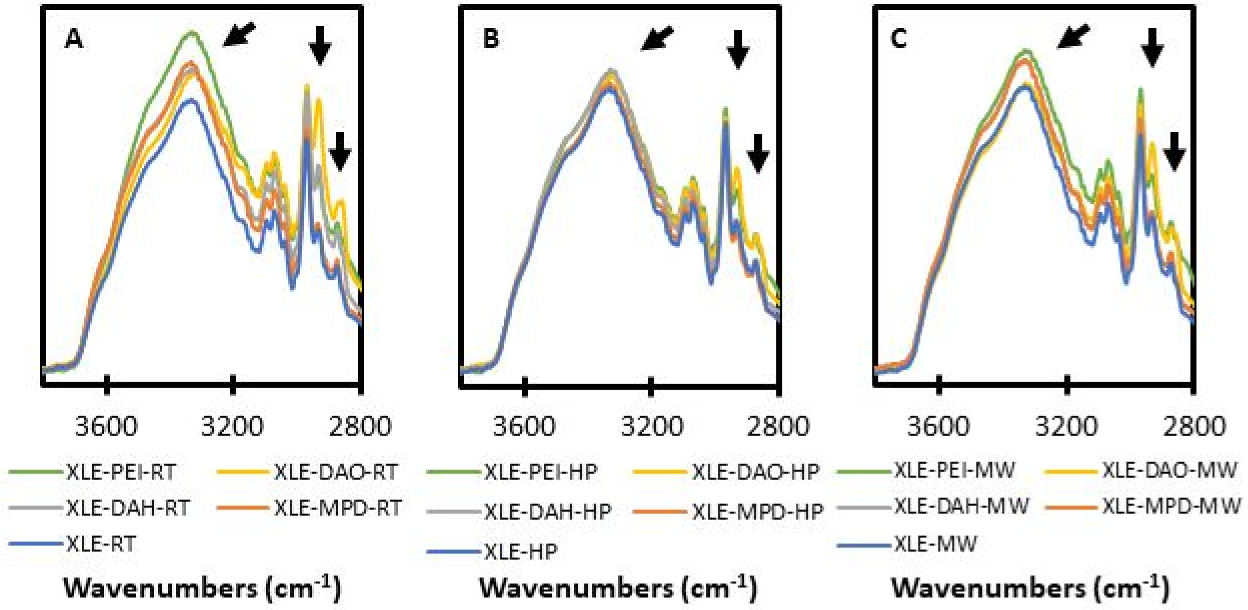

Figure 3. ATR-FTIR spectra of (A) XLE membranes modified with/without amines and no heat treatment (B) XLE membranes modified with/without amines and then heat treated with the hot plate, and (C) XLE membranes modified with/without amines and then heat treated with the microwave.

Characteristic peaks appeared for each membrane at ~1660 cm^{-1}, ~1610 cm^{-1}, and ~1540 cm^{-1} (see the arrows in **Figure S2** in the supporting information). These peaks correspond to the amide I, aromatic amide, and amide II bands present on the polyamide layer, respectively.[38] No shift or change in peak position was observed in amine-modified membranes compared to the control membrane. However, the amine-modified membranes showed very slightly more intense peaks at the amide I, aromatic amide, and amide II bond peaks.

Besides the increase in peak intensity at ~1660 cm^{-1}, ~1610 cm^{-1}, and ~1540 cm^{-1}, an increase in peak intensity at ~3330 cm^{-1} and in the aliphatic -CH$_2$- stretching region of 2800-3000 cm^{-1} also was observed (as indicated with arrows in **Figure 3**). Increasing peak intensities in the region of

2800-3000 cm^{-1} correspond to the conjugation between amines and free carboxylic acid groups. The N-H stretching at 3330 cm^{-1} indicates the presence of amine groups on the polyamide surface. Membranes which did not undergo heat treatment exhibited similar peak intensities at 3330 cm^{-1} and in the aliphatic -CH$_2$- stretching region of 2800-3000 cm^{-1} as membranes which were heat treated using the hot plate or the microwave. This indicates that the thermal treatment did not change the relative number of functional groups on the membrane.

