

# NATIONAL WATER RESEARCH INSTITUTE

## 2016-2018 NWRI Graduate Student Fellows Spring 2018 Final Progress Reports

The NWRI Fellowship program is supported by BioLargo, Inc., American Membrane Technology Association (AMTA), Southern California Salinity Coalition (SCSC), NWRI Member Agencies, NWRI Corporate Associates, and community partners. NWRI is grateful for the support provided by these partners. Under the Fellowship program, NWRI awards Fellowships to graduate students in the U.S. in the areas of water resources and treatment. Supported research must focus on developing and/or enhancing water supplies. Research topics include, but are not limited to: recycled water, treatment technologies, water and energy nexus, exploratory research, desalination, and policy and regulation.

NWRI is pleased to present the first progress report from our 2016-2018 fellows. A brief summary of each project follows:

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## **NWRI Member Agencies**

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## NWRI GRADUATE FELLOW FINAL PROGRESS REPORT

DATE: May 2018

Project Title: A Novel Brine Precipitation with the Aim of Higher Water Recovery

Graduate Fellow: Mojtaba AzadiAghdam

Advisors: Professor Shane Snyder and Professor Jim Farrell

Institution: University of Arizona

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### Introduction

Potable water scarcity has become an important issue over the last few decades due to changes in rainfall patterns and increasing population. Recent estimations demonstrate that more than 1 billion people do not have access to clean potable water, and approximately 2.3 billion people live in regions with water shortages [1]. Therefore, there is an increasing global trend toward using water more efficiently in urban and rural communities. In addition to novel water acquisition and management strategies, such as water transfers, banking and trading, municipalities are turning to water reuse to strengthen their water portfolios [2].

High pressure membrane processes, such as NF and RO, are commonly used to produce drinking water from brackish waters. The RO and NF processes are able to remove both organic and inorganic contaminants and produce clean water [3]. Two major limitations to these processes are membrane fouling and production of a concentrated brine stream [3, 4].

There are four main causes of membrane fouling:

- 1) Microorganism growth;
- 2) Colloidal material adsorption;
- 3) Mineral scale (most commonly divalent cations combined with sulfate and carbonate); and
- 4) Natural organic matter, such as humic and fulvic acids.

Options for concentrate disposal include: deep well injection, discharge to surface water/ocean, and evaporation [5]. Treatment of brine is a site-dependent issue, and the method usually depends on costs, which can be as high as 25% of the overall water treatment costs [6]. The high cost of brine treatment and adverse impacts of brine disposal on the environment are two variables that could be improved by using pretreatment methods that can increase the permeate water recovery and minimize brine generation.

The main goal of this research is to develop a new pretreatment technique for water treatment processes that use membranes. The proposed process consists of pretreatment techniques that will provide a cheaper water treatment option than currently used commercial processes and aims for zero brine waste generation.

The technology to be developed here will enable large-scale inland desalination using RO and NF, which are not commonly practiced in non-coastal areas due to the high costs of brine disposal. Decreasing the volume of brine production by one order of magnitude will make inland RO and NF cost-effective [7]. This will enable both municipally treated wastewater and brackish groundwater to be used as sources of potable/industrial water. These two new sources of water will improve economic development, which was limited by water scarcity in arid regions of the country.

## Progress

During past 2 years, I worked on combining several treatment technologies (fluidized bed crystallization reactor, staged membrane processes, bipolar membrane electrodialysis and ferric chloride coagulation/flocculation) in order to achieve a zero-liquid discharge (ZLD) treatment for secondary wastewater. As previous versions of the project schematics were provided in previous reports, following schematics of the system is the most up to date version which has been improved according to the experiments done on the system.

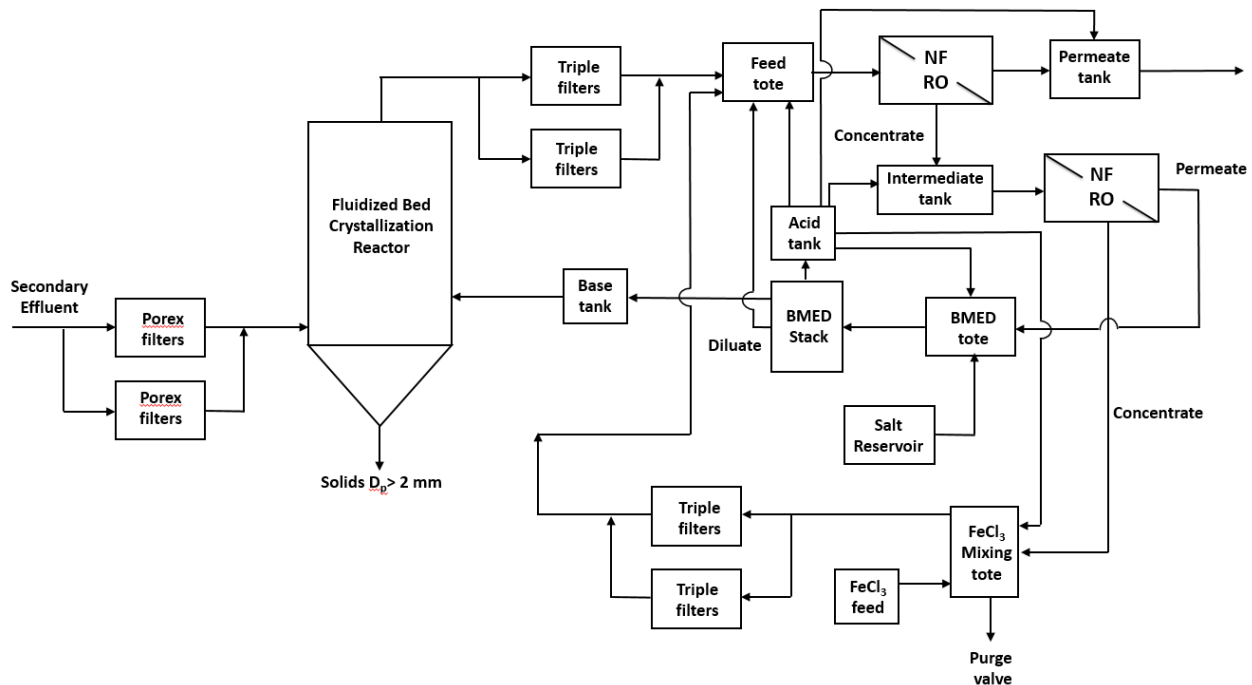


Figure 1 Project schematics

The pH value of the secondary wastewater is increased to 11.5-11.8 in the fluidized bed crystallization reactor (FBCR) and calcium and magnesium are precipitated as calcium carbonate and magnesium hydroxide on the garnet in the FBCR. In optimized conditions (bed is fluidized and pH is above 11.5), over 80% and 70% of the calcium and magnesium are removed, respectively.

The effluent of the FBCR passes through 10-20 micron filters (triple filters) in order to remove the precipitates that are carried over to the next stage. Then, this water enters to the first membrane (RO) and 99% of the monovalent and divalent ions are being removed at this stage. The permeate water exits

the system as clean water produced by the treatment train. The concentrate of this stage (20% of the initial feed volume) is fed to the second membrane (NF to remove the divalent ions. The concentrate of this stream which will be the dirtiest water produced will go to ferric chloride coagulation/flocculation step and the permeate flow will go to bipolar membrane electrodialysis (BMED). Permeate flow of the secondary membrane enters to the BMED which will produce acid and base for the system. Based on the preliminary results, pH values of 1.4 for acid and 12.7 for base are achieved without any elaborate optimization of this stage; therefore, more concentrate acid and base streams are possible with better controlling of the flow and the applied current to the BMED.

