

High-performance porous polybenzimidazole membranes for water treatment using forward osmosis

Final Report

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1. A progress report containing Problem and Research Objectives, Methodology, and Principal Findings and Significance

Abstract

Polybenzimidazole (PBI) is a material with excellent chemical resistance, and thermal and mechanical stability. However, significant drawbacks of PBI that prevent its use as a membrane for water purification applications include hydrophobicity and neutral surface charge at neutral pH values. Surface functionalization was investigated as a means to circumvent these drawbacks by modifying PBI membranes to increase hydrophilicity and surface charge. The modifying agents used for functionalization included: p-phenylene diamine, ethylene diamine, taurine, and poly(acrylamide-co-acrylic acid). Functionalized asymmetric flat sheet PBI membranes were investigated in forward osmosis (FO) applications. The FO process involved semi-permeable flat sheet membranes with an ammonium bicarbonate draw solution and a sodium chloride feed solution. The functionalized membrane surfaces exhibit increased hydrophilicity, surface charge, and reduced pore sizes. Additionally, all membrane modifications show increased water flux and a reduction in sodium chloride transport.

1. Introduction

Forward osmosis (FO) is a technology that shows great potential as an alternative to current desalination techniques. The most attractive features of a FO membrane system include lower operational cost and less energy requirement. Unlike reverse osmosis (RO), that uses hydraulic pressure to create the driving force of water permeation, FO processes use an osmotic pressure gradient between the feed and draw solutions to create the driving force across a semi-permeable membrane. Water flows through the membrane, concentrating a saline feed solution, and diluting a draw solution of much higher osmotic pressure.

While emphasis has been placed on developing FO processes recently [1], two main drawbacks still exist. Most commercially available membranes were designed for RO processes and have proven to be less than ideal for FO systems. RO membranes are built on thick fabric support layers that suffer high levels of internal concentration polarization, significantly reducing membrane flux [2]. The second drawback involves finding an economically viable and easily separable draw solute. Many draw solutes have been examined as possible candidates for FO processes including: ammonium bicarbonate, calcium chloride, potassium bicarbonate, magnesium chloride, magnesium sulfate, and sodium bicarbonate [1, 3-4]. Ammonium bicarbonate was chosen as the draw solution

solute for this study due to its ease of separation to allow for feed solute rejection studies [5-6].

To address the issue of finding a suitable membrane material for FO processes, researchers in Singapore recently developed a PBI nanofiltration (NF) hollow fiber membrane [7-8]. PBI is a polymer that exhibits high mechanical strength, thermal stability, and chemical resistance [9-10]. Through use of the phase inversion technique, asymmetric PBI membranes were formed yielding high water fluxes but low monovalent salt rejection [7-8].

PBI nanofiltration membranes from these studies showed amphoteric behavior with desirable water flux and high rejection of divalent ions. Rejection of ionic species was found to be highly dependent on the solution pH. pH values determine the phases and sizes of the ionic species, in addition to the surface charge characteristics of the PBI membrane [7-8]. It was also shown through surface modification of the PBI membranes that the rejection of aqueous solutes is highly dependent on both the membrane pore size and electrostatic interaction between the solute and membrane. Analysis of virgin and modified PBI membranes in pressure driven systems with single electrolyte solutions at various pH values showed a decrease in solute permeability with modification at neutral pH values, with increasingly higher rejection as the pH increased and the membranes took on higher surface charges [11-13].

In an attempt to enhance the properties of the PBI membranes, the authors have recently demonstrated that asymmetric flat sheet PBI membranes could successfully be cast, and functionalized, using several different modifying agents [12-13]. The previous study used 4-(chloromethyl) benzoic acid (CMBA) for an activation step and p-phenylene diamine (PD), ethylene diamine (ED), and taurine to functionalize the membrane surface. All three modifications resulted in increases in hydrophilicity and membrane surface charge. Additionally, it was hypothesized that the modifications led to decreases in the mean pore size over that of the virgin sample. Previous research with PBI membranes chemically modified with p-xylylene has shown that modification could successfully decrease membrane pore size in the selective layer to a molecular level [11]. Modification with p-xylylene [11] involves a similar reaction to the activation step with CMBA [12-13] described previously by the authors, but has two reactive chloride groups that result in cross-linking of the PBI chains.

Recent studies have indicated that improvements in the wetting of a membrane surface can be critical in improving the membranes water permeability [14]. Lack of sufficient wetting exacerbates internal concentration polarization and disrupts continuity of water throughout the membrane structure. Decreased water continuity within the internal membrane pathways reduces the effective porosity, thus reducing water transport. This study [14] showed that by RO pretreating membranes used in FO application, or through addition of surfactants to the solutions used in the FO process, water permeability could be increased due to the enhanced wetting effect, and subsequent removal of air and vapor trapped in the porous selective layer of the membrane. Each of these techniques affected the various layers of the membrane differently depending on the structure and hydrophobicity of the layer. If the membrane surface is modified to be more hydrophilic, then the wetting effect of the membrane surface can be enhanced.

