NWRI GRADUATE FELLOW SEMI-ANNUAL PROGRESS REPORT

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Project Title: Recovery of Flowback Water from Hydraulic Fracturing Operation Using a Nanoporous Liquid Crystal Polymer Membrane for Simultaneous Removal of Salts and Organics

Graduate Fellow: Sarah Dischinger

Advisor: Professor Douglas L. Gin

Institution: University of Colorado Boulder

Background and Introduction

The process of hydraulic fracturing uses approximately 4 million gallons of water per well, 10-70% of which returns to the surface of the well with high concentrations of both dissolved organic carbon (DOC) and total dissolved solids (TDS) [1]. Given the location and high level of contamination of these wastewaters, an economically viable treatment method for these waters is still under development, and therefore 95% of this water is deep-well injected [2]. Deep-well injection, however, has been associated with the increase in seismic activity and has been shown to compromise the quality of the surface water downstream from these injection sites [2]. The wastewaters produced from hydraulic fracturing eventsare difficult to treat with traditional methods such as biological degradation or filtration because they contain high concentrations of both salt and organics [3-4]. While membranes are the most energy-efficient and cost-effective way to desalinate water [5], development of membrane materials and processes is still needed to make treatment of the more complex hydraulic fracturing wastewater viable.

The bicontinuous cubic lyotropic liquid crystal (LLC) nanofiltration membrane developed in the Gin and Noble research labs at the University of Colorado (CU) Boulder is based on a different selective material than the material used currently in commercial nanofiltration (NF) and reverse osmosis (RO) membranes and could offer an alternative approach to treating hydraulic fracturing wastewater. The monomer and polar solvent of the LLC arrange themselves (i.e., self-assemble) into a nanostructured material with discrete hydrophilic regions (i.e., pores); this nanostructure is locked into place via polymerization [6]. The pores, approximately 1 nm in width, extend continuously throughout the material, creating a pore network through which water and solutes can be transported. The LLC membrane exhibits a similar rejection of uncharged solutes as the commercial NF membrane NF270. However, the LLC membrane exhibits a much higher salt rejection than NF270 [6]. The high salt rejection of the LLC membrane is believed to be due to the positive charges which line the pore walls, enabling the pores to repel charged species (i.e., salts). Compared to the commercial RO membrane SW30HR, the LLC membrane exhibits a slightly decreased rejection and a higher permeance than

SW30HR [6]. Experiments using dead-end filtration units (in which the feed solution is stationary, having no velocity tangential to the membrane) have demonstrated that this novel LLC membrane exhibits a unique rejection profile (i.e., its rejection of charged solutes relative to its rejection of uncharged solutes) compared to commercial NF and RO membranes when treating hydraulic fracturing flowback water (i.e., the water that returns to the surface within the first few weeks of drilling [7])collected from the Denver-Julesburg (DJ) basin in Colorado. The preliminary results provide a proof-of-concept of the novel performance of the LLC membrane. However, further testing is required to confirm the performance of the material and the fouling properties, both of which are best evaluated in the cross-flow configuration, which is used more commonly in industry than the dead-end configuration.

Objective of this Research: The objective of this research project is to evaluate the performance—charged and uncharged solute rejection, water flux, and fouling—of the LLC membrane in treating hydraulic fracturing flowback water. The performance of the LLC is to be directly compared with the performance of commercial NF and RO membranes.

Hypothesis: I hypothesize that the unique performance of the LLC membrane during dead-end filtration will be maintained during cross-flow filtration. Given the localization of charge within the pores, I hypothesize that organic fouling will be reduced in the case of the LLC membrane.

Significance: By completing this research, I will evaluate the applicability of this novel LLC membrane material in contexts relevant to the oil and gas industry. This work is part of a larger collaboration with a research group in the environmental engineering department at CU Boulder to develop a cost-competitive treatment train for handling the hydraulic fracturing wastewater collected from the oil and gas industry located in the DJ basin. In addition to contributing to the development of a treatment train, this research in and of itself will contribute valuable knowledge about membrane filtration of hydraulic fracturing flowback water by evaluating how components of the flowback water interact with membrane materials. This research will contribute to the development of solutions to treat and recover hydraulic fracturing wastewater. Such solutions can decrease water stress in areas of minimal water resources and reduce seismic activity by reducing the volume of water that must be deep-well injected.