According to the newly published research articles, ferric chloride's coagulation ability can be optimized with the pH. The authors of Racar et al. mentioned that ferric chloride had its highest organic matter removal at effluent pH of 5.58 and the iron (III) concentration of 26.38 mg/L [8]. Therefore, the pilot plant design is optimized to include a pH sensor in the ferric chloride mixing tank and a pump for adding acid to the tank using the acid generated by BMED. TOC values will be measured for different pH values and iron concentration to optimize the organic matter removal in this specific wastewater in the next few months.

I have also worked on a controller system for the whole pilot plan to run the system on continuous mode. In order to achieve this goal, I have used multi parameter controllers to measure pH and level to control pump speeds and actuator valves which is discussed in the details of previous progress reports.

## Conclusions

Even though there are several months of experiments left in this project, the preliminary results indicate that high inorganic contamination removal is possible using the FBCR. Furthermore, the amount of the acid and base made using the BMED will be sufficient to have a closed loop system, and we can avoid purchasing acid and base, which is one of the novelties of this system. Previous studies show the effect of pH and iron concentration in organic matter removal in ferric chloride mixing stage that needs to be investigated. However, if the results of these recently published articles can be reproduced, this system will be able to run continuously without early membrane fouling. For the next few months, these and several other hypotheses will be validated and more experiment data will be gathered in order to suggest this treatment system can be commercialized.

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## NWRI GRADUATE FELLOW FINAL PROGRESS REPORT

DATE: May 2018

Project Title: Study of the viability of chlorine photolysis as an advanced oxidation process in water treatment systems

Graduate Fellow: Devon Manley Bulman

Advisor: Christina K. Remucal

Institution: University of Wisconsin-Madison

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Clean drinking water is essential to human life. It is one of the most important issues in developing regions, and as water scarcity increases even developed nations are looking for adaptive strategies to treat their drinking water. One major areas of concern in drinking water treatment is the removal of organic contaminants such as pharmaceuticals, personal care products, pesticides, industrial solvents, and other chemicals. These compounds are difficult to remove from drinking water without costly infrastructure development to install and maintain an advanced oxidation process or activated carbon filter. My research focuses on the mechanism behind an emerging advanced oxidation process, chlorine photolysis, that has the potential to improve drinking water treatment utilizing existing infrastructure in developed regions. The process could be used in regions that currently do not have the resources to build and maintain a drinking water treatment and distribution system.

### Background and Introduction

Advanced oxidation processes are used to remove organic contaminants from drinking water by generating hydroxyl radical. Hydroxyl radical oxidizes organic contaminants, breaking them down into smaller, ideally less-toxic molecules. Previous research shows that reacting hypochlorous acid (i.e. free-available chlorine, or bleach) with UV light creates multiple reactive species including hydroxyl radical, and that this system is capable of degrading some organic contaminants (Remucal and Manley 2016). Very few studies have investigated the formation of degradation products, which means that researchers are unsure if the organic contaminants are reacting with hydroxyl radical or with other reactive oxidant species, including reactive chlorine species. Past research has shown that these reactive chlorine species, such as chlorine radical, can react with organic contaminants and form chlorinated products. Additionally, most past studies have utilized light at 254 nm and neutral pH. While neutral pH is relevant for natural waters and the environment, the 254 nm UV light is the most commonly used wavelength for drinking water treatment. Variation in both pH and wavelength could have an effect of the formation of reactive oxidants. This study seeks to understand how varying pH and wavelength can change the production of reactive oxidants during chlorine photolysis.

Hypothesis. The degradation of chlorine and the production of reactive oxidants will be determined by fundamental parameters such as molar absorptivity and quantum yield.

Study Goals and Research Objectives. The goal of this research is to be able to quantify the production of reactive oxidants during chlorine photolysis. In order to achieve this the study has two objectives:

1. **Experimentally determination the direct chlorine photolysis rate constant and the production of measurable reactive oxidants.**
2. **Develop a kinetic model to quantify the production of other reactive oxidants produced during chlorine photolysis.**

Needs Served. This research fills a current gap in the understanding of how chlorine photolysis degrades organic contaminants. Previous studies have determined the rate constants for many reactions that occur in this system, and other studies have evaluated the degradation of contaminants of interest by reactive oxidants or by chlorine photolysis. Current scientific understanding of what types of reactive oxidants are produced and in what quantities is still lacking. This study seeks to fill that gap by determining reactive oxidant production under different conditions during chlorine photolysis.

### **Progress Since the Beginning of Your NWRI Fellowship**

Objective 1. The first objective of this work is to determine the chlorine photolysis rate constant and reactive oxidant productions under a variety of conditions. The chlorine loss rate constant varies with pH and wavelength due to the change in light absorption by chlorine. Understanding how chlorine degradation changes is important due to regulation of both disinfectant use and efficacy. Quantifying reactive oxidants allows us to determine the most effective treatment conditions.

To measure the chlorine loss rate constant, samples at pH 5-10 and were photolyzed in a Rayonet merry-go-round photoreactor with single-wavelength bulbs at 254, 311, or 365 nm. The chlorine concentration was measured at various times after the reaction began to determine how quickly chlorine was degraded. The concentration of various oxidants was measured using probe compounds, as most oxidants degrade too quickly to be measured directly. The probe compounds react with one or more of the oxidants in a well-understood mechanism, and the degradation of a probe compound or the formation of a known product can be used to determine the concentration of an oxidant such as hydroxyl radical. Nitrobenzene, benzoate, and cinnamic acid were selected as probe compounds due to their selectivity to hydroxyl or chlorine radical, and ozone. Each of these probe compounds also resists direct degradation by UV light. The concentration of the probe compounds was measured using high-performance-liquid-chromatography.

The results from this objective are still preliminary and have not yet been published. **These preliminary results demonstrate that radical production varies by irradiation wavelength, but the concentration remains within an order of magnitude.** We observed trends in both chlorine loss and radical production that can largely be explained by changes in molar absorptivity and quantum yield.

Objective 2. The second objective is to develop a kinetic model to help quantify the formation of reactive oxidants. Previous studies have published kinetic models using literature rate constants and used them to describe qualitative trends in their experimental data. All of the published models were developed to describe the formation of reactive oxidants at 254 nm, ignoring the other wavelengths where oxidant production is different. Additionally, they do not look at the formation of oxidants we determined to be present in objective 1. To correct for this, we added numerous radical reactions to ensure that all reactive oxidant species found to be present in experimental reactions were determined in the model.

The kinetic model is run using the Kintecus modelling software and uses a tableau approach to calculate the variation in concentration of chlorine and reactive oxidants with time. This approach is commonly



used in advanced oxidation processes, and similar models have been developed for the hydrogen peroxide photolysis system, which is a simpler system to model. Current model results using the model developed in this study have improved on the prediction of both chlorine loss and radical production over literature models, though the model does not yet accurately predict experimental results. This is the main focus of current research in this study.