The focus of this study was to investigate the performance of the functionalized flat sheet PBI membranes in a forward osmosis application. The functionalization of membranes studied included the three modifying agents used previously, and an additional fourth modifying agent, poly(acrylamide-co-acrylic acid). Poly(acrylamide-co-acrylic acid) (PAcA) was selected for this study due to its ability to crosslink with the activated PBI membrane and because of its natural properties in aqueous environments. PAcA has both amino (-NH₂) and carboxyl (-COOH) functional groups that can either protonate or deprotonate based on the solution pH, and it is incredibly hydrophilic in nature [15-17]. A summary schematic of the two-step chemical modification procedure is shown in Figure 1. For simplicity, the modification of the PBI repeat unit is only shown at one of the secondary amines for one of the imidazole rings. This reaction could take place at both imidazole rings for the repeat units on the membranes surface.

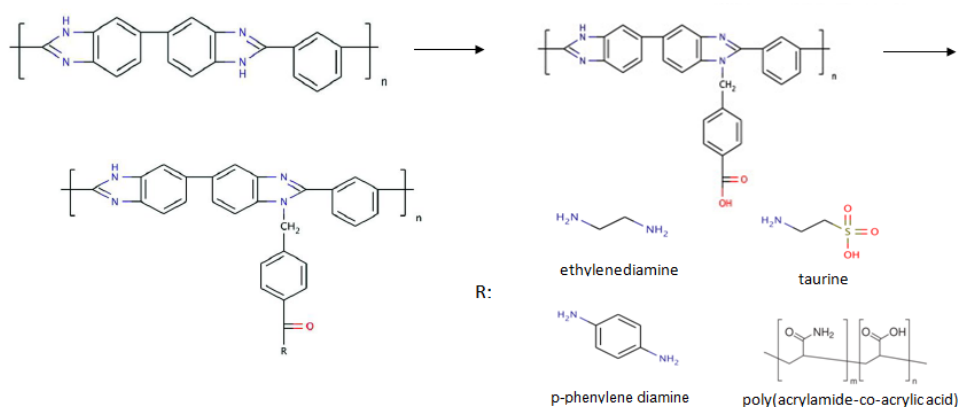


Figure 1. Chemistry for two-step modification procedure.

2. Materials and Methods

2.1. Chemicals

All chemistry required for PBI membrane casting, preparation, and surface modification used in this study has been described previously [12-13]. PBI dope was supplied by PBI Performance Products, Inc. (Charlotte, NC) as a 26 wt% solution. Ammonium bicarbonate, poly(acrylamide-co-acrylic acid), all poly(ethylene glycol) solutes, and sodium chloride were purchased from Sigma-Aldrich (USA). Glycerol, glucose, sucrose, and raffinose were purchased from Fisher Scientific (USA). DI water was supplied by a continuous distillation apparatus.

2.2. Feed and draw solutions

For all experiments the draw solution used was a 2M ammonium bicarbonate (NH₄HCO₃) solution made by dissolving reagent grade ammonium bicarbonate in DI water. The feed solutions for all experiments consisted of a 0.1M sodium chloride (NaCl) solution. The osmotic pressure gradient across the membrane was approximately 65 bar [1, 3].

2.3. Polybenzimidazole forward osmosis membranes

All PBI membranes were cast and modified in house. The casting and two-step modification procedure has been previously described [12-13]. In summary, the PBI flat sheet membranes were cast at 150 μ m with a doctor's blade and formed by way of the

phase inversion technique. The selective layer thickness was found to be approximately 8 μm . After formation, the surface was activated by way of reaction between the highly reactive chloride of the CMBA molecule and the secondary amine in the imidazole ring of the repeat unit in the PBI backbone. The second step involved subsequent modifications performed in a 2-(N-morpholino) ethanesulfonic acid (MES) buffer at pH 6 using N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDCH) and N-hydroxysuccinimide (NHS) chemistry. Figure 2 shows a cross-sectional view of the asymmetric virgin PBI flat sheet membrane taken by environmental scanning electron microscopy (ESEM). An FEI Quanta 3D FEG Dual Beam Electron Microscope (FEI, U.S.A.) was used to image the sample.

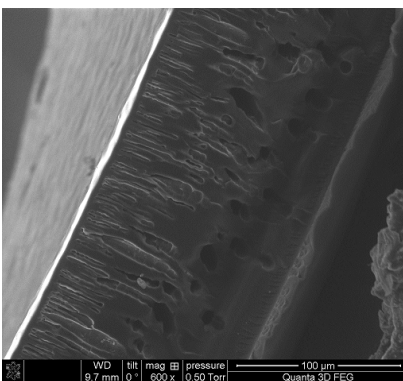


Figure 2. SEM image of the asymmetric PBI flat sheet membrane cross-section.

