

NWRI GRADUATE FELLOW SEMI-ANNUAL PROGRESS REPORT

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Project Title: Charge Mosaic Membranes from Ink-Jet Printing for Improved Water Reuse and Treatment

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Introduction

Desalination by reverse osmosis is an effective method of producing potable water, but the process is energy intensive due to fundamental thermodynamic restrictions.¹ Therefore, in addition to desalination, water reuse will be an important component of the water supply portfolio. Water reuse attempts to use non-traditional sources for a beneficial purpose, (e.g., reclaimed wastewater for irrigation). This process will be another source for potable water and requires a fraction of the energy required by desalination. The presence of dilute ionic contaminants such as nitrate, perchlorate, and heavy metals are a notable concern that hinder the advancement of water reuse due to their well-documented effects on human health.¹ This proposal seeks to develop an innovative technology to remove dilute ionic species from aqueous feed streams for improved water reuse. Specifically, charge mosaic membranes (CMMs) that allow charged solutes to permeate more rapidly than water, will be designed and fabricated. Current technologies such as reverse osmosis remove contaminants from wastewater when water is forced through a size-selective membrane that rejects contaminants too large to flow through the membrane pores. Alternatively, the use of CMMs will make it possible to remove only that small percent of contaminant rather than forcing 99.9% of solution through a size-selective membrane.

Due to past difficulty in producing charge mosaics with well-defined and controlled nanostructures, their development has lagged severely. To overcome these difficulties, our research group recently developed a promising avenue to CMM design by ink-jet printing polymeric materials onto a structural template.² This printing process is versatile, fast, and consistent, and does not require harsh chemical treatments. Figure 1 illustrates the fabrication process of these mosaic membranes. Polyelectrolytes are printed on a

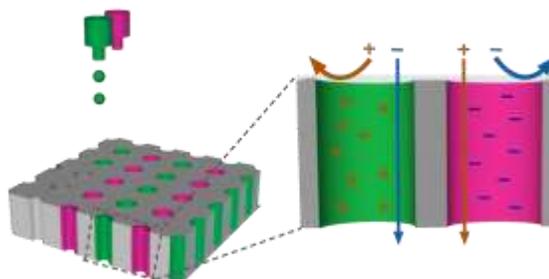


Figure 1 Schematic of the fabrication process for printing the mosaic structure.

polycarbonate track etched membrane into discrete regions. Using the striped pattern, positively charged and negatively charged polyelectrolytes are alternatively printed to form the mosaic. Selecting certain polyelectrolytes and printing conditions offers a wide array of functionalities and nanostructures for this system.³ This ability will enable a fundamental understanding of how the performance of these membranes relates to their basic physio-chemical features—something that is lacking in prior studies and prevents the systematic design of more effective charge mosaics.

Research Plan

Using the control over the nanostructure and chemical functionality of mosaic membranes provided by these new fabrications methods, I will generate rigorous structure-property-performance relationships for these membranes to enable a novel design for CMMs for removal of dilute hazardous contaminants from reclaimed wastewater. By studying the effect of different modifications to the structure on the physical and chemical properties of the membrane, we will elucidate a fundamental understanding of the transport phenomena that determines the performance of these membranes.

CMMs facilitate the transport of dissolved salts because the charged ions are drawn electrostatically to the oppositely charged nanopores. This produces an enrichment of salt, which is a greater concentration of salt in the permeate. This results from salt being preferentially transported over water. Membranes of a single charge reject salt because the coions (i.e. ions of the same charge as the membrane) are electrostatically repelled, and the counterions (i.e. ions of opposite charge) are bound to the coions because of electroneutrality. The constraint of electroneutrality dictates that the overall charge of a solution must be neutral, meaning that there must be an equal concentration of anions and cations. This condition is maintained in a CMM, which allows both ions to flow through oppositely charged regions of the membrane.⁴

Three conditions are necessary for the mosaic to achieve enrichment:

- 1) Charged domains must traverse the entire membrane thickness and be closely packed;
- 2) Charged densities of charged regions should be equal in magnitude and opposite in charge;
- 3) Overall surface charge should be neutral.

Harsh chemical treatments and difficulty in orienting domains perpendicular to the surface have caused development of CMMs to lag severely.

