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

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Background and Introduction

The process of hydraulic fracturing uses around 4 million gallons of water per well, 10-70% of which returns to the surface [1]. An economically viable method to treat water is still under development, resulting in the deep well injection of 95% of the water produced by these operations [2]. Deep well injection, however, has been associated with the increase in seismic activity and has been shown to impact the quality of the surface water downstream from these injection sites [2]. There is a great need for economically viable treatment trains capable of handling these waters. However, the combination of high salt and high organic concentrations makes these waters difficult to treat with traditional wastewater treatment methods. While membranes are the most energy efficient and cost effective way to remove the salinity from this water [3], development of membrane materials and processes is still needed to make treatment viable.

The bicontinuous cubic lyotropic liquid crystal (LLC) nanofiltration membrane developed in the Gin and Noble research labs at the University of Colorado Boulder offers a competitive performance to that of commercial nanofiltration (NF) and reverse osmosis (RO) membranes. Specifically, the LLC membrane has a uncharged solute rejection performance between that of RO and NF, a charged solute rejection performance similar to that of RO, and a thickness-normalized water permeance comparable to RO [4]. The LLC membrane is a nanostructured material with discrete hydrophilic regions formed by the self-assembly of the amphiphilic monomer in combination with a polar solvent [4]. The hydrophilic regions, approximately 1 nm in width, extend continuously throughout the material, creating a pore network through which water and solutes can be transported. The pores are lined with positive charges, enabling the pores to repel charged species (i.e., salts). This LLC membrane exhibits a salt rejection much higher than commercial NF membranes with a similar molecular weight cut off; compared to commercial RO, the LLC membrane exhibits a slightly decreased rejection while having a higher permeance [4]. Experiments using dead-end filtration units have demonstrated that this novel LLC membrane exhibits a unique rejection profile (i.e. rejection of both charged and uncharged solutes) compared to commercial NF and RO membranes when treating hydraulic fracturing flowback water collected from the Denver-Julesburg (DJ) basin in Colorado. This water is generally characterized as having 22,500 mg/L of dissolved solids and 590 mgC/L of dissolved organics [1]. (Since treatment results of this water by the LLC membrane are currently being written-up as a manuscript for publication, I cannot yet disclose the results in a public form.) These 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 a configuration more similar to that found in industry, namely a crossflow orientation rather than a dead-end orientation.

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. **I hypothesize that the unique performance of the LLC membrane during dead-end filtration will be maintained during crossflow filtration.** Given the localization of charge within the pores, I hypothesize that organic fouling will be reduced in the case of LLC membranes. 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 Colorado University Boulder to develop a cost-competitive treatment train for handling the hydraulic fracturing flowback water 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 the various components of the flowback water interact with various membrane materials. Increasing seismic activity due to deep well injection and increasing water stress in areas of minimal access to water are important issues, and this research will contribute to the development of solutions to treat and recover hydraulic fracturing flowback water.

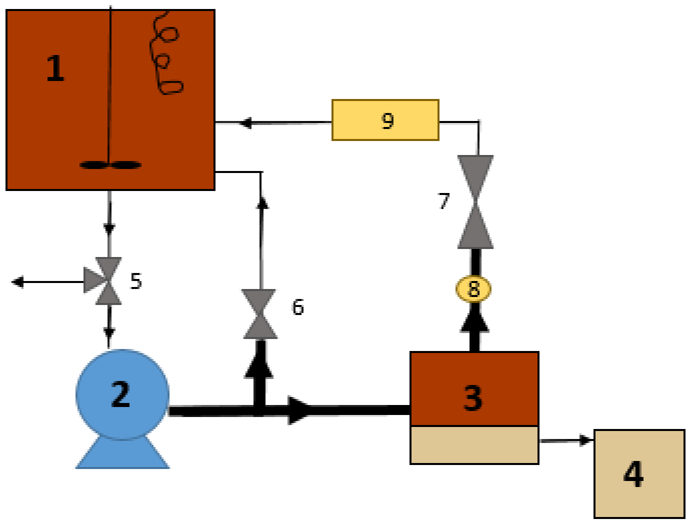
Progress to Date

The first few months of this project have been devoted to developing an experimental plan and working with manufacturers to design the exact bench-top crossflow filtration system to bring the plan to fruition. The objective of this research is to evaluate the performance of the novel LLC membrane in treating hydraulic fracturing flowback water when in a crossflow orientation. Performance will be evaluated in the following ways:

- Water flux: Water flux will be calculated by measuring the mass of permeate collected over time.
- Solute rejection: Solute rejection will be measured by comparing the concentration of various solutes in the initial feed and in the permeate.
- Fouling: Fouling will be observed by a change in the water flux and further analyzed by scanning electron microscopy and elemental analysis of the membrane surface.

