

NWRI GRADUATE FELLOW FINAL 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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Introduction and Background

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 remote location and high level of contamination of this wastewater stream, an economically viable treatment method for this stream is still under development, and therefore 95% of the 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 wastewater 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 (i.e., TDS) and organic compounds [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 hydraulic fracturing wastewater viable.

The bicontinuous cubic (Q_I) lyotropic liquid crystal (LLC) nanofiltration membrane (TFC Q_I membrane) developed in the Gin and Noble research labs at the University of Colorado (CU) Boulder uses a unique selective material to enable 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 pass. The nanostructure distinguishes this TFC Q_I membrane material from its amorphous commercial counterparts. While the pore size of the TFC Q_I membrane is more comparable to that of the commercial nanofiltration (NF) membrane NF270, the salt rejection of the TFC Q_I membrane approaches that of the commercial reverse osmosis (RO) membrane, SW30HR [6]. Applying this selectivity to aqueous industrial streams, it has been shown that this novel TFC Q_I membrane exhibits a unique ability to collect small organic solutes from hydraulic fracturing flowback water (i.e., the water that returns to the surface within the first few weeks of drilling [7]) into a reduced saline permeate stream [8]. The collection of the small organic solutes from hydraulic fracturing waste streams offers a non-traditional treatment approach that could recover value from this waste stream [8]. These results provide a proof-of-concept of the novel performance of the TFC Q_I membrane. However, these proof-of-concept experiments were run using

dead-end filtration, in which the feed solution has no velocity tangential to the membrane, and, while dead-end filtration is valuable for lab studies, it is not commonly used in industry. Therefore, further testing is required understand how the performance of the TFC Q₁ membrane would translate into an industrial context. To accomplish this, the research contained herein studies the TFC Q₁ membrane in the industrially-used cross-flow filtration, in which the feed solution flows tangential to the membrane surface. Such a study enables evaluation of the TFC Q₁ membrane's stability in the hydrodynamic environment of cross-flow feed velocity as well as its fouling propensity.

Hypothesis

I hypothesize that the unique selectivity of the TFC Q₁ membrane observed during dead-end filtration will be maintained during cross-flow filtration. Given the nanostructure of the selective Q₁ layer, I hypothesize that organic fouling will be reduced in the TFC Q₁ membrane relative to its commercial counterparts.

Objectives and Study Goals

The objective of this research is to evaluate the performance—charged and uncharged solute rejection, water flux, and fouling—of the TFC Q₁ membrane during the filtration of hydraulic fracturing wastewater in a more industrially-relevant context. The performance of the TFC Q₁ membrane will be directly compared with the performance of a commercial membrane. By conducting these experiments, I will also gain more knowledge about the TFC Q₁ membrane and cross-flow filtration.

Needs Served by this Research

By completing this research, I will evaluate the applicability of the novel TFC Q₁ membrane 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 Colorado. 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 wastewater by evaluating how solutes present in these wastewaters interact with membrane materials. Developing viable treatment methods for hydraulic fracturing wastewater would decrease water stress in areas having minimal water resources and reduce seismic activity by reducing the volume of water that requires deep-well injection.

Progress since the Beginning of the NWRI Fellowship

Since the beginning of this project, I have brought a bench-top cross-flow filtration system into the Gin and Noble research labs, I have developed experimental methods for evaluating membrane performance in this system, and I have evaluated the performance of the TFC Q₁ membrane using real produced water collected from the oil and gas industry in Colorado.