2.4. Membrane characterization

2.4.1. FTIR, contact angle, and zeta potential

The PBI membranes used in this study have previously been characterized by Fourier transform infrared spectroscopy in attenuated total reflectance mode (FTIR-ATR), contact angle, and zeta potential measurements [12-13]. FTIR analysis was obtained on a Varian Excalibur Series Fourier Transform Infrared instrument, the FTS-4000 Spectrometer and the UMA-600 Microscope (Randolph, MA). Contact angle was determined using a Tantec Model CAM-MICRO Contact Angle Meter (Tantac, Inc., U.S.A.). Surface charge was analyzed by measuring the zeta potential on the membrane surface. Samples were measured using an electrokinetic analyzer (BI-EKA, Brookhaven Instrument Corp., Holtsville, NY), located at Michigan State University. These techniques have shown the effects of PBI surface functionalization on membrane chemistry, hydrophilicity and surface charge [12-13].

2.4.2. Pore size determination

Total organic carbon (TOC) analysis was used to determine the pore sizes of the membranes developed. Concentrations of the solute solutions used for pore size determination were measured with a Tekmar-Dohrmann, Phoenix 8000 UV-persulfate TOC Analyzer (Tekmar Company, OH). The approach involved introducing feed solutions containing uncharged solutes (Table 1) of various Stokes-Einstein radii to the selective layer of the PBI membranes in an Amicon 8010 dead-end filtration cell (Millipore, USA). All experiments were performed as single solute permeation runs. The diluted permeate

and original feed solutions were sampled in the TOC to determine solute rejection. The apparent solute rejection R (%) was calculated by Equation 1:

$$R = (1 - C_p/C_f) \times 100\% \quad (1)$$

where C_p and C_f are the solute concentrations in the permeate and feed solutions, respectively. The uncharged solute samples are shown in Table 1 along with their Stokes-Einstein radii [7, 15]. Nonionic molecules have been used to determine membrane pore sizes by previous researchers [7, 11, 18-20] and a similar procedure was followed for this study.

Table 1. Molecular weights and Stokes-Einstein radii of neutral solutes for pore size determinations.

Solute	Mw (g mol ⁻¹)	Stokes radii (nm)
Glycerol	92	0.26
Glucose	180	0.37
Sucrose	342	0.47
Raffinose	504	0.58
PEG	600	0.61
PEG	1000	0.80
PEG	2000	1.41
PEG	4600	1.75
PEG	8000	2.31

200 ppm solutions were made of each individual solute in DI water. Each separation experiment involved permeation of a single solute in a pressure driven dead-end flow cell at 4.82 bar. Every membrane-solute combination was repeated three times so the average value could be calculated. The rejection values for all solutes were used to determine the mean effective pore size and the molecular weight cut-off (MWCO) for each membrane modification. The MWCO of a membrane is the molecular weight of the solute that is 90% retained by the membrane [18].

2.5. Forward osmosis operational set-up

The FO process used in this study is shown in Figure 3. The membrane filtration cell was a Sterlitech CF042 acrylic filtration cell (Sterlitech Corporation, Kent, WA) modified for forward osmosis to allow for water to flow through rectangular channels on both sides of the membrane. The channel dimensions of 8.25 cm length and 5.1 cm height provided a total membrane area of 42 cm². The 0.1M sodium chloride feed solution flowed across the selective (dense layer) side of the membrane and the 2M ammonium bicarbonate draw solution across the permeate side of the membrane. Polypropylene mesh feed spacers were used in the channels to provide membrane support and to enhance turbulence and mass transport. Variable speed peristaltic pumps (Fischer Scientific) were used to pump the liquids in co-current flow and at equal flow rates. Due to the endothermic disassociation of ammonium bicarbonate, the draw solution was allowed to equilibrate to room temperature before the FO experiments were begun. The solution was continuously mixed during the equilibration period. Both the feed and draw solutions were run at room temperature for all experiments.

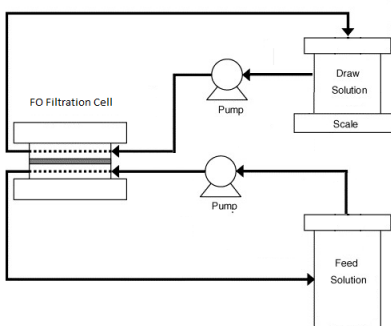


Figure 3. Schematic of co-current flow forward osmosis system.

This experimental set-up allowed for minimization of strain to the membrane as a result of unequal pressure across the length of the membrane; and to reduce the effect that additional parameters (temperature gradient, different fluid velocities, counter-current flow, etc.), other than concentration gradient, would have on the transport of feed solution across the membrane. The initial experimental approach involved testing a 2M ammonium bicarbonate solution against feed solutions of 0.1M sodium chloride solutions, at both pH 7 and pH 10. The pH adjustments were made with concentrated sodium hydroxide solution. The flow rates of both the feed and draw solution were approximately 65 mL/min. The osmotic pressure gradient between the bulk feed and draw solutions was approximately 65 bar [1, 3].

2.6. Transport properties

Mass transport across the membrane was determined by measuring the weight change of the draw solution in one hour intervals over a five hour period. The weight of the draw solution increases as water permeates across the membrane from the feed solution by way of osmosis. The volumetric increase divided by the membrane area and the selected time period gives the water flux.