Progress to Date

Synthesis of the monomer

The novel LLC membrane being evaluated in this work is a thin-film composite (TFC) membrane in which the selective layer (i.e., the layer that determines the rejection performance of the membrane) is the nanostructured LLC polymer. The formation of the nanostructure, which gives this material its selectivity, depends on the properties of the amphiphilic monomer used to form the nanostructure, the polar solvent mixed with the molecules, and the temperature (Figure 1). As seen in Figure 1, monomer **1** used here consists of two single-tailed imidazolium-based surfactant molecules tethered together by an alkyl spacer. This monomer cannot be purchased from any commercial chemical company, but rather is synthesized in-house through a sequence of eight steps. A single 3-gram batch of this monomer takes about 25 days to synthesize from the commercially available precursors. During

this period, I synthesized enough monomer to fabricate about ten TFC Q_I membranes for testing, which will be sufficient for the needs of this project.

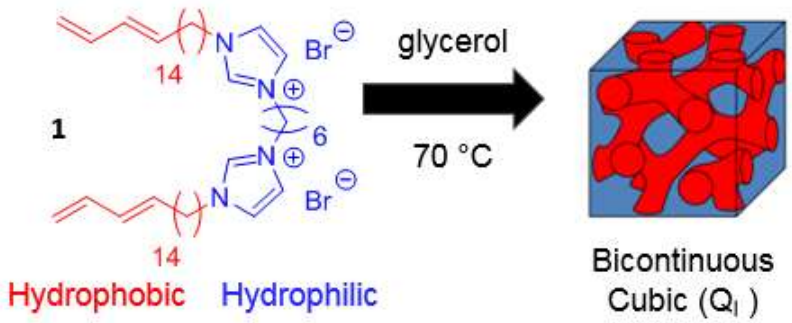

Figure 1. When the imidazolium-based monomer **1** is combined with glycerol and raised to 70°C, the desired bicontinuous cubic phase is formed.

Assembling the cross-flow system

The central goal of this project is to evaluate a new membrane material in an industrially relevant context within the lab, namely a table-top cross-flow filtration system. During the last reporting period of this project, I, with help from the Sterlitech technical representatives, designed the cross-flow unit and purchased the various components. During the current reporting period, I received and assembled the components. However, this system is more complex than I have worked with in the past, and therefore required me to solve some mechanical and electrical engineering problems.

In my dead-end filtration system, pressurized nitrogen gas is used to create a pressure difference across the membrane. However, in a cross-flow orientation, a pump is required to pressurize the liquid in order to create the needed pressure difference. The type of pump capable of providing the necessary pressure and flow rate requires a higher voltage than is commonly provided by wall outlets. Therefore, in order to make this cross-flow system as versatile and mobile as possible, a variable frequency drive (VFD) was added to the pump. Using a VFD not only increases my control over the flow rate of the system by allowing me to change the speed of the pump, but it also converts the single-phase 120V electricity source available from most common outlets to a 3-phase 230V source required by the pump. Figure 2a shows the pump and its associated VFD. In order to move electricity from the wall to the pump, it was necessary to hardwire an extension cord to the VFD and then hardwire a cord from the VFD to the pump. With the help of the departmental electrician, I learned how to hardwire, ground the system, and prevent compromised connections induced by the weight and torque of the cord (Figure 2b).

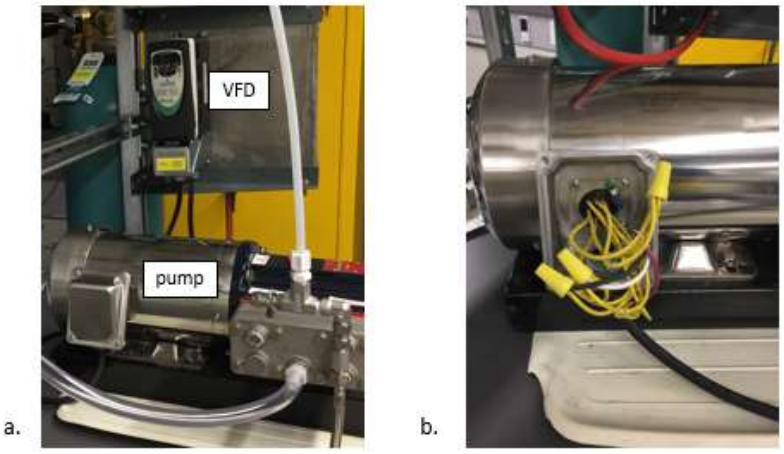

Figure 2. (a) The VFD and pump, and (b) a picture of the hardwired electrical connections to the pump.