### Discussion of Results.

The preliminary results suggest that hydroxyl radical, chlorine radical, and other oxidant species are produced during chlorine photolysis, making chlorine photolysis an effective advanced oxidation process. At all wavelengths the chlorine loss rate constant and probe loss are predicted by fundamental parameters (molar absorptivity and quantum yield). The wavelength of irradiation in these studies include both the traditional treatment wavelength (254 nm) and light within the solar spectrum (311 and 365 nm). This means that hydroxyl radical is produced by chlorine photolysis under conditions found on the Earth's surface, and chlorine photolysis could be utilized in solar treatment applications. The production of hydroxyl radical is produced at similar concentrations across a pH range, requiring less chemical input to ensure adequate reactive oxidant production. Both the kinetic model and the experimental results predict the formation of previously overlooked oxidants.

### **Conclusions**

Chlorine photolysis is a good candidate for removing organic contaminants from drinking water. The photolysis of free available chlorine produces reactive oxidants at all pH and wavelength conditions in this study. The model is still in development, but preliminary results suggest that it will be able to quantify the reactive oxidants produced. Quantifying reactive oxidant production during chlorine photolysis is important because reactive oxidant concentrations determine the efficacy of contaminant removal, which is the ultimate goal of any advanced oxidation process.

### **Next Steps**

Understanding the rates and mechanisms of reactive oxidant production is the first step in validating chlorine photolysis as an advanced oxidation process. In order to complete this work, we need to complete the kinetic model by determining the cause of over produced species at high pH.

Additionally, we need to complete the probe experiments using cinnamic acid to complete the picture drawn by the nitrobenzene and benzoate experiments. Once these steps are complete the research will move on to the next phase, looking at the formation of potentially harmful disinfection by-products (a result of reaction between oxidants and naturally occurring organic matter) during chlorine photolysis.

### **Presentations**

Devon Manley Bulman and Christina K. Remucal (2018) "Effect of solution conditions on reactive oxidant production during chlorine photolysis" (*Poster Presentation*) AEESP special symposium for the AEESP Distinguished Lecture Series.

Devon Manley Bulman and Christina K. Remucal (2018) "Effect of solution conditions on reactive oxidant production during chlorine photolysis" (*Poster Presentation*) Water @ UW Symposium.

Christina Remucal and Devon Manley Bulman (2017) "Effect of solution conditions on reactive oxidant production during chlorine photolysis" (*Poster Presentation*) Association of Environmental Engineering and Science Professors Conference, Ann Arbor, MI

Devon Manley and Christina K. Remucal (2017) "Effect of solution conditions on reactive oxidant production during chlorine photolysis" 253rd National Meeting of the American Chemical Society, San Francisco, CA

**Citations**

Remucal, Christina K., Devon Manley. "The efficacy of chlorine photolysis as an advanced oxidation process for drinking water treatment." *Environmental Science: Water Research and Technology* (2016):2(4) pp. 565-579.

## NWRI GRADUATE FELLOW FINAL PROGRESS REPORT

DATE: May 2018

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

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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 Q<sub>i</sub> membrane would translate into an industrial context. To accomplish this, the research contained herein studies the TFC Q<sub>i</sub> 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 Q<sub>i</sub> 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 Q<sub>i</sub> membrane observed during dead-end filtration will be maintained during cross-flow filtration. Given the nanostructure of the selective Q<sub>i</sub> layer, I hypothesize that organic fouling will be reduced in the TFC Q<sub>i</sub> 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 Q<sub>i</sub> membrane during the filtration of hydraulic fracturing wastewater in a more industrially-relevant context. The performance of the TFC Q<sub>i</sub> 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 Q<sub>i</sub> membrane and cross-flow filtration.

### *Needs Served by this Research*

By completing this research, I will evaluate the applicability of the novel TFC Q<sub>i</sub> 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 Q<sub>i</sub> 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<sub>1</sub> Membrane in Cross-Flow Filtration*

The TFC Q<sub>1</sub> membrane performance during cross-flow filtration was not significantly different from its performance in dead-end filtration. Before studying the TFC Q<sub>1</sub> 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<sub>1</sub> membrane using simple solutions of water and sodium chloride. A TFC Q<sub>1</sub> 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<sub>1</sub> membrane in these two types of filtration, despite a 15x difference in membrane active area, indicates that the TFC Q<sub>1</sub> 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<sub>1</sub> 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 <sup>2</sup> )	flux (L m <sup>-2</sup> h <sup>-1</sup> )	salt rejection (%)
dead-end	2.8	0.5 ± 0.1	98 ± 1
cross-flow	42	0.55	98

**Table 1.** TFC Q<sub>1</sub> 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<sub>1</sub> Membrane Filtration of Produced Water*

The performance of the TFC Q<sub>1</sub> 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<sub>i</sub> membrane during the treatment of produced water demonstrates the feasibility of using the TFC Q<sub>i</sub> membrane in an industrial context. The TFC Q<sub>i</sub> 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<sub>i</sub> membrane was only about one third the flux of the commercial NF90 membrane, which, taking into account the fact that the TFC Q<sub>i</sub> selective layer is 25x thicker than the selective layer of the NF90 membrane [6,11], demonstrates that the TFC Q<sub>i</sub> membrane is in the range of commercial membrane flux. While a slow decline in TFC Q<sub>i</sub> 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<sub>i</sub> membrane. The CIP process did increase the flux through the TFC Q<sub>i</sub> membrane while minimally impacting the rejection, indicating that the TFC Q<sub>i</sub> membrane maintains its integrity through a CIP process. These preliminary results suggest that the recently-developed TFC Q<sub>i</sub> membrane can withstand exposure to produced water during cross-flow filtration and exposure to CIP processes.

The TFC Q<sub>i</sub> 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<sub>i</sub> 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<sub>i</sub> 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<sub>i</sub> 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<sub>i</sub> 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<sub>i</sub> membrane retains its unique selectivity in more industrially-relevant contexts.

Membrane	DOC Rejection (%)	TDS Rejection (%)
TFC Q <sub>i</sub>	39	85
NF90	76	98

**Table 2.** Rejection of DOC and TDS present in pretreated produced water by the TFC Q<sub>i</sub> and NF90 membranes while in cross-flow filtration at 400 psi.

The fouling propensity of the TFC Q<sub>i</sub> membrane remains unclear due to the significantly different hydrodynamic environments experienced by the NF90 and TFC Q<sub>i</sub> membranes. The selective layer of the TFC Q<sub>i</sub> 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<sub>i</sub> 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<sub>i</sub> 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<sub>i</sub> and NF90 membranes in terms of material properties rather than hydrodynamic conditions.

## Conclusions

The TFC Q<sub>i</sub> 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<sub>i</sub> membrane can perform in cross-flow filtration and withstand CIP processes, motivating further development of the TFC Q<sub>i</sub> 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<sub>i</sub> membrane to industry, more work is required to confirm the TFC Q<sub>i</sub> membrane as an alternative to commercial NF materials. Specifically, the TFC Q<sub>i</sub> 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<sub>i</sub> 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<sub>i</sub> membrane, the fabrication method of the TFC Q<sub>i</sub> 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<sub>i</sub> membrane as an industrially-relevant alternative treatment for hydraulic fracturing wastewater.

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## SCSC-NWRI GRADUATE FELLOW FINAL PROGRESS REPORT

DATE: May 2018

Project Title: Impacts of Long-Term Exposure to Flow with Elevated Salinity and Temperature on Hydrophobicity of Membranes used for Membrane Distillation

Graduate Fellow: Ryan Gustafson

Advisor: Amy Childress, Ph.D.