Since PEI contains a greater number of N-H bonds than DAH, DAO, or MPD, PEI-modified XLE membranes exhibited the greatest N-H stretching. Additionally, it was expected that PEI-modified membranes would have the maximum intensity in the aliphatic -CH$_2$- stretching region of 2800-3000 cm^{-1}. However, the peaks in the aliphatic stretching region for PEI were similar to that of DAO modified membranes. This indicated that the extent of PEI attachment to the XLE membrane was not as expected, which was also reflected in the membrane performance. As compared to the control membrane, MPD-modified membranes exhibited very similar peak intensities in the aliphatic -CH$_2$- stretching region; however, their peak intensities were comparatively lower than those of DAH-, DAO-, or PEI-modified membranes.

3.2.2. *Static angle contact angle goniometry*

An analysis of static water contact angles was conducted to determine how the modification affected the hydrophobicity/hydrophilicity of XLE membranes. The water contact angle data for the modified XLE membranes which did not undergo heat treatment and modified XLE membranes which were heat treated using a hot plate or a microwave are shown in **Figure 4**. A statistical difference in the water contact angles was observed between the amine-modified membranes and the control XLE membrane. It was found that DAH-, DAO-, and MPD-modified membranes had a higher water contact angle than the control XLE membranes, indicating an increased hydrophobicity of the polyamide layer. Statistical analyses are shown in **Table S5** of the Supporting Data. The SEM images of the membranes (see **Figures S3, S4 and S5** in the supporting information) showed the typical RO membrane ridge-and-valley structures with no visible differences in surface morphology of the modified membranes compared to the control membrane. So, we assumed that the surface roughness was similar for all membranes. By attaching an amine, hydrophilic carboxylic acid moieties were decreased, and hydrophobic aliphatic chains or aromatic rings were increased when the membranes were modified with DAH, DAO, or MPD. There was a significant decrease in water contact angle for the PEI-modified membranes compared to control and other amine modified membranes. This reduction can be attributed to the abundance of -NH- and -NH_2 groups in PEI. The contact angles of membranes which underwent heat treatment via either a hot water bath or a microwave did not differ significantly from those membranes which did not undergo heat treatment.

