ND*nano* Summer Undergraduate Research
2016 Project Summary

1. Student name: Ryan J. LaRue

2. Faculty mentor name: Dr. William A. Phillip

3. Project title:
"Tailoring the chemistry of copolymer-based membrane adsorbers for heavy metals removal via high-throughput evaluation techniques"

4. Briefly describe any new skills you acquired during your summer research:
New skills that I acquired during my research include the fabrication of SNIPS membranes, post-production functionalization of these membranes, and methods to analyze and quantify the ability of membrane adsorbers to capture heavy metals.

5. Briefly share a practical application/end use of your research:
Like we have seen recently with the events in Flint, Michigan, and with other places around the world, providing people with safe, clean drinking water can often be a challenge. The copolymer membrane adsorbers which I am developing could be used as effective water treatment devices to remove heavy metals from water supplies, or to purify industrial wastewaters in order to preserve water quality.

Begin two-paragraph project summary here (~ one type-written page) to describe problem and project goal and your activities / results:

The ability to provide people with safe, clean drinking water is one of the defining challenges of this era. Due to factors such as growing populations, pollution and climate change, we are applying greater stresses on already scarce freshwater resources. Particularly, the contamination of water bodies with heavy metals is a significant nuisance in many parts of the world. Known for their often-toxic or carcinogenic effects, heavy metals can be present in water due to soil chemistry or industrial pollution. Here, we describe the development of a family of nanoporous membranes incorporating self-assembled copolymer precursors which show promise as novel separation and purification devices. Of particular interest, poly(acrylonitrile-*r*-oligo(ethylene glycol) methyl ether methacrylate-*r*-glycidyl methacrylate) (poly(AN-OEGMA-GMA) membranes fabricated via the self-assembly and nonsolvent-induced phase separation (SNIPS) procedure possess highly-tunable, well-defined nanostructures. Further post-fabrication functionalization can precisely tailor the material surface chemistries to adsorb heavy metals from aqueous solutions. However, the traditional approach to improving the performance of these membrane adsorbers has relied on evaluating membrane structures and surface chemistries in a slow, sequential fashion using a stirred-cell apparatus. This approach significantly limits the pace at which new membranes can be developed.

Using membranes produced via the SNIPS procedure, we have developed a process by which amino acids can be grafted onto the surface of the material. Certain amino acids are known to have significant affinities for aqueous metal ions, enabling capture by the functionalized membranes. We have shown that via a $ZnCl_2$ catalyst in butanone, glycine (Gly), glutamic acid (Glu), cysteine (Cys) and histidine (His) can be coupled to the poly(AN-OEGMA-GMA) membranes, as indicated through FTIR analysis. Furthermore, the Cys-functionalized membrane (seen in Figure 1) has shown to effectively uptake Pb^{2+} ions. Using the Langmuir absorption model, it was calculated that a Cys-membrane has a maximum Pb adsorption of 1.41 ± 0.01 mmol/g of membrane—on par with other membrane-based adsorber systems. Our investigations aim at evaluating the amino acid membranes for the capture of other heavy metals—a process that requires efficient testing procedures to screen wide varieties of ions and membrane chemistries. To this end, we designed a microscale, high-throughput test apparatus that allows for six experiments to be conducted simultaneously. Individual experiments employ a flat-sheet membrane (active area ~ 1.5 cm^2), with mixing above the surface achieved by a tumble stirrer. A schematic of the high-throughput stirred cell (HTSC) setup can be found in Figure 2. In order to validate the HTSC against the standard stirred cell, both devices were used to evaluate the hydraulic permeability of a standard Millipore 30 kDa MWCO polyethersulfone membrane. It was found that the stirred cell and HTSC produce statistically-equivalent permeability values: 208 L m^{-2} h^{-1} bar^{-1} (LMH/bar) for the HTSC with a 95% confidence interval of (172, 264) LMH/bar, and 225 LMH/bar for the stirred cell with a 95% confidence interval of (192, 259) LMH/bar. Future work aims to validate the HTSC against the stirred cell by collecting sieving data of high molecular weight polysaccharides.

Figure 1: A Cys-membrane (left) immersed in a Au^+ solution turns yellow (center), visually indicating the presence of cysteine. A dime (right) is shown for scale.

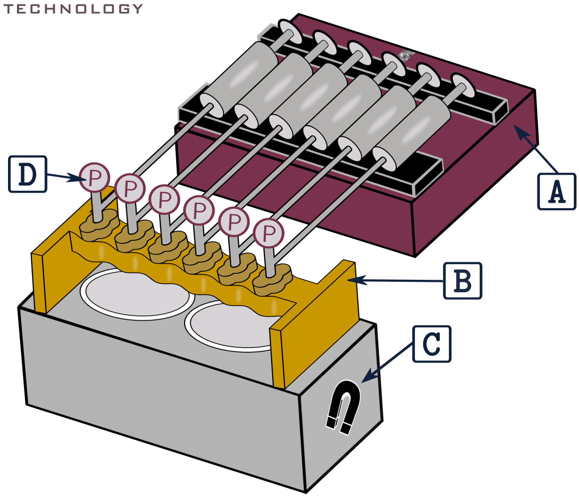

Figure 2: The HTSC setup consists of a syringe pump [A] to provide a constant flux, the 3D-printed membrane test unit [B], a magnetic tumble stirrer [C] for constant mixing over the membrane surface, and pressure transducers [D] to monitor pressure in each of the wells.

Publications (papers/posters/presentations):

Poster:

Novel High-Throughput Techniques for Membrane Evaluation. R.J. LaRue, D.R. Latulippe & W.A. Phillip, Research Experience for Undergraduates Summer Poster Session, University of Notre Dame, Indiana, July 26, 2016.

Presentations:

Tailoring the chemistry of copolymer-based membrane adsorbers for heavy metals removal via high-throughput evaluation techniques. R.J. LaRue, T.J. Dilenschneider, S. Qu, W.A. Phillip, & D.R. Latulippe, Canadian Chemical Engineering Conference, Quebec City, Quebec, October 2016.

Papers (forthcoming):

A manuscript (in preparation) to *Biotechnology & Bioengineering* establishing that our high-throughput device provides identical membrane performance data as a stirred cell, yet is more efficient. A second manuscript highlighting our novel copolymer membrane adsorbers for heavy metal capture.