Institution: University of Southern California

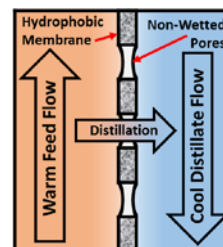
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### Background and Introduction

Drinking water sources throughout the world are becoming increasingly saline over time. This increase in water resource salinity has a number of different causes, including: urban runoff, residential water treatment systems (e.g., water softeners), industrial uses (e.g., cooling towers), agricultural practices (e.g., fertilizers and animal wastes), and water and wastewater treatment systems (e.g., brines and chemicals used in treatment). The increased salinity of drinking water sources has spurred interest in desalination technologies. Additionally, historic droughts like the one recently experienced in California reduce the reliability of traditional water systems that import water from water-rich regions to water-scarce regions. For these reasons, water managers in areas with scarce water resources are turning to water reuse and desalination to meet their water supply needs.

Although water reuse and desalination technologies are a viable option to enhance local water supplies, these processes can consume larger amounts of electrical energy than conventional water treatment technologies [1]. Consequently, these technologies may contribute more greenhouse gases to the atmosphere than conventional water treatment processes do, thereby exacerbating concerns regarding climate change. These concerns create the need for water treatment technologies that require low levels of electrical energy. To achieve this end, my research project focuses on an option for a low-energy desalination process.

Membrane distillation (MD) is an innovative water treatment technology that can be driven by alternative energy sources like solar energy or low-grade (waste) heat [2]. In direct contact MD, the feed solution (e.g., wastewater, seawater, or brine) is heated and passed along one side of a membrane, while a cooler pure water solution (the distillate) is passed along the other side of the membrane (Figure 1). The membranes used in MD are microporous—meaning that they have pore sizes less than one micrometer—and hydrophobic—meaning that they repel water. In MD, water evaporates at the feed membrane surface, passes through the membrane pores, and condenses upon contact with the cool distillate stream. Because the vapor pressure driving force is unaffected by salinity, MD can be used to treat high-salinity process streams that are challenging or impossible for conventional technologies to treat. The vapor phase separation results in a characteristically high rejection of non-volatile contaminants, but the high rejection of non-volatile contaminants can only be maintained as long as the



**Figure 1:**  
Membrane distillation diagram.

hydrophobicity of the membrane is maintained. If the hydrophobicity is not maintained, the pores will become flooded with feed water, allowing passage of feed solution and its contaminants into the distillate solution.

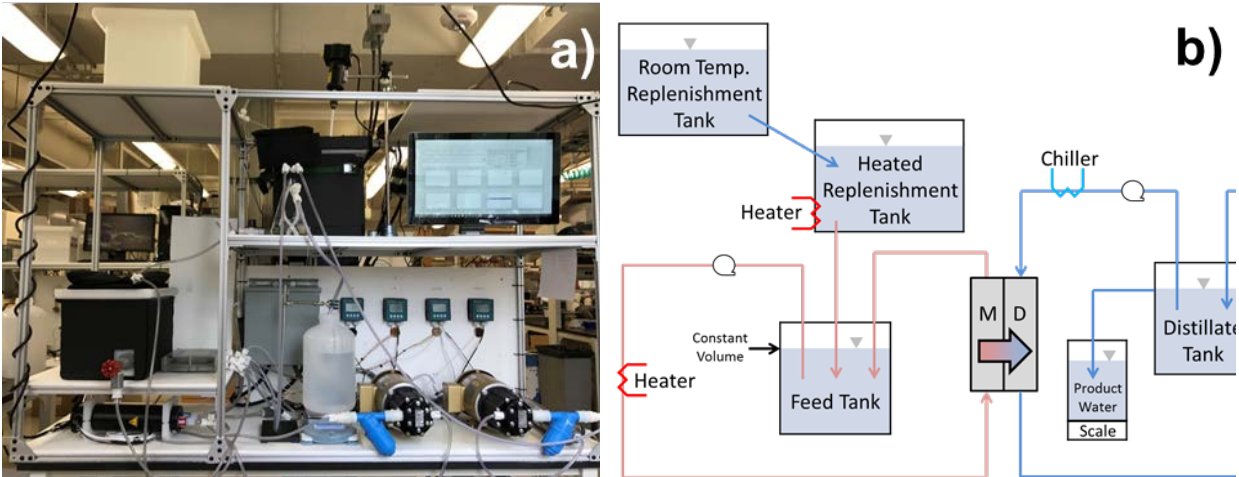
Similar to how the flow of water in a river smooths the rocky surface of a riverbed, **it is my hypothesis that long-term exposure of MD membranes to viscous flow (e.g. wastewater, seawater, or brine) reduces surface roughness over time.** Because surfaces with a higher roughness are more hydrophobic [3], a reduction in MD membrane surface roughness would result in a reduction in membrane hydrophobicity and therefore a lower rejection of contaminants in the feed solution. Additionally, feed solution salinity and temperature impact membrane hydrophobicity. A smaller pore size and a higher liquid surface tension result in a higher liquid entry pressure and therefore a higher hydrophobicity, as described by the modified Young Laplace equation [4]. Because a higher salinity solution has a higher surface tension, membrane hydrophobicity would be expected to be higher for a higher salinity solution. However, higher temperatures have been demonstrated to result in pore size expansion [5], which would result in a lower membrane hydrophobicity. This indicates that the net effect on MD membranes of temperature, salinity, and potential changes in membrane surface roughness over time is unknown. The interplay between temperature, salinity, and surface roughness in affecting long-term MD membrane hydrophobicity is not well-described in the scientific literature, and my research addresses this concern.

The objective of the research described in this report is to determine (a) whether long-term exposure to viscous flow results in a reduction in MD membrane surface roughness over time, (b) the net effect of long-term exposure of MD membranes to viscous flow, elevated temperature, and salinity on membrane hydrophobicity, and (c) the relative contributions of each of these three variables to changes in membrane surface properties over time.

## **Progress Since the Beginning of the Project**

### *Experimental System Development*

The first stage of research involved the design and construction of a bench-scale MD system that was capable of continuous operation for long time periods while maintaining constant operating conditions and withstanding high temperatures. A photo and schematic of the long-term MD system are shown in Figure 2. A key feature of the design was to use non-metallic or titanium parts, in order to avoid accumulation of corrosion byproducts on the membrane surface during long-term experiments. The feed solution's concentration was kept constant through the use of an automated valve switching system that periodically replenished the feed tank with pre-heated distilled water over time. The thermal driving force was provided by a plastic-coated inline heater and a recirculating chiller connected to a titanium heat exchanger.



**Figure 2:** (a) Photo and (b) schematic of long-term bench-scale membrane distillation testing system.

*Experiments and Methods*

Numerous experiments were performed with a flat-sheet, expanded polytetrafluoroethylene (ePTFE) membrane, and these experiments were performed in two phases. Phase 1 involved operation of a long-term 100-day experiment and operation of a shorter-term 20-day experiment with scaling. The first experiment was used to determine if membrane hydrophobicity decreases during long-term exposure to viscous flow with elevated temperature and high salinity. The second experiment provided opportunity for comparison of changes to the membrane surface with and without scaling, and provided the opportunity to evaluate changes in membrane surface properties during shorter exposure periods. Phase 2 involved a series of three 30-day experiments that were used to separate the effects of temperature and salinity on changes in the membrane surface over time. The experimental conditions are summarized in Table 1.

