NDnano
Notre Dame Nanoscience and Technology

NDnano Undergraduate Research Fellowship (NURF)
2022 Project Summary

1. *Student name & home university:* Aaron Peaslee, Michigan Technological University

2. *ND faculty name & department:* Professor Kyle Doudrick Civil and Environmental Engineering and Earth Sciences

3. *Summer project title:* Nanocatalytic Membranes for Water Treatment

4. *Briefly describe new skills you acquired during your summer research:*
During the summer, I acquired many invaluable skills related to working successfully as a team member in a research laboratory. These skills included very simple things such as quantitatively pipetting, but also how to synthesize novel polymer membranes and subsequently how to attach palladium nanoparticles to the synthesized membranes to create nanocatalytic membranes. I learned how to use a UV-visible spectrophotometer to quantify the amount of palladium adsorption to the membrane and to measure the results of NO_2^- flowthrough tests performed on these nanocatalytic membranes.

5. *Briefly share a practical application/end use of your research:*
Nanocatalytic membranes can be used to eliminate drinking water contaminants such as nitrites (NO_2^-) and nitrates (NO_3^-). If they are shown to be effective, the membranes can be fabricated as hollow tubes, which would allow them to be retrofitted into existing water treatment and distribution infrastructure, as well as being made into household filters.

6. *50- to 75-word abstract of your project:*
Nanocatalytic membranes have been fabricated that utilize palladium nanoparticles as a catalyst for H_2 and oxidized contaminants in water (*e.g.,* NO_2^-). Previously, the cost of palladium has made the process of creating these types of membranes prohibitively expensive, but by adsorbing the palladium onto the membrane as nanoparticles costs are cut down significantly, making nanocatalytic membranes a competitive option for water treatment to remove contaminants.

7. References for papers, posters, or presentations of your research:
Randal Marks, Joseph Seaman, Patricia Perez-Calleja, Junyeol Kim, Robert Nerenberg, and Kyle Doudrick, "Catalytic Hydrogel Membrane Reactor for Treatment of Aqueous Contaminants" *Environ. Sci. Technol.* 2019, 53, 11, 6492–6500. doi: 10.1021/acs.est.9b01667
"Fact Sheet Date: March 12, 1998 New York State - Epa.gov." EPA, 1998, https://www.epa.gov/sites/default/files/2015-06/documents/ny_hh_364_w_03121998.pdf.
"Fact Sheet Date: March 12, 1998 New York State - US EPA." EPA, 1998, https://www.epa.gov/sites/default/files/2015-06/documents/ny_hh_644_w_03121998.pdf.

One-page project summary that describes problem, project goal and your activities / results:

Modern farming techniques utilize large quantities of fertilizer to achieve high crop yields. These fertilizers typically end up in runoff from rainfall, and eventually end up in ground water and surface water, contaminating important sources of drinking water. Two of the main contaminants from fertilizer are nitrite (NO_2^-) and nitrate (NO_3^-), which the EPA limits to 1 mg/L and 10 mg/L respectively.

The end goal of my research was to develop filtering membranes with palladium (Pd) nanoparticles attached to the surface that are capable of removing nitrite from the water. Pd is used for these filters as it is an extremely effective catalyst for reducing contaminants such as nitrate and nitrite with H_2 gas. Until recent developments, Pd has always been too expensive to be practical in this application, but by attaching very small amounts of Pd to the membranes as nanoparticles, the use of Pd is likely to be much more practical and economically viable in large scale applications.

There are many different materials that can be used as membranes to which Pd can be attached such as nylon, but I started by attempting to synthesize my own P4VP and P4VP quaternized with methyl iodide (P4VP+) membranes. This was done by adding small amounts of polysulfone to a solvent, heating the solution at 80°C for 24-48 hours, then adding P4VP or P4VP+ to the solution before heating at 80°C for another 24-48 hours. I then would synthesize the membranes by pipetting the solution onto a glass slide in a humidity chamber, spreading the solution to an even thickness with a doctor blade. The solution reacts with water in the air to harden into a solid, but once the solution thickens enough, I would submerge the slide in a water bath to finish the hardening process. The final steps of the membrane synthesis process are to cut out circular sections of the membrane, and then soak them in ethanol for 6 hours, before returning the membranes to water for storage.

After synthesizing the membranes, the Pd could be attached by soaking the membranes in solutions of $PdCl_4^{2-}$ or $PdNO_3$ (Pd^{2+}) for 24 hours and then reducing the Pd attached to the membranes using $NaBH_4$. The amount of palladium attached to the membranes can be quantified by measuring the initial and final concentration of Pd in the solutions that the membranes were soaked in.