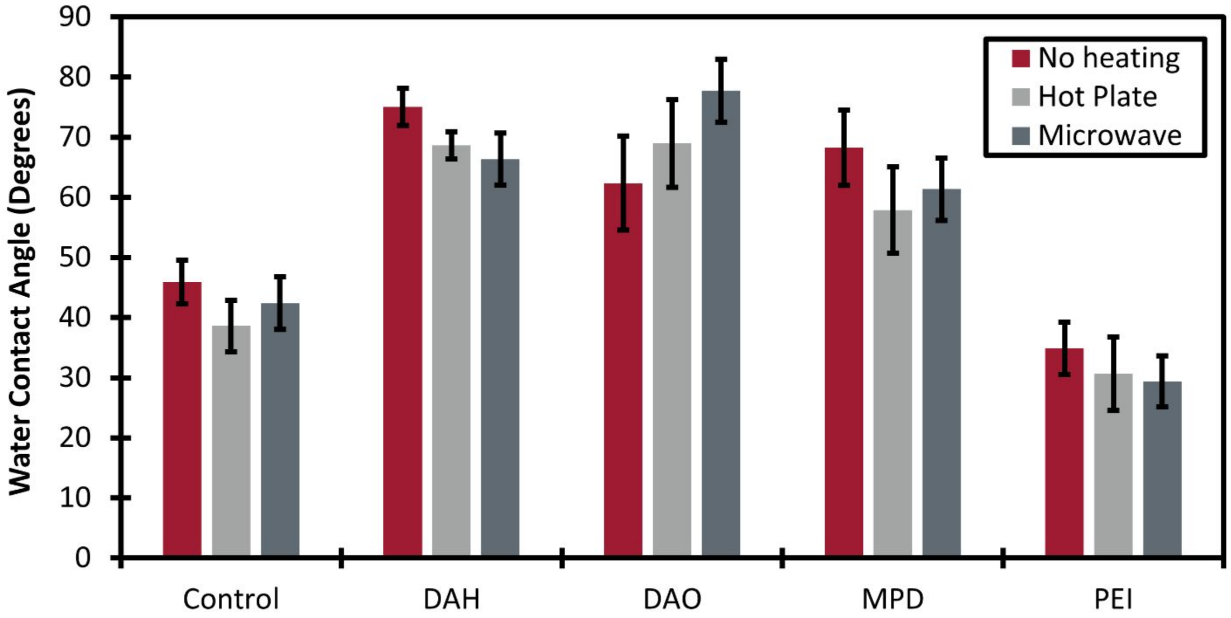

Figure 4. Static water contact angle for the control and modified XLE membranes. The error bars represent one standard deviation among three membrane samples.

3.2.3. *Streaming potential analysis*

The zeta potential of each membrane was measured sequentially at pH 6, 9, and 3 to examine the effect of amine modification on membrane surface charge. The results from the zeta potential analysis can be found in **Figure 5**. Both the control and modified XLE membranes exhibited positive surface charges at pH 3. It was found that at pH values of 3, 6, and 9, the amine modified XLE membranes displayed more positive surface charges than the control XLE membrane. At pH 9, the modified XLE membranes exhibited a reduced negative surface charge. This is likely a result of the protonated amine groups from the newly incorporated amine molecules having a greater positive charge density than the negatively charged deprotonated carboxylic acid groups.

We compared the zeta potentials of the amine-modified membranes which underwent no heat treatment, heat treatment in a hot water bath, and heat treatment in a microwave. The membranes which were modified with linear diamines or a branched polyamine showed more positive surface charges in all pH values compared to the control and MPD-modified membranes. We believe the pK_a value of the amines plays an important role in the difference between the zeta potential value of membranes modified with linear diamines or PEI and membranes modified with aromatic diamines. The pK_a values of the linear diamines and PEI were found to be higher than MPD (See **Table S6** in the supporting information). This explains why there are more positive surface charges at all pH values for membranes modified with DAH, DAO, or PEI as compared to the control membranes and membranes modified with MPD.