**Table 1:** Experimental matrix.

Experiment Number	Feed Inlet Temperature (°C)	Distillate Inlet Temperature (°C)	Feed Salinity (g/L NaCl)	Flow Rate (L/min)	Time (days)
1	65	38	200	1.5	100
2	65	38	200	1.5	20
3	45	38	200	1.5	30
4	65	38	5	1.5	30
5	65	38	200	1.5	30

MD system performance was evaluated through monitoring of water flux over time, and membrane surface characterization was carried out through surface roughness measurements with atomic force microscopy (AFM), surface imaging with scanning electron microscopy (SEM), and surface elemental composition analysis with energy-dispersive x-ray spectroscopy (EDS). Membrane hydrophobicity was quantified with the contact angle – the angle between the membrane surface and a drop of water placed on that surface.

*Results and Discussion*

The results of the 100-day experiment clearly demonstrated a significant change in membrane surface properties and a decrease in performance (i.e., water flux) that correlated with a decrease in membrane hydrophobicity. A significant decrease in membrane surface roughness was observed on the feed (hot) and distillate (cool) sides of the membrane, and these decreases in surface roughness correlated with decreased contact angles (i.e., hydrophobicity) on both sides of the membrane. SEM images appeared to show a fouling layer on the feed side; elemental analysis with EDS confirmed the presence of a fouling layer. Results from the 20-day experiment, which included short-term scaling of the membrane with NaCl crystals approximately halfway through the experiment, also demonstrated the presence of a fouling layer confirmed with SEM and EDS analyses. The results of this 20-day experiment also demonstrated significant decreases in water flux over time, and membrane surface roughness and contact angle on the feed and distillate sides.

While the membrane surface was fully covered by a fouling and/or scaling layer on the feed side of the membrane in both the 100- and 20-day experiments, significant changes to the actual membrane surface were able to be observed on the distillate side in both experiments. These results indicated that significant changes to the membrane surface could be observed even in twenty days of operation. The results also indicated that the system design needed to be altered to prevent foulants from entering the system, so that changes to feed-side membrane properties could be observed. The most likely pathway that foulants were determined to be entering the system was through the heated replenishment tank (see Figure 2b), which had a partly open top required for insertion of the submerged heater and mixer. Considering this, the heated replenishment tank was removed from the system, and the feed tank was replenished with room-temperature water. Initial testing indicated that this did not negatively impact temperature stability in the MD system, so the series of three 30-day experiments were operated without the heated replenishment tank.

The first 30-day experiment (Experiment 3 in Table 1), with a 45 °C and 200 g/L feed solution, served as the low-temperature feed solution experiment. The second 30-day experiment (Experiment 4 in Table 1), with a 65 °C and 5 g/L feed solution, served as the high-temperature feed solution experiment. The third 30-day experiment (Experiment 5 in Table 1), with a 65 °C and 200 g/L feed solution, served as a comparison experiment for the first and second 30-day experiments to separate the effects of temperature and salinity on changes to the membrane surface. Significant changes in feed-side membrane surface properties were observed qualitatively by comparing SEM images of virgin membranes to those of used membranes for all three experiments; similar changes were observed on the distillate side, but to a lesser extent. EDS results showed that the used membrane samples were composed solely of membrane material, and were not coated with a fouling or scaling layer. These results indicate that long-term exposure to viscous flow with elevated temperature and high salinity can result in permanent changes to the membrane surface structure.

Comparison of SEM images from the three 30-day experiments shows much more significant changes to the membrane surface in the two experiments with a 65 °C feed solution, indicating that higher temperatures result in more significant changes to the membrane surface. Comparison of SEM images from the two 65 °C experiments – one with a 5 g/L and the other with a 200 g/L feed solution – does not show a significant difference in changes to the membrane surface. This indicates that salinity does not play a significant role in the changes to the membrane surface during long-term experiments. These qualitative results (SEM images) were confirmed by measured decreases in membrane surface roughness and contact angle, indicating that changes in membrane surface characteristics caused by long-term exposure to flow with elevated temperature can reduce membrane hydrophobicity over time

– even in the absence of fouling or scaling. The observed decreases in membrane hydrophobicity (i.e., contact angle) also correlated with a decrease in water flux over time in all three 30-day experiments, indicating that the decreases in hydrophobicity result in decreases in MD system performance.

## **Conclusions**

The results presented indicate that long-term operation of MD systems can result in significant changes in membrane surface characteristics, on a time-scale as short as twenty days. Changes in membrane surface properties were measured qualitatively with SEM imaging, and elemental analysis results using EDS confirmed that the observed changes were due to changes in the membrane surface structure, rather than fouling or scaling. The qualitative changes to the membrane surface observed through SEM imaging were confirmed quantitatively through decreased surface roughness and contact angle in each experiment. Decreased contact angle is indicative of decreased hydrophobicity. Comparison of SEM images and measurements of membrane surface roughness between experiments indicated that feed solution salinity did not play a significant role in the changes to the membrane surface, but high-temperature was responsible for the majority of the changes to the membrane surface. The observed decreases in contact angle (i.e., hydrophobicity) in each experiment correlated with decreased water flux over time, indicating that long-term exposure to flow with elevated temperature can result in changes in membrane hydrophobicity that negatively affect MD system performance.

MD can provide significant benefits to the water treatment community through its ability to effectively treat high-salinity feed solutions, while using alternative energy sources such as solar thermal or low-grade waste heat. However, the long-term performance of membranes that are commonly used in MD, like ePTFE, must be adequately assessed before they can be implemented in order to realize the benefits that MD can provide to the water treatment community. The results of this study are important because they assess the ability of ePTFE membranes, which are already used for other fully commercialized water treatment processes like microfiltration, to maintain satisfactory performance under the unique operating conditions in long-term MD experiments (high temperature and salinity). Because the ePTFE membranes presented in this research have been shown to have difficulty maintaining adequate performance during long-term experiments, further research should focus on identifying whether similar behavior occurs with other widely available hydrophobic membranes like those made from polyvinylidene fluoride or polypropylene. Further research could also be focused on the development of hydrophobic coatings that are more resilient and less prone to the types of changes in surface properties observed in this research. This research serves the greater good by identifying the major causes of decreased performance of MD membranes during long-term experiments, while providing information that can be used to design better membranes for use in MD systems, allowing the benefits of MD for desalination and water reuse applications to be fully realized.

## **Journal Articles Associated with this Research**

A.L. McGaughey, R.D. Gustafson, A.E. Childress, Effect of long-term operation on membrane surface characteristics and performance in membrane distillation, *Journal of Membrane Science*, 543 (2017) 143-150.

R.D. Gustafson, A.L. McGaughey, S. McVety, A.E. Childress, Effects of solution temperature and salinity on changes in membrane hydrophobicity in long-term membrane distillation experiments, *Journal of Membrane Science* – In preparation for submission in May 2018

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## NWRI GRADUATE FELLOW FINAL PROGRESS REPORT

DATE: May 2018

Project Title: Mechanisms and Sustainability of Wavelength-Tailored Ultraviolet Drinking Water Disinfection for Small Systems

Graduate Fellow: Natalie Hull

Advisor: Dr. Karl Linden

Institution: University of Colorado Boulder

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### Introduction

This research was part of the EPA-funded DeRISK (Design of Risk-reducing, Innovative-implementable Small-system Knowledge) research center investigating solutions for sustainable water treatment technologies and strategies that are appropriate for small systems in the U.S. I investigated novel sources of ultraviolet (UV) light that output specific wavelengths, including light emitting diodes (LEDs) and excimer lamps, for drinking water disinfection. My research uses fundamental molecular biology investigations to expand understanding of how UV disinfection works, so that we can optimize based on wavelength specific responses. This research expands existing knowledge beyond the understanding that genome damage causes UV disinfection. Growing evidence indicates that protein damage also causes UV disinfection<sup>1</sup>. My research also evaluated and piloted a novel mercury free UV-LED reactor to prove how this research translates in to the field.