Sodium chloride transport was determined by taking a sample of draw solution, after a complete FO run, and boiling the solution until the solvent had completely evaporated. The boiling process resulted in the decomposition of ammonium bicarbonate into ammonia and carbon dioxide gases [5-6] leaving only sodium chloride and sodium hydroxide crystals remaining. The weight of the remaining crystals was measured after boiling, and the crystals were then diluted with a known volume of DI water after which the pH and conductivity were measured. The concentrations of sodium chloride solutions were measured with a conductivity meter. All solution pH values were measured with a Corning 430 glass pH-electrode and a pH meter (Corning, NY). Pure water permeability from a pressure driven process at 4.82 bar was reported previously by the authors [12-13] and were used for comparison.

In order to determine the true rejection of the chloride ion by the selective layer of the PBI membranes tested, a chloride selective electrode would be needed. However, since this was not available, a second approach involving calculating the sodium hydroxide concentration from the pH measurements of the diluted salt solutions was used. The weight of the sodium hydroxide present was determined and subtracted from the total

weight of the dried salt permeate weighed before dilution. The weight of the sodium chloride sample could then be divided by the weight of the water permeate and presented as the weight fraction to be compared against the other membranes.

3. Results and Discussion

3.1. Membrane characterization

3.1.1. FTIR

The FTIR-ATR spectrum for PBI and the functionalized membranes (Figure 4 and Table 2) is described in detail in Hausman et al [13] for the modifications using ED, PD, and taurine. PAcA modification is confirmed by the C=O band around 1620cm^{-1} , the band around 1645cm^{-1} associated with the N-H and NH_2 bonds, and the alkane stretch around 2900cm^{-1} . The use of this technique verified the successful modification for the CMBA surface activation and for each of the final membrane modifications.

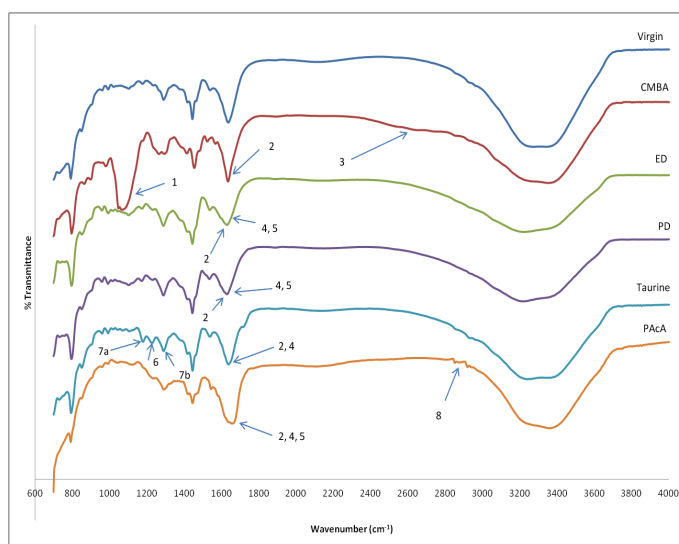


Figure 4. FTIR results for all membrane samples.

Table 2. FTIR functional group location.

Number	Functional group	Wave number (cm^{-1})
1	C-O	1057
2	C=O	1620-1640
3	OH	~ 2670
4	Secondary amine N-H	1645
5	Primary amine NH_2	1645
6	S=O	1215
7a	SO_2 (symmetrical)	1168
7b	SO_2 (anti-symmetrical)	1285
8	Alkane stretch C-H	2850-3000

3.1.2. Zeta potential

In previous studies [12-13] using the modification technique discussed here the final surface modifications for p-phenylene diamine, ethylene diamine, and taurine showed more charged surfaces than the virgin PBI membranes. The addition of poly(acrylamide-co-acrylic acid) for use in this study is expected to yield an even higher surface charge than the other modifications. PAcA has both amino (-NH₂) and carboxyl (-COOH) functional groups that can either protonate or deprotonate based on the solution pH. In this study the pH of the feed and draw solutions for all runs equilibrated to approximately 8.3. At this pH value it is expected the carboxyl groups on the PAcA membranes would be deprotonated to a significant degree (isoelectric point around 4.75) [15-16]. A membrane with a negative surface charge is expected to have a high rejection of anionic species in the feed solution.

3.1.3. Contact angle

Contact angle measurements for the virgin, CMBA activated, and all final modifications are shown in Figure 5. The hydrophilicity increased for all membrane modifications.

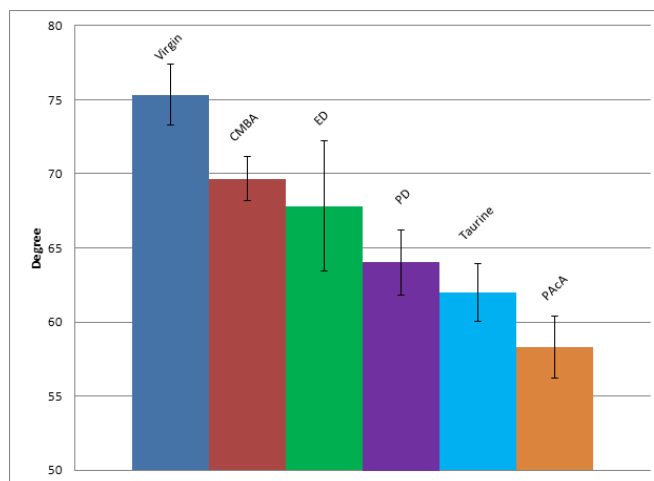


Figure 5. Contact angle measurements for all membrane samples.