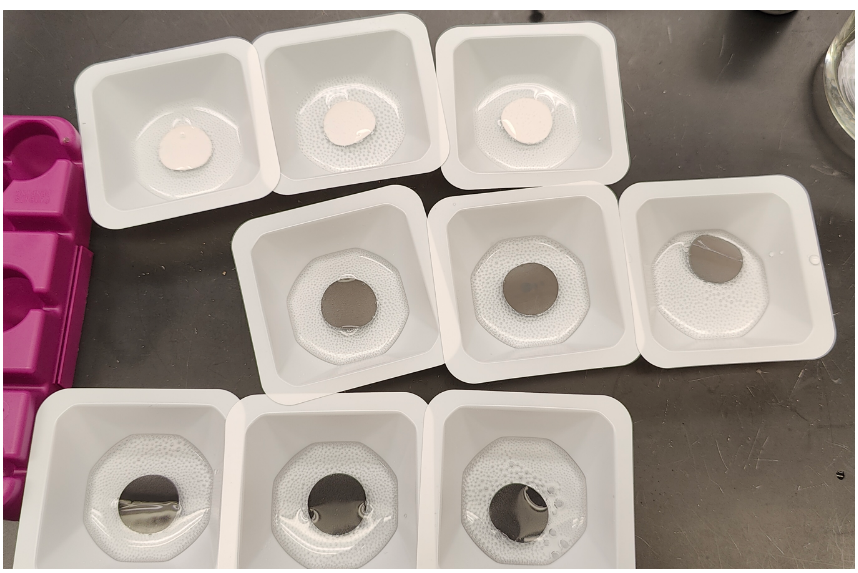

Figure 1. Nylon membranes after being soaked in various concentrations of Pd^{2+} and reduced

While P4VP and P4VP+ membranes should yield better results than Nylon membranes, they are much more fragile, and much less consistent due to human error in the fabrication process. Because of this, I eventually switched to using Nylon membranes for better consistency in my results.

The final step of my research was testing the membranes to find how much nitrite they would remove from water. There are two different methods for testing the membranes. One method is flowthrough testing, where a solution of nitrite and $NaBH_4$ is loaded into a syringe and passed through the membrane at multiple different flowrates. The other method is batch testing, where the membrane is submerged into the same solution of nitrite and $NaBH_4$, and then left for 6 hours. In flowthrough testing an initial and final measurement of the nitrite concentration is taken to quantify its removal, while in batch testing an initial measurement is taken, as well as one measurement every hour for 6 hours after the membrane is submerged in the nitrite solution.

As of the end of my research fellowship, we don't have all the data for the updated testing methods performed on Nylon membranes, but I am hopeful that if they are successful, the results can be used to iterate and evolve the process to make P4VP and P4VP+ membranes consistently and hopefully even more effective than Nylon membranes.

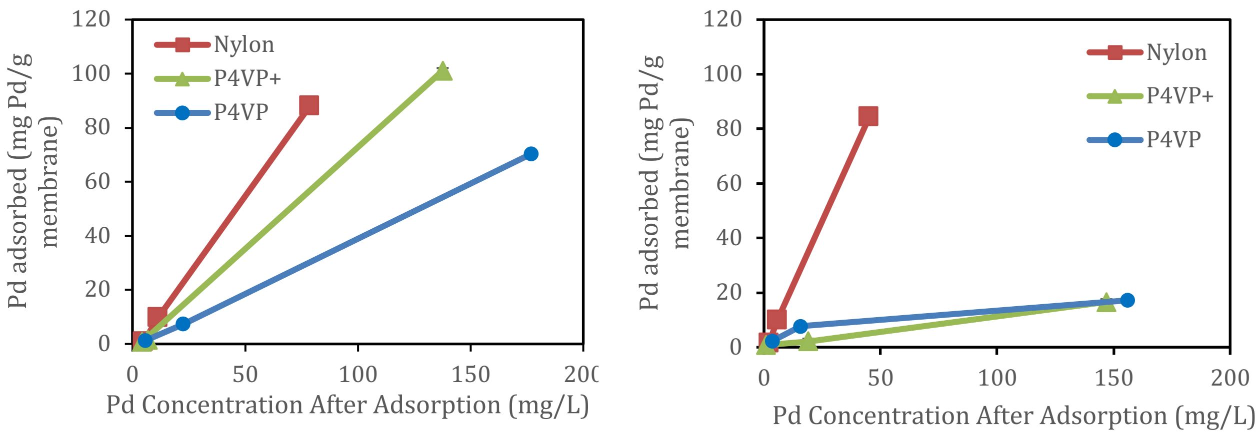

Figure 2. (Left) $PdCl_4^{2}$ adsorption on membranes. (Right) Pd^{2+} adsorption on membranes