LEDs and excimer lamps are new UV sources that can be designed to emit specific wavelengths, as shown in Figure 1. These new sources could be more sustainable than traditional UV lamps because they do not contain toxic mercury, have lower power requirements, are more compact, and are becoming more efficient as materials science advances. Because disinfection does not depend on the UV lamp type, these sources disinfect bacteria, protozoa, and viruses just as well as traditional mercury UV lamps for a given dose and wavelength<sup>2</sup>.

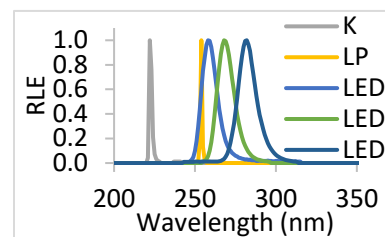


Figure 2 - Relative Lamp Emission (RLE) spectra for the KrCl excimer lamp (K), low pressure mercury lamp (LP), and light emitting diodes (LEDs) used in this study.

U.S. EPA guidance for UV disinfection of drinking water is governed by virus inactivation using traditional low pressure (LP) mercury lamps that emit a single UV wavelength<sup>3</sup>. Because viruses are resistant to this wavelength, the UV dose needed to achieve required 4-log viral inactivation (99.99% reduction) is high enough to sometimes be cost-prohibitive for small systems. However, microorganisms vary in their sensitivity to different UV wavelengths<sup>4</sup>. For example, adenovirus is resistant to single-wavelength (monochromatic at 254 nm) LP UV disinfection, but is more susceptible to multi-wavelength (polychromatic) medium pressure (MP) UV disinfection<sup>5</sup>. This varying wavelength sensitivity offers an opportunity to optimize UV disinfection. Additionally, draft regulatory guidance will allow future UV disinfection to be credited for disinfection at all wavelengths across the UV-C spectrum.<sup>6</sup>

*Hypotheses:*

- (1) By optimizing wavelength selection, reactor design, and operation of mercury-free UV sources, we can achieve equivalent or better disinfection performance with less electricity, thereby improving the sustainability of the UV disinfection process.
- (2) When optimized wavelengths are used, lower UV doses will be required, increasing the attainability (affordability and feasibility of implementation) of this technology for small systems.

*Objectives:*

- (1) Determine wavelength-specific protein damage, genome damage, and inactivation for indicator organisms and pathogens using single or sequential exposures of mercury-free (LED and excimer lamp) and/or traditional UV sources.
- (2) Validate disinfection performance at the bench and implement in a local small system the first commercially available LED flow-through reactor to study sustainability, robustness, and disinfection performance over time.

**Progress**

*Approach:*

A benchtop UV LED system emitting various peak wavelengths from 255 – 285 nm shown in Figure 1 was supplied to our lab through an industry partnership. A KrCl excimer lamp emitting at 222 nm was also supplied through another industry partnership. We tested these wavelengths to more efficiently target absorbance of DNA and proteins, to simulate the disinfection advantages previously identified for polychromatic MP UV emissions<sup>7</sup>. We are testing these novel, non-mercury UV sources when illuminated individually or in sequence to determine the optimum disinfection wavelength or combination(s) of wavelengths. These UV sources were also tested with a traditional LP lamp to determine if wavelength-specific sources targeting DNA and proteins can enhance LP disinfection to lower the required dose to achieve 4-log virus disinfection for regulatory compliance. The ability to disinfect was being measured by viral infectivity assays molecular assays for protein and nucleic acid damage. The effectiveness of disinfection was normalized to UV dose (fluence) and energy use, enabling comparisons between UV source combinations and modes of operation.



A flow-through LED reactor was designed using input from previous studies from our lab. We evaluated it at bench-scale and it is being piloted at a local small system. Over the course of 1 year as shown in Figure 2, the UV transmittance (UVT) in the UV reactor influent was measured daily, and correlated with temperature, pH, and turbidity. Bi-weekly samples were collected in the treatment plant influent, slow sand filter effluent, and existing chlorine disinfection effluent for comparison to the pilot UV LED disinfection effluent, as shown in the water treatment plant schematic in Figure 2. Analytes for these bi-weekly samples included ATP, total coliform, *E. coli*, and TOC. Continued disinfection performance was monitored using quarterly indicator virus challenge tests. Data on electrical and maintenance requirements were collected for life cycle sustainability analyses performed by partner DeRISK researchers.

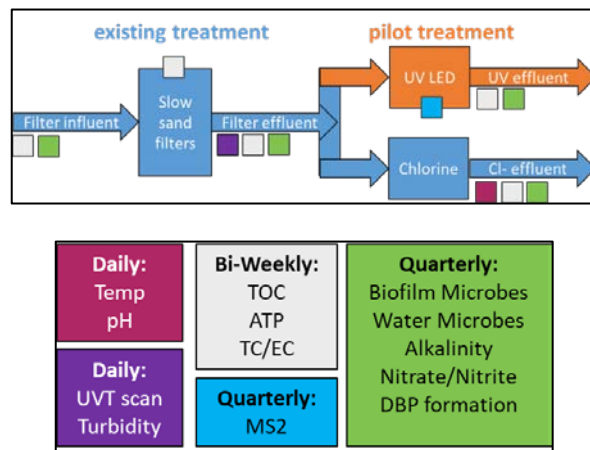


Figure 3 Schematic of existing treatment and pilot UV LED disinfection, showing color-coded sampling locations and schedule for the pilot study.

### Results:

Research for this project built on our lab's previous evaluation of UV LEDs for inactivating *E. coli* bacteria, MS2 coliphage (nonpathogenic surrogate virus), adenovirus 2 (pathogenic virus), and *B. pumilus* bacterial spores<sup>8</sup>, and studies of the contribution of wavelength-specific protein damage to adenovirus inactivation<sup>1</sup>. My study used the same techniques to measure wavelength-specific damage to MS2 proteins and demonstrated that protein damage similarly contributes to MS2 inactivation, likely because both viruses rely on protein integrity to attach to and infect their host cell. I also used a novel enzyme-linked immunosorbent assay (ELISA) to directly quantify wavelength-specific contribution of genome damage to both adenovirus and MS2 inactivation to complement previous research in our lab using indirect (enzyme based) methods to quantify wavelength specific genome damage to MS2 and adenovirus<sup>9,10</sup>. These mechanistic studies demonstrated that the viral surrogate MS2 has similar molecular disinfection response to the target pathogen adenovirus.

The KrCl excimer lamp was tested to determine MS2 inactivation dose-responses for the first time. The excilamp and LEDs were tested alone and when combined sequentially together or with an LP UV lamp. We found the excilamp to be most effective based on a given UV dose, and that disinfection was improved over LP alone when combining the LP and excilamps in sequential exposures. We also found synergy from the order of exposure when MS2 was exposed to either the excimer or the LP lamp before LEDs. When considering electricity requirements for a given level of disinfection, the excilamp is already competitive with LP UV, and all sequential exposures are competitive with MP UV.