3.1.4. Pore size determination

Table 3 shows the mean pore radius, the molecular weight cut-off, and the pore radius where the molecular weight cut off is reached. The effective mean pore sizes of all virgin and modified membranes fall in the nanofiltration range (0.5-2 nm in diameter) [7]. The effective mean pore radius of the unmodified membrane was 0.61 nm.

Table 3. Pore size data

	Virgin	CMBA	ED	PAcA	Taurine	PD
Mean radii (nm)	0.61	0.45	0.38	0.41	0.37	0.33
MWCO (Da)	7977	4161	1994	1399	1287	886
MWCO radii (nm)	2.31	1.66	1.14	0.95	0.91	0.75

From Table 3 it is observed that every membrane modification showed a reduced pore size over that of the virgin. Additionally, all the final modifications showed reduced

pore sizes over the CMBA activated. The ED membrane had a smaller mean pore size than the PAcA but a larger MWCO. This is believed to be attributed to the large size ($M_w = 5,000,000$) and cross-linking ability of the PAcA. If the large PAcA molecules are bonding to multiple sites across the membrane surface in random order, the effects of steric exclusion are expected to be more pronounced on larger solutes [18-20]. As expected the taurine and PD molecules resulted in smaller pore sizes than the ED. They also showed smaller pore sizes than the PAcA. The smaller pore sizes of the PD and taurine modifications over the PAcA are believed to be due to the smaller size of these modifying agents. The PD and taurine are small enough to permeate the pores of the activated membrane and react to a greater degree than the PAcA. The large size of the PAcA molecules restricts them from penetrating into the membranes pores. The effective mean pore size and MWCO for each membrane sample was calculated from a polynomial equation of the third degree. The typical rejection curves for uncharged solutes (Table 1) followed s-shaped rejection curves [18] that were analyzed with polynomial trendlines.

3.2. Forward osmosis flux results

While water flux through all the modified membranes was lower than that of the virgin membranes in pressure-driven mode (Figure 6), water flux through all modified membranes was greater than flux through the virgin membranes in FO mode (Figure 7). Figure 7 shows the results of the FO flux data measured for all the membranes where the starting pH of the feed was 7. Each membrane modification was run three separate times to determine average membrane flux values. Relating this to the pure water flux data obtained for the process driven by hydraulic pressure, (pressure-driven nanofiltration process, Figure 6), it was observed that the behavior of the membranes was reversed. In the pressure-driven process [12-13], the driving force for water permeation was the hydraulic pressure (4.82 bar) applied to the membrane. In the pressure driven process, the primary resistance to water flux stemmed from the membrane morphology: mean pore size, pore size distribution, tortuosity, membrane thickness, etc. The CMBA pure water flux was found to be approximately 30% lower than the virgin membrane flux and the modified samples were all found to be 50-60% lower than the CMBA, or 65-75% lower than the virgin.

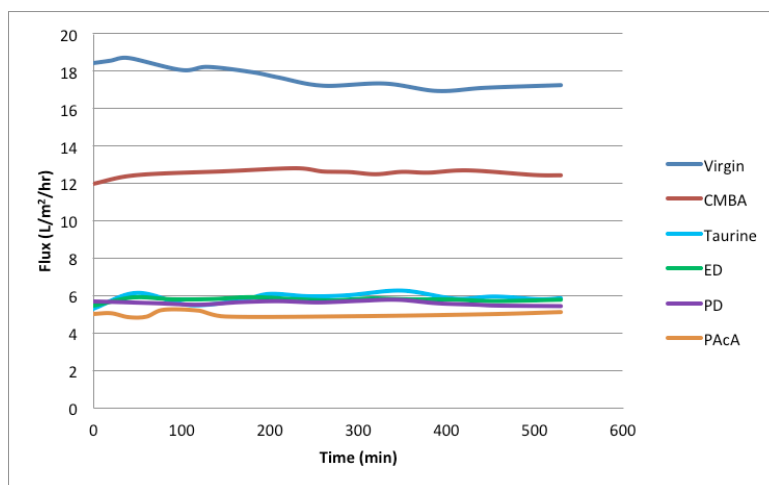


Figure 6. Flux data for all membranes in pressure driven system at a hydraulic pressure of 4.82 bar.