Our lab group has already published two articles on printing membranes using an inkjet printer.^{2,5} In the second paper, we described how we produced the CMM structure using poly(vinyl alcohol) (PVA) blended with either a polycation or polyanion to produce positively-charged or negatively-charged regions, respectively. Our membranes demonstrate the characteristic salt enrichment of CMMs with significantly easier processing conditions and shorter processing times than typical CMMs. We now hypothesize that these membranes can be used for separations of other solutes of interest.

Acetic acid is a common aqueous byproduct in the synthesis of aspirin. To reuse the acetic acid, it must be separated from water, but due to the near equal volatilities of water and acetic acid, this separation

is very energy intensive. Typically, this separation is done by distillation, which involves a lot of energy due to water's unusually high latent heat. We propose a membrane separation to extract acetic acid. The energy involved for membrane separations scales with performance; applying large pressures generates larger throughput.

The CMMs we designed have proven capable of separating inorganic salts by exploiting electrostatic interactions. Acetic acid can disassociate and form charged acetate and hydrogen ions. We hypothesize that the CMMs will facilitate diffusion of these ions. Using a weak organic acid, this allows us to explore the effects of other intermolecular interactions on the transport phenomena of these membranes.

Progress to Date

Rejection measurements were carried out in an Amicon® stirred cell using 1 and 10 mM acetic acid solutions at 12 and 60 psi. Percent rejection (%R) and enrichment (%E) were calculated by the following equation:

$$\%R = -\%E = 1 - \frac{C_p}{C_f}$$

where C_p and C_f are the concentrations in the permeate and feed, respectively, measured by Total Organic Carbon (TOC) instrument analysis.

The current design of the CMMs used poly(diallyldimethylammonium chloride) (PDADMAC) as the polycation and poly(styrene sulfonate) (PSS) as the polyanion. We examined the performance of separating 1 and 10 mM aqueous acetic acid solutions at applied pressures of 12 and 60 psi. The lower concentrations and pressures produced high enrichment ~60%, where little to no enrichment was achieved at all for 10 mM concentration. Increasing the pressure to 60 psi lowered the enrichment of 1 mM solutions. The flow of ions is diffusion driven, having a greater dependence upon electrostatic interactions, while the flow of water is convection driven. Higher pressures permeate higher concentrations of water, lowering the enrichment of acetic acid.

The membranes have a limited surface charge, and thus can transport only a limited number of ions. While higher concentrations do not limit the flow of ions, the relative rates of transport appear lower for higher concentrations than lower concentrations.

To explore the effect of hydrophobic interactions on the flow of acetic acid, we printed membranes using poly(allylamine hydrochloride) (PAH) as the polycation instead of PDADMAC. PAH is a more hydrophobic (water-loving) polycation. We expected that membranes printed with PAH to yield lower enrichments than ones printed with PDADMAC due to the greater affinity of PAH than PDADMAC for water over acetic acid. Our results confirmed this, as the enrichments for all experiments was lower in membranes using PAH as the polycation. The same trends as noted above with concentration and applied pressure were consistent.

Since acetic acid is a weak acid, the degree of ionization varies with pH. The previous experiments were all performed using a pH 7.0 solution to ensure that 99% of the acetic acid was in the deprotonated form. We used the same membranes and measured enrichment of 1 mM acetic acid solutions that had been adjusted so that 0, 50, and 99% of the acetic acid was deprotonated. As expected, greater protonation showed lower enrichment due to limited electrostatic interactions.

Conclusions

We have shown that it is possible to separate acetic acid from water using a CMM. Higher concentrations and pressure result in lower enrichment due to the limited membrane surface charge and higher throughput of water, respectively. Additional intermolecular interactions were investigated and confirmed to play a role in this separation by using a different polycation in the printing of the CMMs. Finally, the importance of electrostatic interactions was confirmed by investigating the effect of varying the degree of protonation of acetic acid in solution.

Next Steps

We will continue to explore the effects of different polycations, concentrations of acetic acid, and transmembrane applied pressures on the enrichment of acetic acid. We look to increase enrichment by varying different design parameters involved in printing. These parameters include polyelectrolyte concentration, number of overcoats (*i.e.* the number of times the print head passes over a single point), and template pore diameter.

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