The MS2 disinfection performance of the flow-through UV LED reactor was measured at various flowrates and UVTs measured at 285 nm (the wavelength emitted by the LEDs) at the bench in dechlorinated tap water. MS2 disinfection was measured in slow sand filter effluent water after installation at the local small system in January (Figure 3), and once per quarter over the course of one year. Experimental results of MS2 disinfection upon installation, and in November and the following January aligned well with the novel approach of combined variable model<sup>11</sup> predictions from bench testing. In May and August, MS2 was disinfected more effectively than predicted, possibly due to light scattering or photosensitization. The UV-LED reactor was resilient for one year with zero maintenance to maintain disinfection performance. The LEDs lost only 25% power after continuous operation, and the unit cost an estimated <\$25 to run, treating 0.5 lpm at an MS2 reduction equivalent dose of at least ~40 mJ/cm<sup>2</sup> all year.



Figure 4 (a) UV-LED at Jamestown, CO drinking

## Conclusions

This research increased knowledge of how different UV wavelengths damage the molecules that make up infectious agents. Molecular studies of viral surrogate and pathogen contribute confidence to validations and test results for novel wavelength combinations using this viral surrogate. Use of a simple viral surrogate, MS2 coliphage, to assess genome and protein damage is a novel technique for evaluation of performance of these UV sources, and could be useful after further method development for on-site analysis of UV-induced damage for faster and more accurate UV validations. These molecular tools may also eventually prove useful for on-site or even online monitoring of UV disinfection system performance.

This research also showed that synergy can be achieved to minimize electricity requirements and maximize disinfection, when using a tailored wavelength combination of these novel mercury free sources. This could increase sustainability of UV disinfection for systems of all scales, including small systems. This is new and exciting because synergies between wavelength-specific excimer lamps, LEDs, and traditional LP lamps have not previously been investigated to determine how molecular protein and nucleic acid damage contribute to increased UV disinfection efficiency (especially at low wavelengths). Future research should investigate whether simultaneous exposure to these various types of UV sources results in synergy, and whether operation of these sources in pulsed mode (excilamps and LEDs but not LP lamps) results in increased disinfection and/or electrical efficiency.

This first longitudinal evaluation of a flow-through UV LED system provides data necessary for practical operation, life cycle analyses, design improvements, and scale-up, allowing faster adoption of wavelength tailored UV disinfection systems in the future. Future studies should examine scaled-up systems implemented at scaled suitable for meeting full municipal flow needs. Future studies should also optimize reactor design for lower water qualities to prove efficacy of wavelength tailored disinfection for reclaimed and waste water.

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### Relevant Presentations and Publications

**Hull NM** and Linden KG (Feb 2018, conference presentation). Sequential LED and excimer lamp exposures for viral UV disinfection. IUVA Americas, Redondo Beach, CA.

***NMH won 1<sup>st</sup> place student presentation***

Linden KG, **Hull NM** (presenter), Sholtes KA, and Beck SE (Oct 2017, conference presentation). UV LEDs for small systems: a revolution in robust and effective disinfection? International IWA S2Small Conference on Sustainable Solutions for Small Water and Wastewater Treatment Systems, Nantes, France.

**Hull NM** and Linden KG (Oct 2017, invited presentation). Mechanisms and Sustainability of Wavelength-Tailored Ultraviolet Drinking Water Disinfection for Small Systems. Environmental Engineering Seminar, CU Boulder, CO.

**Hull NM** and Linden KG (Sep 2017, conference presentation). Longitudinal Disinfection Performance of a UV LED Reactor Piloted at a Drinking Water Plant. IUVA World Congress, Dubrovnik, Croatia.

***NMH tied for 2<sup>nd</sup> place student presentation***

**Hull NM**, and Sholtes KA (co-first authors) (Feb 2017, invited presentation). UVC LEDs and Disinfection. UVC LED Review Workshop for IUVA Americas, Austin, TX.

**Hull, NM** and Linden KG (Jan 2017, webinar). UV Wavelength-Specific Damage and Inactivation of MS2. DeRISK Center Drinking Water Webinar, Hosted in Boulder, CO.

**Hull, NM**, Linden KG (Nov 2016, conference presentation). Ultraviolet Wavelength- and Dose-Dependent Inactivation and Molecular Damage of MS2 Coliphage. WQTC, Indianapolis, IN.

Beck SE, **Hull NM** (presenter), and Linden KG (Feb 2016, conference presentation). Ultraviolet Wavelength- and Dose-Dependent Damage of Adenovirus Proteins. IUVA World Congress, Vancouver, BC, Canada.

***NMH won 2<sup>nd</sup> place student presentation***

Beck SE, **Hull NM**, Poepping C, and Linden KG (2017). Wavelength-Dependent Damage of Adenovirus Proteins Across the Germicidal UV Spectrum. *ES&T* 52(1):223-229.

**Hull NM**, Beck SE, and Linden KG (manuscript in preparation 2018). Molecular Damage of MS2 and Adenovirus Across the Germicidal UV Spectrum.

**Hull NM**, and Linden KG (manuscript in preparation 2018). Validation and Small-System Implementation of the First Commercial UV-C LED Water Treatment Reactor.

**Hull NM** and Linden KG (submitted to *Water Research*). Combining Novel UV Sources for Viral Disinfection Compliance at Lower Doses than Conventional Mercury Lamps.

## NWRI GRADUATE FELLOW SEMI-ANNUAL PROGRESS REPORT

DATE: May 2018

Project Title: Charge Mosaic Membranes from Ink-Jet Printing for Improved Water Reuse and Treatment

Graduate Fellow: Mark J. Summe

Advisor: William A. Phillip

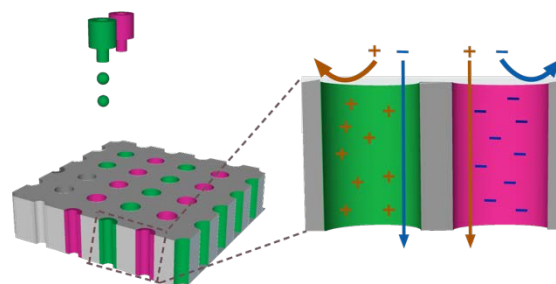
Institution: University of Notre Dame

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### Introduction

Desalination by reverse osmosis is an effective method of producing potable water, but the process is energy intensive due to fundamental thermodynamic restrictions.<sup>1</sup> Therefore, in addition to desalination, water reuse will be an important component of the water supply portfolio. Water reuse attempts to use non-traditional sources for a beneficial purpose, (e.g., reclaimed wastewater for irrigation). This process will be another source for potable water and requires a fraction of the energy required by desalination. The presence of dilute ionic contaminants such as nitrate, perchlorate, and heavy metals are a notable concern that hinder the advancement of water reuse due to their well-documented effects on human health.<sup>1</sup> This proposal seeks to develop an innovative technology to remove dilute ionic species from aqueous feed streams for improved water reuse. Specifically, charge mosaic membranes (CMMs) that allow charged solutes to permeate more rapidly than water, will be designed and fabricated. Previously, to remove contaminants from wastewater, water is forced through a size-selective membrane that rejects contaminants too large to flow through the membrane pores. Alternatively, the use of CMMs will make it possible to remove only that small percent of contaminant rather than forcing 99.9% of solution through a size-selective membrane.