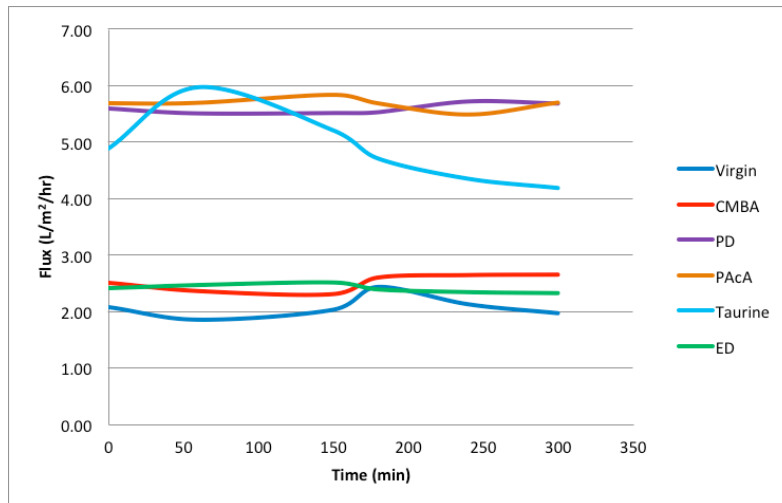


Figure 7. Flux data for all membranes in FO system

The results of the FO experiments were the reverse of those in the pressure driven experiments. The two membranes with the lowest flux in the dead-end cell were the PD and PAcA membranes. In the FO process these were the two membranes with the highest flux results. The virgin flux results were 63% and 64% lower than the PD and PAcA, respectively. The virgin was 17% lower than the CMBA and the CMBA was 55% and 56% lower than the PD and PAcA, respectively. The ED and CMBA flux values were very close to one another and not much higher than the virgin. The taurine modified membranes showed an early flux close to the PD and PAcA but began to drop lower as the run time progressed.

The performance of the membranes in FO, as opposed to the pressure driven experiments, was primarily believed to be attributed to the increased hydrophilicity of the modified membranes. In pressure driven experiments, water is forced through the membrane by hydraulic pressure, where-as in the FO system the water solution flows freely past the membrane surface. The increase in hydrophilicity of the modified membranes caused the system to favor water transport. Contact angle measurements for each of the membranes, shown in Figure 5, displayed an increased hydrophilicity after functionalization.

The contact angle for the ED membrane was the highest of the modified samples, and ED had the lowest water flux of the final modifications. Additionally, ED was the smallest of the modifying agents, but still caused a 38% decrease in the membrane pore size. The CMBA activation caused a 25% decrease. Since the hydrophilicity was slightly higher with a smaller pore size, this could explain the similar water flux between the ED and CMBA membranes. Additionally, the mean ED contact angle value was lower than the CMBA but the standard deviation was the largest and actually overlapped the lower end of the virgin standard deviation.

Despite the similar water fluxes, the weight fraction of sodium chloride in the permeate was significantly lower for the ED membranes. Previous work has shown zeta potential results for the ED modified membrane with a higher surface charge than the CMBA [12-13]. The higher surface charge and reduced pore size seems to explain the

lower weight fraction of sodium chloride in the permeate while the water flux remains roughly the same as the CMBA membrane.

It is interesting to note that water transport was far lower in the FO system than the pressure-driven cell. The osmotic pressure gradient between the two bulk solutions was roughly 65 bar [1, 3], whereas the hydraulic pressure in the pressure-driven cell was only 4.82 bar. This behavior was expected and has been reported previously. Low flux results in FO systems were the result of internal concentration polarization [1-4]. Concentration polarization reduces the osmotic pressure gradient across the membrane to the point where it is significantly lower than that of the bulk. This affects the performance of the trans-membrane water transport, resulting in much lower water flux across the membrane than would be expected from the bulk osmotic pressure gradient.

3.3. Salt transport

3.3.1. Salt permeability

Due to the buffering effect of ammonium bicarbonate and sodium bicarbonate, the pH of the draw and feed solutions for the FO experiments equilibrated to a slightly basic value (approximately 8.3) where all the membranes were expected to have some degree of surface charge [12-13]. From the previous zeta potential studies involving virgin, CMBA activated, taurine, ED and PD modified at pHs 7 and 10, the readings were approximately 1.7, 4.2, -0.4, -4.5, and -7.2 mV, respectively for pH 7 and 0.1, 4.2, -3.7, -7.3, and -11.5 mV, respectively for pH 10. The rejection of 0.1M sodium chloride solutions for all modified membranes in the FO system was significantly higher than the virgin.

In a typical membrane filtration system, the percent rejection is quantified by determining the concentration of salt in the feed solution, and the concentration of the salt that permeates the membrane. Since the relationship between concentration and conductivity of sodium chloride is linear, concentration can be determined by taking conductivity measurements of the feed initially and of the draw solution after the ammonium bicarbonate has been removed. Use of this technique would not be ideal for the process used for this discussion because the rejection values would be for a bench scale system where both the feed and draw solutions were recycled past the membrane many times over. For the 65 mL/min flow rate selected for both streams, the 1000 mL draw solution was recycled past the membrane roughly 19.5 times over a five-hour period. With 19.5 turnovers per experiment, the percent rejection values were deemed subjective. The most relevant technique for relating salt permeate data in this system is with the salt weight fractions measured for each membrane. This way, the performances of the membrane modifications can be related to one another and the virgin.