Introducing a Cross-Flow System: System Design and Assembly, Method Development

In order to achieve the project objective of evaluating a recently-developed membrane material in the context of industrially-relevant cross-flow filtration, it was necessary to first assemble a system in which I could run such studies. With guidance from the manufacturer of the cross-flow membrane cell, I designed a cross-flow filtration system for the needs of the project and assembled the system in our lab. After some preliminary runs, I was able to improve the system by increasing control over some of the parameters that influence membrane performance (e.g., temperature and trans-membrane pressure (TMP)), as well as increase the ease-of-use of the system (e.g., high-pressure quick-connect fittings). After assembly and system optimization, it was possible to set and maintain the temperature, TMP, and cross-flow velocity independently, each of which were essential for achieving the experimental conditions I was interested in studying. With the cross-flow system ready for testing, it was necessary to develop experimental methods that reduced the variation due to sample collection and also that maintained the feed composition. While the time spent developing the system and methods did not produce results directly related to the project objectives, such development was necessary to ensure that the results collected from the system would be valuable.



Figure 1. The cross-flow filtration system assembled in our lab.

Performance of the TFC Q_i Membrane in Cross-Flow Filtration

The TFC Q_i membrane performance during cross-flow filtration was not significantly different from its performance in dead-end filtration. Before studying the TFC Q_i membrane in a new filtration environment using a complex aqueous stream (i.e., hydraulic fracturing wastewater), it was important to evaluate the performance of the TFC Q_i membrane using simple solutions of water and sodium chloride. A TFC Q_i membrane was run under cross-flow filtration conditions for 50 continuous days, demonstrating the membrane's stability in the cross-flow environment. As can be seen from Table 1, the flux and the salt rejection were not significantly different between cross-flow and dead-end filtration. The similarity in performance of the TFC Q_i membrane in these two types of filtration, despite a 15x difference in membrane active area, indicates that the TFC Q_i membrane is fairly uniform over the larger area and that there are no large defects in the larger area present in cross-flow filtration. These results demonstrate that the TFC Q_i membrane has a stable performance in the more industrially-relevant context of cross-flow filtration and justify extending the experiments to include the more complex hydraulic fracturing wastewater.

filtration type	membrane active area (cm ²)	flux (L m ⁻² h ⁻¹)	salt rejection (%)
dead-end	2.8	0.5 ± 0.1	98 ± 1
cross-flow	42	0.55	98

Table 1. TFC Q_i membrane performance in both dead-end and cross-flow filtration. Salt rejection was measured with a 0.01 M sodium chloride solution. Error represents one standard deviation.

TFC Q_i Membrane Filtration of Produced Water

The performance of the TFC Q_i membrane during treatment of actual produced water collected from a basin in northeastern Colorado was evaluated and compared to the performance of the commercial NF

membrane NF90. NF90 was chosen as a commercial NF comparison due to its high salt rejection and its previous use in produced water treatment research [9,10]. For this comparison, TMP, cross-flow velocity, feed temperature, duration of exposure, and recovery were held constant while flux and rejection of TDS and DOC were measured. The produced water used for these experiments was pretreated via micro- and ultra- filtration in order to simulate the types of pretreatment that would be used in an industrial setting.

The stable performance of the TFC Q_i membrane during the treatment of produced water demonstrates the feasibility of using the TFC Q_i membrane in an industrial context. The TFC Q_i membrane was exposed to pretreated produced water for 60h, with a clean-in-place (CIP) process implemented after the first 20h. During filtration of produced water, the flux of the TFC Q_i membrane was only about one third the flux of the commercial NF90 membrane, which, taking into account the fact that the TFC Q_i selective layer is 25x thicker than the selective layer of the NF90 membrane [6,11], demonstrates that the TFC Q_i membrane is in the range of commercial membrane flux. While a slow decline in TFC Q_i membrane flux was observed and attributed to fouling, the absence of significant changes in flux suggests that the membrane integrity was maintained for the duration of the 60h exposure. The sustained DOC and TDS rejection across the 60h exposure also demonstrates the stability of the TFC Q_i membrane. The CIP process did increase the flux through the TFC Q_i membrane while minimally impacting the rejection, indicating that the TFC Q_i membrane maintains its integrity through a CIP process. These preliminary results suggest that the recently-developed TFC Q_i membrane can withstand exposure to produced water during cross-flow filtration and exposure to CIP processes.

