NWRI GRADUATE FELLOW SEMI-ANNUAL PROGRESS REPORT

DATE:	December 1, 2017
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

Overview

The process of hydraulic fracturing uses approximately 4 million gallons of water per well, 10-70% of which returns to the earth's surface 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 an increase in seismic activity and has been shown to reduce the quality of the surface water downstream from these injection sites [2]. The wastewaters produced from hydraulic fracturing events are 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], further development of membrane materials and processes is 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 lower rejection and a similar permeability (i.e., thickness- and pressure-normalized water flux) [6]. Dead-end filtration experiments, in which the feed solution has no velocity tangential to the membrane, have demonstrated that this novel LLC membrane exhibits a unique selectivity for small organic solutes as compared to commercial NF and RO membranes. More specifically, it has a lower rejection of small, uncharged organic solutes relative to its high rejection of charged solutes [6,7]. In the context of treating hydraulic fracturing flowback water (i.e., the water that returns to the surface within the first few weeks of drilling [8]), the LLC membrane offers a non-traditional treatment approach that could improve the economics of treatment [7]. 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 the cross-flow configuration, which is the configuration used more commonly in industry than the dead-end configuration.

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 LLC membrane as compared to its commercial counterparts.

Objectives and Study Goals

The objective of this research project is to evaluate the performance—charged and uncharged solute rejection, water permeability, and fouling—of the LLC membrane during the filtration of hydraulic fracturing flowback water in a more industrially relevant context. The performance of the LLC is to be directly compared with the performance of commercial NF and RO membranes. By conducting these experiments, I will also gain more knowledge about the LLC membrane as well as cross-flow filtration.

Needs Served by this Research

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 solutes present in flowback water interact with membrane materials. Developing viable treatment methods for hydraulic fracturing flowback water would decrease water stress in areas having minimal water resources and reduce seismic activity by reducing the volume of water that must be deep-well injected.

Progress to Date

The central goal of this project is to evaluate a new membrane material in an industrially relevant context within the lab through the use of a table-top cross-flow filtration system. During the last reporting period of this project, I received and assembled the components of the filtration system and resolved the electrical and mechanical problems that arose during the assembly. During this reporting period, I identified limitations of the initial system and implemented improvements. With the improvements in place, I was able to develop methods for running the system. Further, I ran a preliminary filtration experiment with an LLC membrane in this new cross-flow filtration system to compare its performance in cross-flow vs. dead-end filtration.

Improving the Cross-Flow Filtration System

Unit Operation	
1	feed tank with stir rod
2	positive displacement pump
3	crossflow membrane filtration unit
5	heat exchanger
6	permeate collection tank
Valves	
7	drain valve
8	pressure relief valve
9	backpressure regulator
Metering Devices	
4	volumetric flow meter
10	high-pressure gauge
11	thermometer

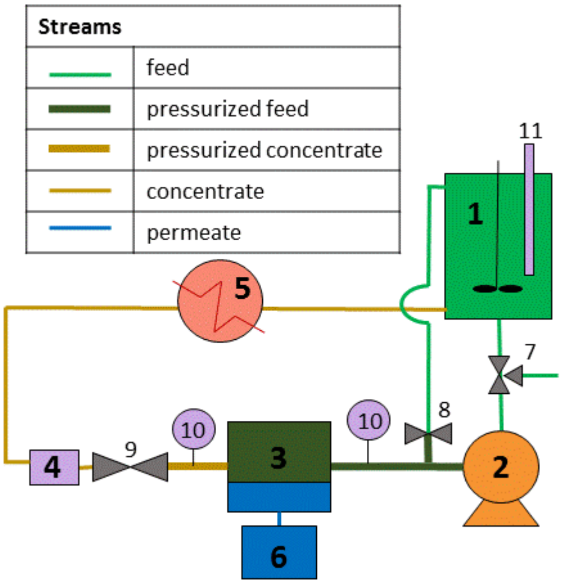
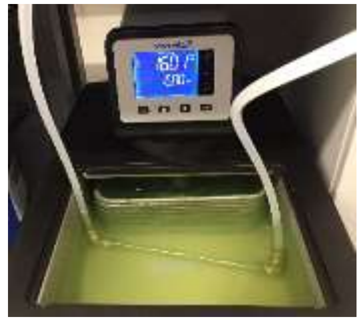


Figure 1. Schematic of the improved cross-flow filtration system

Figure 1 is an updated schematic of the cross-flow filtration system as it is currently being used. Changes to the initial system were made to improve the control of the feed temperature and the pressure. To improve control over the temperature of the feed, a heat exchanger (5 in Figure 1) was added to the concentrate stream (instead of removing the heat at the feed tank itself, as in the initial system). The heat exchanger consists of a stainless steel tube that is submerged in a chilled bath (Figure 2a). The amount of heat removed from the concentrate as it passes through the steel tube depends on the flow rate of the solution and the temperature of the solution entering the tube, both of which will be constant for the duration of the experiment. This has proven to be an effective way to control the temperature of the solution in the feed tank for the duration of the experiment. To gain control over the pressure of the system, the high-pressure control valve was replaced by a backpressure regulator (Figure 2b). The regulator is able to maintain a constant backpressure at various flow rates because the degree of openness of the valve depends on the force of a spring (the force is set by the user). By using the regulator, backpressure and flow rate are decoupled because backpressure is determined by the force of the spring while flow rate is determined by the speed of the pump. With these improvements, I have gained control over the variables of temperature, pressure, and flow rate and can manipulate them independently, making the system ready for testing.