Figure 8 shows the transport ratios for the weight fraction of the sodium chloride and sodium hydroxide per water permeating the membranes, and the weight fraction of sodium chloride that permeated through the membranes. The thin bar in the back is the weight fraction of the total salt content remaining after the solvent boil off and the thicker bar in the front is the weight fraction for just the sodium chloride. From Figure 8, it is clear that every modified surface yielded higher rejection of sodium chloride over that of the virgin. The surface charges of the modified membranes were greater than the virgin at these slightly basic pH values. Additionally, the pore sizes of the modified membranes

were smaller and resulted in better rejection. Due to the hygroscopic nature of sodium hydroxide and sodium chloride, the weight readings of the dried salt samples were not entirely accurate. As the heated beaker and remaining salt sample were left to cool some water moisture was trapped and added to the final weight. While the inaccuracy of the salt measurements may negate this as quantitative data, the weight measurements do provide excellent qualitative data to compare the modified samples to one another and to the unmodified.

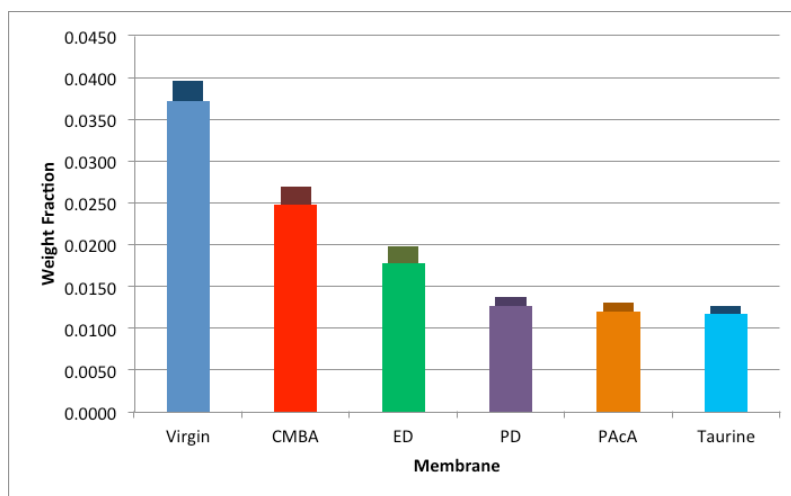


Figure 8. Total salt (back, thin bar) and sodium chloride (front, thick bar) weight fractions for each membrane.

3.3.2. pH effects

It was clear after only a few experimental runs that testing a feed solution at pH 10 was an impractical endeavor since the buffering strength of the much more concentrated ammonium bicarbonate draw solution equilibrated the pH of both feed and draw solution streams. This effect was observed because both the feed and draw solutions were recycled past the membrane surface, resulting in several turnovers of the process volumes. In addition, one experiment was attempted to bring the draw solution pH up to 10, using ACS grade ammonium hydroxide, but resulted in such a large dilution that the approach was discredited. To bring the pH of 1L of draw solution to 9.98 required 400mL of ACS grade ammonium hydroxide (28-30%), diluting the solution to only 1.43M ammonium bicarbonate, and lowering the osmotic pressure gradient to approximately 47 bar. In a true desalination process, the feed solution would not be recycled past the membrane, and the pH equilibration would not be as prevalent. Even after this experiment however, when the solutions were boiled down and rehydrated to determine sodium chloride rejection, the pH of the final salt solutions of both the feed and draw followed the same trend as seen with all the other samples.

It was observed for all membrane-pH samples that after the five hour run time, the pH of both feed and draw solutions were equilibrated. Previous studies have shown high rates of reverse salt diffusion for ammonium bicarbonate draw solutions [3-4]. For the samples where there was no pH adjustment for either the feed or draw solutions, and also for the samples where the feed was adjusted to pH 10, the final pH of the feed and draw solutions was always between 8.2-8.4 (this pH range is resultant of the presence of sodium

bicarbonate and sodium carbonate which buffer in this pH range). For the experiment with both feed and draw pH values initially around 10, both streams remained around 10.

At the end of a full FO run, a known volume of draw solution was boiled down until all the water evaporated. During this boiling process, all the dissolved ammonium salts decompose into ammonia and carbon dioxide. The remaining solid was then diluted with DI water to the original volume, so information about the salt rejection and membrane performance could be obtained. All the membrane experiments, including the experiment where the initial pH values were both at 10, followed the same behavior. After the boil off, and subsequent dilution, the pH of the draw solution was over 10, and the pH of the feed solutions was neutral.

These results indicate membrane selectivity of the sodium ions over the chloride ions in the feed stream. This membrane behavior was expected for the slightly basic environment where the membrane takes on a negative surface charge. In addition to surface charge, the anionic species are larger than the cationic. The larger size of the anions leads to an increased size exclusion effect from the dense membrane structure. Considering the pH equilibration for the readings taken immediately after the five-hour experimentation time, but the large pH discrepancy after the solutions were boiled down and diluted, it seems the membrane allowed passage of sodium and ammonium ions much more freely than their anion counterparts.