The TFC Q_i membrane isolates organic solutes in a reduced saline feed during the treatment of produced water. As can be observed in Table 2, the TFC Q_i membrane had a lower DOC rejection relative to its TDS rejection when compared to the commercial NF90 membrane. The NF90 membrane rejected TDS to a high degree and DOC to a fair degree, producing a permeate with low concentrations of both salts and organic solutes. The TFC Q_i membrane, on the other hand, allowed a significant portion of the organic solutes to pass through the membrane while still rejecting salts. Therefore, the TFC Q_i membrane separated the organic solutes from a large portion of the salinity by passing the organic solutes into the permeate and retaining the salts in the concentrate. This comparison exhibits the TFC Q_i membrane's unique selectivity for small organic compounds. Such a selectivity offers an alternative approach to the treatment train by enabling the possibility of biodegradation post-desalination rather than pre-desalination, as is traditionally done. These results agree with experiments run in dead-end filtration [8]; the TFC Q_i membrane retains its unique selectivity in more industrially-relevant contexts.

Membrane	DOC Rejection (%)	TDS Rejection (%)
TFC Q _i	39	85
NF90	76	98

Table 2. Rejection of DOC and TDS present in pretreated produced water by the TFC Q_i and NF90 membranes while in cross-flow filtration at 400 psi.

The fouling propensity of the TFC Q_i membrane remains unclear due to the significantly different hydrodynamic environments experienced by the NF90 and TFC Q_i membranes. The selective layer of the TFC Q_i membrane is about 25x thicker than that of the commercial membrane NF90. The consequence of this difference is that the water flux is an order of magnitude different between the two membranes when both membranes are exposed to the same TMP. Therefore, while the TFC Q_i membrane did experience over 90% flux recovery after completion of the 60h exposure to pretreated produced water,

no statement can be made comparing its fouling propensity to the commercial NF90 membrane. The only statement that can be made from the current set of results is that the TFC Q_i membrane does not foul at low flux, validating further investigation. Experiments are currently being run in order to better compare the fouling propensity of the TFC Q_i and NF90 membranes in terms of material properties rather than hydrodynamic conditions.

Conclusions

The TFC Q_i membrane offers an alternative approach to the treatment of hydraulic fracturing wastewater through the application of its unique selectivity. The research presented herein demonstrates the membrane's stable performance in cross-flow filtration and its ability to isolate organic solutes from the high salinity environment of produced water. Such a separation could enable biodegradation to occur post-desalination, reducing the volume of the waste stream requiring deep-well injection and potentially recovering value from this waste stream. The research presented herein specifically demonstrates that the recently-developed TFC Q_i membrane can perform in cross-flow filtration and withstand CIP processes, motivating further development of the TFC Q_i membrane for industrial application. The development of a novel material that enables an alternative approach to water treatment challenges paradigms about treatment and could contribute to solutions for treating some of the most difficult waste streams, including those produced by hydraulic fracturing. By recovering more water from hydraulic fracturing waste streams, water scarcity could be reduced in the arid regions where hydraulic fracturing is occurring; the seismic activity associated with deep-well injection could be reduced as well.

While this research presents preliminary results that support the feasibility of applying the TFC Q_i membrane to industry, more work is required to confirm the TFC Q_i membrane as an alternative to commercial NF materials. Specifically, the TFC Q_i membrane should be tested with produced waters collected from more basins (since the quality of the water varies significantly from basin to basin), for longer periods of time, and through more CIP cycles. As discussed above, the fouling propensity of the TFC Q_i membrane material should be compared to that of commercial membranes through careful control of the hydrodynamic environment experienced by each membrane during filtration. To improve the industrial relevance of the TFC Q_i membrane, the fabrication method of the TFC Q_i membrane should be adjusted so as to achieve a thinner selective layer and a correspondingly higher flux. While more experiments and material development is required, the research presented herein motivates further investigation of the TFC Q_i membrane as an industrially-relevant alternative treatment for hydraulic fracturing wastewater.

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