Figure 2. a.) heat exchanger: stainless steel tube submerged in a chilled bath, and b.) backpressure regulator attached in-line with the filtration system, with the previously used control valve sitting in front

a.) 

b.) 

Method Development

With any new experimental setup, it is important to develop a clear experimental method. For the cross-flow filtration system developed here, such method development includes not only establishing values for the parameters of flow rate, applied pressure, temperature, feed spacer, membrane type, and solution type, but also procedures for start-up, shut-down, changing of the feed solution, and cleaning. I ran some studies to determine the hold-up volume of the cross-flow filtration system (from the outlet of the feed tank to the inlet of the feed tank, where the concentrate returns) and using that value, developed methods to change the feed solution efficiently without contaminating the new feed solution. Based on literature and previous experience, I have determined the temperature, pressure, flow rate, and feed spacer I will use for experiments [7,9,10]. These preliminary methods may be optimized as my experience grows and as my research develops, however, I have a sufficient base on which to begin collecting data.

Preliminary Results

Having established a methodology for filtration experiments, I was able to start collecting baseline information about how the LLC membrane performs in this new filtration system. To date, the performance data of the LLC membrane is in the context of dead-end filtration. In terms of the actual filtration performance, there are two main differences between the dead-end filtration and cross-flow filtration systems. The first is the active area. The active area of the cross-flow filtration system (6.5 square inches) is fifteen times larger than that of the dead-end filtration system (0.43 square inches). The concern arises as to whether the smaller area evaluated in dead-end filtration is a good representation of the larger area, or if, upon increasing the active area, more defects are present and compromise the performance. In order to identify consequences of increasing the active area, water permeance and salt rejection were evaluated. The permeance of the LLC membrane in dead-end filtration is $1.9 \times 10^{-3} \pm 7 \times 10^{-4}$ L m^{-2} h^{-1} psi^{-1} while the permeance of a LLC membrane in cross-flow filtration is 1.9×10^{-3} L m^{-2} h^{-1} psi^{-1}. The salt rejection of the LLC membrane during dead-end filtration is 98 ± 1 % (300 psi, 0.01 M NaCl solution), and the salt rejection of the LLC membrane during cross-flow filtration under the same conditions is 97.5%. The similarity of the permeance and the salt rejection between dead-end and cross-flow filtration suggests that the larger active area of the LLC membrane being tested in the cross-flow system does not have significantly more defects than the smaller piece isolated for dead-end filtration.

During the preliminary test of the LLC membrane, the cross-flow system was run continuously for 42 days, only pausing for short periods in order to change the feed solution. While actual experiments are not expected to take this long, such an extended run period demonstrates the robustness of both the cross-flow filtration system as well as the membrane. One of the studies done during this run considered the impact of cross-flow velocity on DI water permeance through the membrane. It was observed that below a cross-flow velocity of about 20 cm/s, the permeance began to decrease. Given that the feed solution was DI water, the cause of the decreasing permeance was attributed to biofouling rather than fouling of solutes onto the membrane surface. A CIP procedure was implemented and recovered about 84% of the initial permeance, however, the constant decrease in permeance persisted. Biological growth was observed in the plastic tubing, further supporting the hypothesis that the cause of permeance decline was biofouling. Because biofouling is so prevalent in my system, I need to develop ways to not only remove biofouling, but also to prevent biofouling from forming in the future. In the context of filtering complex solutions, it will be important to identify whether the observed permeance decline is due to biofouling or to fouling by solutes in the feed stream.

Conclusions

Any recently acquired experimental equipment requires some time to troubleshoot, optimize, develop experimental methods, and collect baseline data. The cross-flow system I am currently using has proven to be robust and enables me to control the independent variables (i.e., temperature, pressure, and flow rate). I also gained enough experience with the system to have developed experimental methods and procedures for handling the system and limited resources (i.e., hydraulic fracturing flowback water) efficiently.

With a robust system and established methodology in hand, I was able to collect some baseline information about the performance of the LLC membrane during cross-flow filtration. These results show that the performance of this membrane in cross-flow orientation and with a larger active area is comparable to its performance in dead-end filtration, suggesting that meaningful data can be collected from LLC membrane filtration in cross-flow orientation. The goal of this work it to evaluate the novel LLC membrane in more industrially-relevant contexts in order to determine if it can contribute to the treatment of hydraulic fracturing flowback water. A treatment option for this waste stream would reduce the water stress in arid drilling regions as it recovers reusable water, as well as reduce the volume of solution that requires deep-well injection.

Next Steps

The next step in this research is to run the experiments of interest. These experiments will evaluate the membrane filtration performance (permeance and rejection of organic and inorganic solutes) of the LLC membrane in the presence of hydraulic fracturing flowback water (or synthetic water of similar properties, depending on the availability of the flowback water). The performance of the LLC membrane will be compared to commercial membranes of similar characteristics. Fouling will also be observed as the permeance changes with time, and fouling will be analyzed post-filtration to identify if the cause of fouling is organic, inorganic, or biological.

One unexpected challenge that needs to be addressed before moving forward is the prevalence of biofouling. Methods need to be put in place to remove biofouling already present as well as prevent biofouling from occurring in the future. Through literature review and talking with people who have more experience than I with these types of filtration systems, I hope to improve my methods and mitigate the occurrence of biofouling.

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