The selectivity of the membrane for sodium ions was balanced by the reverse diffusion of the small and positively charged ammonium ions, thus obeying the electroneutrality principle. The excess of sodium ions permeating the PBI membranes yielded the higher pH values in the diluted draw solutions. When the draw solution was boiled down the ammonium and bicarbonate ions degrade into ammonia, carbon dioxide, and water. The remaining solute crystals, after completion of boiling, were a mixture of sodium chloride and sodium hydroxide. In the feed solution however, the thermal decomposition of the ionic species leads to a breakdown of all the ammonium and bicarbonate ions. The excess ammonium and chloride ions decomposed into ammonia and hydrogen chloride. With the continued heating, the hydrogen chloride was also boiled off as vapor, and the remaining salt was simply sodium chloride. The pH of the diluted salt solution for the feed was thus neutral.

This pH phenomenon is a qualitative confirmation of the membranes selectivity for the cationic species, and higher rejection of the anionic species. The higher rejection was attributed to both steric exclusion and Donnan exclusion. The presence of sodium hydroxide in the diluted solution gave an elevated conductivity reading, and thus shows a lower sodium chloride rejection value when conductivity readings are taken. If conductivity readings were used solely to measure salt rejection then the percent rejection values would appear far lower than the actual values.

4. Conclusion

The overall lower mass transport across the virgin membrane in FO mode, despite the larger pore sizes, was believed to be due to the membranes higher hydrophobicity. All the modified membranes were more hydrophilic than the unmodified samples. The more hydrophilic surfaces should undergo an increased wetting effect, where the membrane-

fluid interactions favored water transport. In addition to the effect of the more hydrophilic surfaces, the charged membrane surfaces showed a higher degree of sodium chloride rejection when examined as weight fractions of the permeate transporting through the membranes.

The results of PBI surface functionalization with the intent to increase hydrophilicity, increase surface charge, and decrease the membrane pore size show enhanced membrane performance both with respect to water flux and salt rejection. The reduced pore size coupled with the use of a feed stream carrying divalent or larger ions mixed with colloidal particles may have the ability to yield excellent results and high purity water. In addition, if the cations chosen were much larger (e.g. transition metals or contaminants in industrial wastewaters) then the overall salt rejection would be expected to increase.

To further verify the effectiveness of the membrane modifications, additional experimentation should include testing of both unmodified and modified membranes in both FO and RO set-ups. In future experiments, both unmodified and modified PBI membranes should be tested in true RO conditions, at multiple hydraulic pressures, and in FO over several osmotic pressure gradients. The authors recommend that a chloride ion selective electrode (ISE) be used for determining salt rejection. Additionally, zeta-potential values should be determined for the PACA modification.

5. *References*

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2. Publication citations (all journal articles, proceedings and presentations at conferences)

Peer-Reviewed Journal Article:

Flanagan M., and I.C. Escobar (2013). Novel Charged and Hydrophilized Polybenzimidazole (PBI) Membranes for Forward Osmosis, *Journal of Membrane Science*, **434**: 85-92.

Peer-Reviewed Book Chapter:

Flanagan, M., Hausman, R., Digman B., I.C. Escobar, M.R. Coleman, and T-S Chung (2011). Surface Functionalization of Polybenzimidazole Membranes to Increase Hydrophilicity and Charge. In: Escobar I.C. and B. Van der Bruggen (eds.), *Modern Applications in Membrane Science and Technology*. ACS Symposium Series; American Chemical Society: Washington, DC, pages 303-322.

Conference Presentations:

Flanagan M. and I.C. Escobar (2012). "Charged and Hydrophilized Polybenzimidazole (PBI) Membranes for Forward Osmosis," 2012 AIChE Annual Meeting, Pittsburgh, PA, October 28-November 2, 2012.

Flanagan M., and I.C. Escobar (2012) "Novel Charged and Hydrophilized Polybenzimidazole (PBI) Nanofiltration Membranes," 2012 Euromembrane Conference, London, England, September 23-27, 2012.

Flanagan M., R. Hausman, and I.C. Escobar (2011). "Polybenzimidazole Forward Osmosis Membranes Functionalized to Impart Surface Charge and An Increase In Hydrophilicity," 2011 AIChE Annual Meeting, Minneapolis, MN, October 16-21, 2011.

Flanagan M., R. Hausman, I.C. Escobar, M. Coleman, and T-S Chung (2011). "Polybenzimidazole Forward Osmosis Membranes Functionalized for Increased Surface Charge and Hydrophilicity," 2011 NAMS Annual Meeting, Las Vegas, NV, June 4-8, 2011.

3. Number of students supported by the project (MS/PhD/undergraduate/post docs) as well as their majors

One MS student – Michael Flanagan (Technical Manager at Whitaker Finishing LLC)

One undergraduate student – Jordan Morales (now, junior in Chemical Engineering, at The University of Toledo)

4. Awards or Achievements (patents, copyrights)

Faculty (Isabel Escobar) Award: 2011 American Institute of Chemical Engineers (AIChE) Separations Division FRI/John G. Kunesh Award: recognizes outstanding contributions to the academic, scientific, technological, industrial, or service areas involving separations technologies for individuals under the age of 40. Criteria considered in selecting an awardee include: Significant discoveries, important research, development of new processes and products, introduction of new education concepts, service to the Separations Division, or outstanding service to the separations community.

Student (Michael Flanagan) Award: Winner of 2012 University of Toledo, College of Engineering Outstanding MS Thesis Award.