Due to past difficulty in producing charge mosaics with well-defined and controlled nanostructures, their development has lagged severely. To overcome these difficulties, our research group recently developed a promising avenue to CMM design by ink-jet printing polymeric materials onto a structural template.<sup>2</sup> which is versatile, fast, and consistent and does not require harsh chemical treatments. Figure 1 illustrates the fabrication process of these mosaic membranes. Polyelectrolytes are printed on a polycarbonate track etched membrane into discrete regions. Using the striped pattern, positively charged and negatively charged polyelectrolytes are alternatively printed to form the mosaic. Selecting certain polyelectrolytes and printing conditions offers a wide array of functionalities and nanostructures for this system.<sup>3</sup> This ability will enable a fundamental understanding of how the performance of these membranes relates to their basic physio-chemical features—something that is lacking in prior studies and prevents the systematic design of more effective charge mosaics.



*Figure 5 Schematic of the fabrication process for printing the mosaic structure.*

## Research Plan

Using the control over the nanostructure and chemical functionality of mosaic membranes provided by these new fabrications methods, I will generate rigorous structure-property-performance relationships for these membranes to enable a novel design for CMMs for removal of dilute hazardous contaminants from reclaimed wastewater. By studying the effect different modifications to the structure has on the physical and chemical properties of the membrane, we will elucidate a fundamental understanding of the transport phenomena that dictates the performance of these membranes, which has previously been lacking.

CMMs facilitate the transport of dissolved salts because the charged ions are drawn electrostatically to the oppositely charged nanopores. This produces an enrichment of salt, which is a greater concentration of salt in the permeate. This results from salt being preferentially transported over water. Membranes of a single charge reject salt because the coions (i.e. ions of the same charge as the membrane) are electrostatically repelled, and the counterions (i.e. ions of opposite charge) are bound to the coions because of electroneutrality. The constraint of electroneutrality dictates that the overall charge of a solution must be neutral, meaning that there must be an equal concentration of anions and cations. This condition is maintained in a CMM, which allows both ions to flow through oppositely charged regions of the membrane.<sup>4</sup>

Three conditions are necessary for the mosaic to achieve enrichment:

- 1) Charged domains must traverse the entire membrane thickness and be closely packed;
- 2) Charged densities of charged regions should be equal in magnitude and opposite in charge;
- 3) Overall surface charge should be neutral.

Harsh chemical treatments and difficulty in orienting domains perpendicular to the surface have caused development of CMMs to lag severely.

Our lab group has already published two articles on printing membranes using an inkjet printer.<sup>2,5</sup> In the second paper, we described how we produced the CMM structure using poly(vinyl alcohol) (PVA) blended with either a polycation or polyanion to produce positively-charged or negatively-charged regions, respectively. Our membranes demonstrate the characteristic salt enrichment of CMMs with significantly easier processing conditions and shorter processing times than typical CMMs. This simple and rapid method of producing CMMs will provide an avenue for exploring the fundamental ion transport mechanism driving this enrichment behavior.

To understand the ion transport mechanism, we examine our flux equation below:

$$\mathbf{j}_i = \mathbf{j}_i^{\text{conv}} + \mathbf{j}_i^{\text{diff}} + j_i^{\text{em}} = \vec{\mathbf{u}}C_i - D_i\nabla C_i - \mu_i\mathcal{F}C_i\nabla\varphi$$

where  $j_i^{\text{conv}}$ ,  $j_i^{\text{diff}}$ ,  $j_i^{\text{em}}$  are the convective, diffusive, and electromigratory flux components, respectively, which correspond each to a different driving force, namely a pressure drop, concentration gradient, and electrostatic potential gradient, respectively, as shown in the right-hand side of the equation. Initially these experiments were executed in a dead-end filtration set-up, where the convection of the solvent tends to dominate over the other terms.

To isolate the diffusion and electromigration terms, the membranes were loaded into a diffusion cell, where the membrane is placed between two reservoirs. One reservoir contained a salt solution of known concentration, and the other contained DI water. The concentration and electrostatic potential gradients drive the transport of ions across the membrane. Plotting the downstream concentration as a function of time yields a diffusion curve of which the slope is proportional to  $P$ , the salt permeability, which is representative of the flux of ions across the membrane. Using these diffusion cell experiments, we will investigate the ion transport mechanisms of different salts across different types of membranes (*i.e.* anionic, cationic, and CMM) by comparing the permeability values across these salts and membranes.

### Progress to Date

The current design of the CMMs used poly(diallyldimethylammonium chloride) (PDADMAC) as the polycation and poly(styrene sulfonate) (PSS) as the polyanion. We examined the performance of two symmetric salts (*i.e.* KCl and  $\text{MgSO}_4$ ) and two asymmetric salts (*i.e.*  $\text{K}_2\text{SO}_4$  and  $\text{MgCl}_2$ ) at different concentrations and through membranes monofunctionalized with PDADMAC (positively-charged) and PSS (negatively-charged) each and a CMM.

For the monofunctionalized membranes, the asymmetric salts dominated the flux, with the divalent counterion (*e.g.*  $\text{Mg}^{2+}$  for PSS) had the highest flux, and the divalent coion (*e.g.*  $\text{SO}_4^{2-}$ ) had the lowest flux. This seems to indicate that the electrostatic interactions are dominating. The strong electrostatic attraction between the charges on the membrane and the divalent counterion drives the ions to the boundary layer and across the membrane. Conversely, the strong electrostatic repulsion between the membrane and its coion restrict passage of the ion. The need to maintain electroneutrality controls the co-transport of salt's corresponding monovalent ion.

However, in the case of the CMM, it is the symmetric salts that have the highest and lowest transport. In particular, the symmetric monovalent salt, KCl, has the highest permeability value. This is attributed to the ability of the membrane to electrostatically attract the ions at even rates, transporting them rapidly across the membrane and maintaining electroneutrality. By comparing this to a membrane with no surface charge, which removes an electrostatic contribution, we found that the KCl permeability is much higher through a CMM than an uncharged membrane. This indicates that there is some additional interaction beyond diffusion at play to increase the KCl transport, namely electrostatic attraction.

Furthermore, we developed a theoretical model from the governing ion flux equations based on Donnan theory and the electric double layer to predict how permeability changes with upstream concentration for the different membrane types. It was found that increasing salt concentration increases permeability in single-charged membranes but decreases permeability in CMMs. This is consistent with experimental results and is explained by the different electrostatic partitioning. The exclusion of the membrane's coion coupled with electroneutrality restricts entrance of salt into single-charged membranes until concentrations are sufficiently high enough to screen the surface charge. CMMs facilitate transport *via* electrostatic attraction of both ion, and high concentrations screen these favorable interactions, resulting in a lower permeability.

### Conclusions

We have identified that electrostatic attraction plays a significant factor in driving salt ions across charged membranes. For the CMM, the symmetric monovalent salt has the highest permeability. This is

because both ions from the salt are transported evenly. There is an uneven electrostatic attraction/repulsion for the asymmetric salts through a CMM. This differs from the monofunctionalized membrane where the asymmetric salts have the highest and lowest transport due to strong electrostatic attraction and repulsion for the divalent counterion and coion, respectively.

### **Next Steps**

We will continue to explore the effects of different salts on the transport through a charge mosaic membrane, particularly by investigating the effect of different monovalent anions and cations.

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