The two dominant sources of variation in these experiments are (1) membrane sample, and (2) age of the flowback water. Through experiment replication and a random run sequence of experiment replicates, I will account for these variations.

To mitigate the variation due to membrane sample, at least three membrane samples that have demonstrated good quality will be evaluated. To mitigate variation due to aging of the water, the system volume must be designed to minimize experiment duration for 50% recovery of the feed while still collecting a sufficient amount of sample for analysis and further treatment, if necessary. Temperature, pressure, and tangential flow velocity along the membrane could impact the transport properties of solutes through the membrane, therefore these properties will be adjustable and monitored in the crossflow filtration system. Discussion with a manufacturer of bench-top crossflow filtration units (Sterlitech) also provided valuable input to the development of this system. Considering the research objectives, limitations on time and sample size, and comments from the manufacturer, a system has been designed as shown in Figure 1.



Unit Operation	
1	feed tank with stir rod and cooling coil
2	positive displacement pump
3	crossflow membrane filtration unit
4	permeate collection tank
Valves/Controllers	
5	drain valve
6	flow-controller valve
7	high-pressure valve
Metering Devices	
8	high-pressure gauge
9	flow meter

Figure 1. The schematic of the crossflow filtration system. Thick lines identify high pressure streams. Adapted from Sterlitech.com

Conclusions

Preliminary results using dead-end filtration units demonstrate that the LLC membrane offers a novel way of treating hydraulic fracturing wastewater. By using the LLC membrane to isolate the biologically degradable component of hydraulic fracturing wastewater from conditions that inhibit biological degradation (namely, high salt concentrations), a more economically competitive treatment train for handling these waters is possible. Such a treatment train could motivate the reduction of deep-well injection of these contaminated waters while recovering water for local reuse. This would impact not only oil and gas companies, but also local communities.

Unfortunately, the preliminary study was limited by the dead-end filtration units used for testing. These units have a small feed volume and minimal active membrane area; this means that 50% recovery of the feed is only 11 mL of permeate over a 5-day period. With such a small sample volume, characterization and biological degradation experiments with these samples were limited. The cross-flow filtration system developed above will collect permeate samples on the order of 500 mL, enabling the same sample to be characterized and used in multiple biodegradation experiments. In addition to producing more sample for characterization and treatment train development, the cross-flow filtration unit will enable a study of fouling of the LLC membrane in industrially relevant flow orientations. Fouling is of huge concern in the treatment of wastewaters, and having a hydrodynamic environment similar to what the membrane would experience in industrial applications is essential. This work is important in realizing the application of LLC membranes for the treatment of hydraulic fracturing wastewaters, furthering the treatment of wastewaters the majority of which are not currently being treated.

Next Steps

The designed system in Figure 1 is ready to be assembled. The focus of these next few months will be on assembling the crossflow unit and establishing an experimental procedure based on preliminary filtration experiments. Baseline performance of the membranes will be measured in terms of water flux and rejection of single solute solutions, both charged and uncharged.

During the assembly of the crossflow system, I will also be synthesizing the monomer to necessary make the LLC material, and I will fabricate and confirm the quality of membranes for testing. Below is the project plan for the next few months.

		Nov-16	Dec-16	Jan-17	Feb-17	Mar-17	Apr-17	May-17
1	**Develop a crossflow filtration system**							
1a	Design the crossflow filtration system							
1b	Build the crossflow filtration system							
1c	Collect baseline filtration data							
1d	*Establish an experimental procedure based on 1c*							
2	**Make TFC Q_I membranes**							
2a	Synthesize LLC monomer							
2b	Fabricate TFC Q_I membranes							
2c	*Have TFC Q_I membranes of confirmed quality for testing*							
3	**Evaluate membrane performance in treating hydraulic fracturing flowback water**							
3a	Run filtration of commercial RO membrane							
3b	Run filtration of commercial NF membrane							
3c	Run filtration of TFC Q_I membrane							
3d	Analyze feed and permeate solutions							

References

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