The feed tank also required some design work. High density polyethylene was chosen as the material for the feed tank because containers made from this material are already used to collect and store the wastewater. In order to ensure that the system never runs dry, the minimum volume at any given time in the feed tank must be no less than 1 L. Given that the volume of the piping in the cross-flow system itself is about 0.5 L and experiments will be run to about 50% recovery of the feed, a container volume of at least a 3 L is needed. To provide for extra capacity, a 4 L feed tank was chosen for this system. In order to maximize the degree of mixing induced by the stir rod at the center of the tank, I chose a narrower, taller tank instead of a wider, shorter tank. An outlet from the center of the bottom of the tank feeds the pump and is raised about 6 in above the pump inlet to allow the pump to be gravity-fed. Tubing returns the concentrate and the relief-valve streams to the feed tank via ports in the lid of the tank. The stir rod also enters the feed tank from the top. The hole around the shaft of the stir rod will be loosely wrapped in order to allow for free rotation of the shaft and pressure equalization while preventing foreign objects from entering the tank. The feed tank is wrapped by a chilling coil in order to maintain the feed temperature. Figure 3 shows how the feed tank is currently set up.

Figure 3. The feed tank, with inlet and outlet connections, a chilling coil, and a stir rod.

The individual components are connected to complete the cross-flow system. Figure 4 presents the cross-flow system in its entirety, including elements not mentioned above. As with any system, testing and redesign are a central part to improving the system. One major improvement that will be made is

securing all the apparatuses to a plate such that the rigid tubing does not exert stress on the various joints. The chilling coil will also be insulated. Once testing begins, more improvements will be identified and implemented.

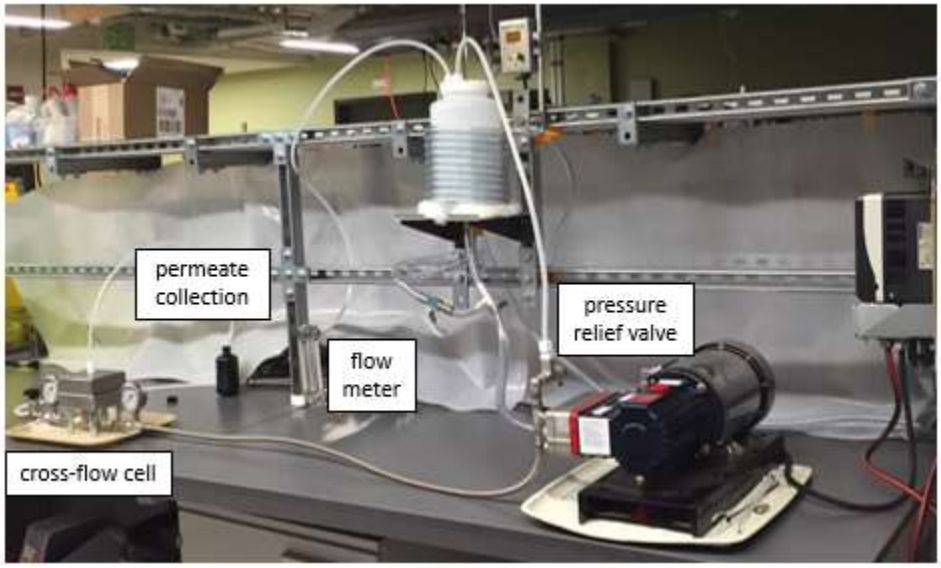

Figure 4. The cross-flow system in its entirety.

Conclusions

This project aims to evaluate a new material under conditions that are more industrially relevant through the use of a new cross-flow filtration system. As such, both the material and the new system must be made or built before evaluation can begin. While there are no analytical results to present during this period, I have synthesized the monomer and assembled the system necessary to run the proposed experiments. This means that in moving forward with this project, (1) I have sufficient monomer (the most difficult material to acquire in this project), and (2) I should be able to use and adjust the cross-flow system efficiently because I designed the system to be user-friendly and flexible. Valuable and reproducible results depend on a robust and well-designed system, so time put into setting up a system is well invested.

This work contributes to the development of membranes for the treatment of wastewaters having complex compositions, such as hydraulic fracturing wastewater. Such development could ease the competition for water among various industries in water-scarce regions by recovering a portion of the wastewater for reuse applications. In addition to contributing to the development of a treatment for a specific wastewater source, the evaluation of a novel membrane material in a more industrially relevant context could motivate the development of other of nanofiltration materials, progressing the field and addressing problems in new ways.

Next Steps

Moving forward, there are a few adjustments that need to be made to the cross-flow system before filtration begins. Once the system is complete, I will establish an experimental method so that results

are replicable and comparable. The experimental method should include flowrate, applied pressure, feed temperature, and experiment duration, along with the associated parameters required to maintain each value. Also, I will run preliminary tests to determine if the parameters will need to be adjusted for each type of membrane tested. With an established experimental method, I can begin filtration experiments with hydraulic fracturing wastewater. Filtration experiments will consist of exposing the various membrane types to cycles of water and wastewater while evaluating the selectivity, flux, and flux recovery of each membrane. The membrane surfaces will then be analyzed in order to study the fouling that is occurring on each membrane.

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