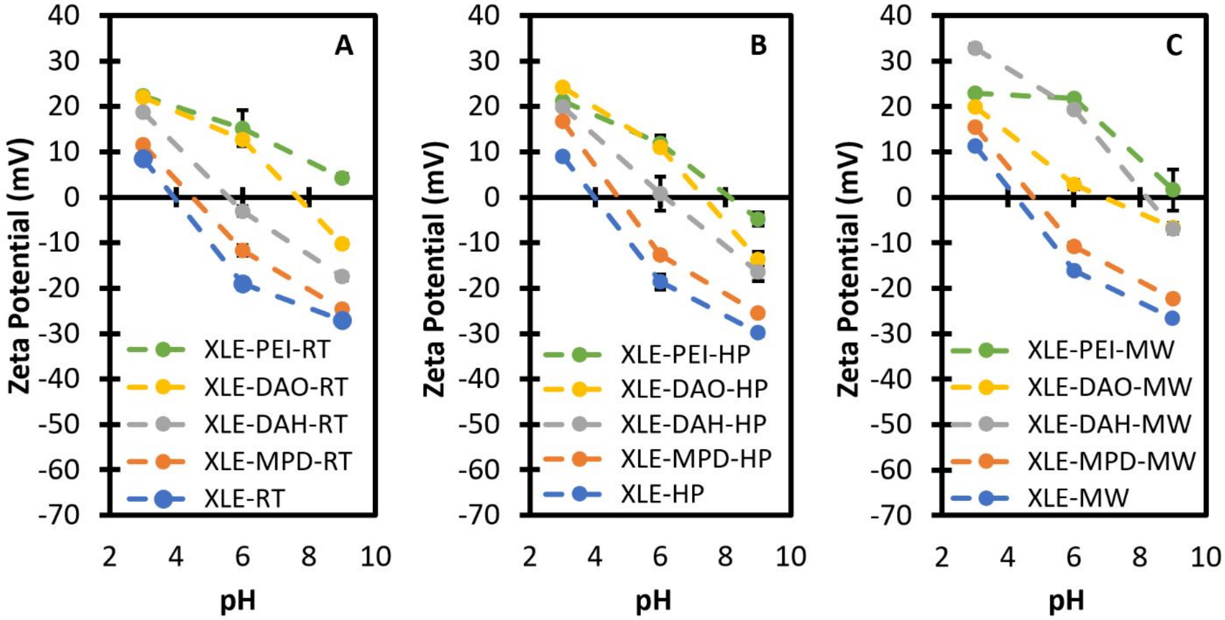

Figure 5. Zeta potential of (A) XLE membranes modified with/without amines and without heat treatment, (B) XLE membranes modified with/without amines and then heat treated with the hot plate, and (C) XLE membranes modified with/without amines and then heat treated with the microwave, at pH 3, pH 6 and pH 9. The error bars represent one standard deviation among three tests. The dashed lines between data points are included to aid in the visual comparison of the different modifications.

3.3. Mechanism

Figure 6 shows the proposed modification schematic for the XLE membranes using the carbodiimide chemistry. As mentioned in the introduction, polyamide membranes exhibit incomplete crosslinking due to the fast, chaotic nature of the IP reaction. This can lead to sizeable free volume holes in the polyamide layer as depicted on the left-most image of **Figure 6**. Werber et al. have demonstrated that the XLE membrane has more free carboxylic acid groups than most other RO membranes, indicating more uncross-linked areas in the membrane.[39] Additionally, the

EDC-NHS coupling approach should modify almost exclusively the surface -COOH groups due to EDC and NHS being larger molecules than what typically permeates through the membrane.

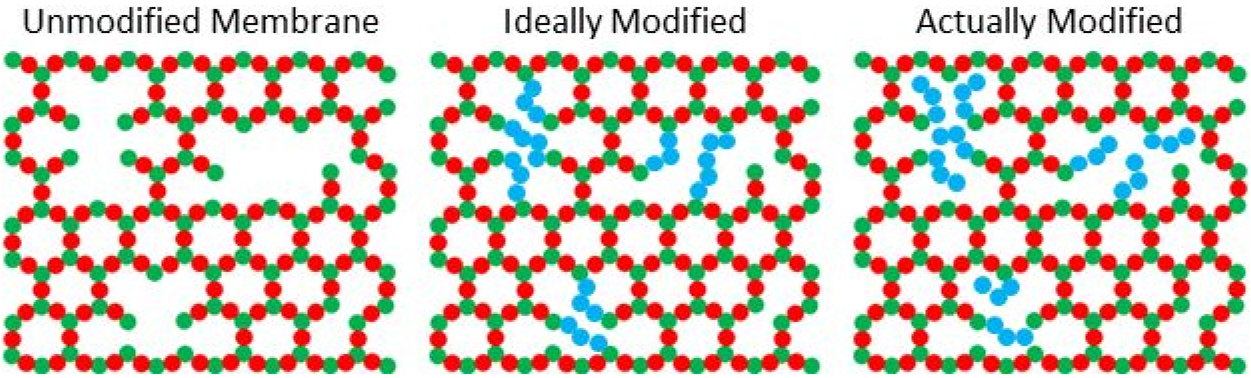

Figure 6. Proposed modification mechanism using carbodiimide chemistry on XLE membranes. The green circles are TMC, the red circles are MPD, and the blue chains are the diamines.

In an ideal world, the amine coupling would facilitate such that one amine couples to two free carboxylic acid groups on the membrane (see center image of **Figure 6**). However, to achieve this, one would need to use a tiny amount of amine. Using the data reported by Werber et al., the free carboxylic group density is 37 groups per nm^2 for the XLE membrane, resulting in approximately 6.42×10^{10} carboxylic acid groups present on a membrane area of 1735 mm^2 (the area of a 47 mm diameter circle used in the dead-end cell).[39] Note that this number is higher than what is likely accessible to the EDC-NHS coupling chemistry on the membrane surface, but we will move forward with it nonetheless. That means to have a 2:1 ratio between free carboxylic acid groups and diamines, 3.21×10^{10} diamine molecules are needed in the reaction solution (assuming a 100% reaction efficiency). In a 100 mL reaction solution using DAO, this means approximately 5.33×10^{-14} moles of DAO are needed or a wt% of 7.7×10^{-10}. Needless to say, these numbers are incredibly low and many orders of magnitude lower than the 2 wt% we used in this study. Therefore, the center mechanism is unlikely to occur at a significant level in our study.

Thus, the modification depicted in the right-most image of **Figure 6** is the most likely scenario that is occurring. There are more than enough amines to have one diamine coupled to each carboxylic acid group present on the membrane surface. These diamines are filling in some of the free volume space causing the demonstrated increase in small molecule rejection. We are attempting to determine the free volume hole size of these membranes using PALS, which will be shared in a future communication from our lab.

4. Conclusion

In this work, commercial RO membranes were chemically modified and heat treated to enhance the rejection of SNMs. Unexploited carboxylic acid groups on the surface of the polyamide layer were activated using carbodiimide chemistry. An amine was subsequently coupled to activated attachment sites on the surface of the membrane. Various types of diamines as well as a branched polyamine were evaluated. Amine attachment was followed by heat treatment using either a microwave or hot water bath. Compared to control XLE membranes with a 21% urea rejection, modified XLE membranes had a 32-61% urea rejection rate, depending on the amine type and the nature of heat treatment.

For the urea rejection test, the DAO-modified membranes without heat treatment and heat treated with either a microwave or hot water bath showed significantly higher urea rejection compared to the other membranes modified without and with heat treatment. Among all the heat-treated amine modified membranes, we saw the lowest average urea rejection of 47% for the PEI-modified membranes. The urea rejection of the membranes modified with the hot plate did not show any significant difference from the urea rejection of the membranes modified with the microwave. Therefore, the microwave is a time effective way to achieve the benefits of the 24 h heat treatment in 1.5 min. In the case of the boron rejection, the modified membranes showed significantly higher boron rejection (41-59%) compared to the control XLE membranes (23%). The water permeance of the modified membranes decreased (by 25-90%) significantly from that of the control XLE membrane, as is expected with a reduced free volume space. The salt rejecting performance of the control XLE membrane was maintained in the modified membranes. The XLE-DAH-HP and XLE-MPD-HP membranes showed the best average results with pure water permeances of 3.3 and 3.0 LMH/bar, NaCl rejections of 93% and 88% (similar to or great than the pristine XLE membrane), but with the fourth and third highest urea rejection of 53% and 57% (compared to 61% as the highest) and the highest boron rejections of 58% and 59%.

Even though we observed a reduction in the pure water permeance, even the lowest water permeance (provided by hot plate treated DAO-modified membrane) was comparable to some commercial RO membranes (0.54 – 0.83 LMH/bar) which are generally used for seawater desalination.[40] Besides treating the effluent from irrigation and fertilizer industries, we believe, our modified membranes have the potential for producing ultrapure water (UPW) used in the manufacturing industry, where the presence of SNMs creates problems with manufacturing desired products. For example, in 1992, at Intel Corporation in the US, defective products were manufactured and an investigation revealed that the defect was caused by inadequate removal of urea from the UPW process.[41] Currently, we are exploring alternative chemical modification strategies, including evaluating the effects of different surfactants during RO synthesis to increase SNM rejection and water permeance. We also are working to estimate the change in free volume hole size using PALS measurements.

Data availability

Data will be made available on request.

CRediT authorship contribution statement

Shahriar Habib: Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Validation, Visualization, Writing - original draft, Writing - review & editing.

Madison A. Wilkins: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Validation, Visualization, Writing - original draft, Writing - review & editing.

Steven T. Weinman: Conceptualization, Formal analysis, Funding acquisition, Methodology, Project administration, Supervision, Validation, Visualization, Writing - review & editing.

Declaration of Competing Interest

The authors declare no conflict of interest.

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