

# **NATIONAL WATER RESEARCH INSTITUTE**

## **2008 - 2009 NWRI Fellowship Program Progress Reports**

June 2009

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## NWRI Fellows Award Year 2008 – 2009

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## NWRI Fellowship Program Summary

Our nation faces a number of challenges in meeting the needs of a growing population requiring more water resources and protection against emerging issues, such as water scarcity and the quality of our water supplies. Under the Fellowship Program, NWRI awards fellowship funding to graduate conducting research related to water supply, water resources, water quality, and technologies and treatment.

The Fellowship Program was established to:

- Support and encourage graduate students to investigate and develop the innovative procedures, technologies, and policies crucial to resolving our critical water needs.
- Advance the state-of-knowledge in the areas of water treatment technologies, water quality, water policy and economics, engineering, public health, risk assessment, and water resources management.
- Highlight the water and wastewater industries as attractive career choices.

### *Selection Process*

The Fellowship Committee, a subcommittee of the Research Advisory Board, selects fellowship recipients based on the merit and strength of their application, as well as the demonstrative promise of their proposed research towards improving public health, water resources, and technology.

### *Program Funding*

Fellowship recipients are typically awarded up to \$10,000 a year (limited to 3 years). NWRI's Fellowship program is underwritten by the Joan Irvine Smith & Athalie R. Clarke Foundation, NWRI Member Agencies, NWRI Corporate Associates and community partners.

NWRI Member Agencies Include:

- Inland Empire Utilities Agency
- Irvine Ranch Water District
- Orange County Sanitation District
- Orange County Water District
- Los Angeles Department of Water and Power
- West Basin Municipal Water District

NWRI's Corporate Associates include:

- Cargill, Inc.
- Carollo
- CDM
- CH2M HILL
- Kennedy/Jenks Consultants
- MWH
- Malcolm Pirnie, Inc.
- United Water - SUEZ

Current community partners include:

- American Membrane Technologies Association (AMTA)
- Southern California Salinity Coalition (SCSC)

### *NWRI Graduate Fellowship Research Conference*

One of the highlights of the Fellowship Program is the NWRI Graduate Fellowship Research Conference. Fellowship recipients are given the opportunity to present their research and receive valuable feedback from the audience, which includes industry professionals, members of academia, and policy makers. The product of this conference is the *NWRI Annual Graduate Fellowship Research Conference Proceedings*, a set of proceedings that includes extended abstracts.

More information about the Fellowship Program may be found at [www.nwri-usa.org/fellowship.htm](http://www.nwri-usa.org/fellowship.htm).

**Brian Badgley**  
University of South Florida

*Potential For Benthic Vegetated Habitats To Serve As An Important Refuge For Water  
Quality Indicator Bacteria In A Subtropical Watershed*

Expected Graduation Date: May 2009  
Advisor: Valerie Harwood, Ph.D.

**Brian Badgley, University of Florida  
Ph.D. Program Progress Report**

I am currently finishing my fifth year of my Ph.D. program at the University of South Florida. I am anticipating the completion of my dissertation during the summer of 2009, with an expected graduation date of Fall 2009. As of the writing of this progress report, I have fulfilled the following programmatic requirements for my degree:

- All required coursework has been completed and the required number of credit hours will be completed by my expected graduation date.
- I have completed a dissertation proposal that has been approved by my advisory committee.
- I have passed both my written and oral qualifying examinations and advanced to candidacy.

My research progress has also been progressing well and I am on track to complete all of my proposed research in time for my anticipated graduation date. In terms of my NWRI proposal, I outlined the following research goals:

- Goal 1: Determine if *Enterococcus* routinely persists in natural vegetated bottoms of lakes and rivers and if particular strains are surviving more successfully than others.
- Goal 2: Examine the potential for benthic *Enterococcus* strains associated with vegetation to be resuspended into the water column during high flow events and how resuspension rates are affected by important variables such as hydrodynamics, cell counts, and vegetative biomass.

Sampling for Goal #1 was completed in May of 2008, and analysis and modeling of the importance of enterococci densities has been completed as was reported in the October 2008 progress report. Since then, I have been completing the molecular analysis of enterococci isolates that will allow me to determine population structure for my samples, and begin to analyze differences in strain diversity and persistence in the environment. I currently have about 80% of the strains completed and should finish the remaining isolates in the next month or two. That will conclude the data analysis for this chapter of my dissertation, and I plan to draft a manuscript for publication over the summer.

Data collection for the second goal outlined above (examining the potential for the resuspension of benthic enterococci) was attempted last summer and early winter of 2009, but was found to be difficult to do experimentally. Under the advisement of my committee, we have decided to take a theoretical approach to this problem, and I am currently working with a faculty member in the Department of Geology here at USF to determine the best means of doing this. Using real measurements of hydrodynamic data, as well as estimates of wave data during storm events, I am attempting to estimate sediment resuspension under a range of conditions for several of my sites. These estimates, coupled with the landscape data and modeling work from the previous chapter

of my dissertation, will allow me to estimate resuspension of enterococci and determine the potential for such resuspension events to interfere with water quality assessment. I expect the analysis will be completed by June 2009, and the manuscript will be written over the rest of the summer.

My third chapter, the mesocosm work which was outlined in my October 2008 progress report, is complete and has been submitted to *Environmental Microbiology* for peer-reviewed publication.

### **Submitted Manuscripts:**

**Badgley BD, Harwood VJ** (submitted) The effects of submerged aquatic vegetation on the persistence of environmental populations of *Enterococcus spp.* in outdoor mesocosms.

### **Related Oral Presentations:**

**Badgley BD, Harwood VJ** (2007) The effects of submerged aquatic vegetation and temperature on the survival of enterococci bacteria in controlled mesocosms. *Southeastern Branch of the American Society for Microbiology*, Auburn, AL.

**Badgley BD, Harwood VJ** (2008) The potential for benthic vegetated habitats to serve as an important refuge for water quality indicator bacteria in a subtropical watershed. *National Water Research Institute Graduate Fellowship Research Conference*, Washington, DC

**Badgley BD, Harwood VJ** (2008) Gauging The Relative Importance of Sediment and Submerged Aquatic Vegetation as Reservoirs for Fecal Indicator Bacteria and Their Potential Impact to Water Quality Monitoring. *Southeastern Branch of the American Society for Microbiology*, Jacksonville, FL.

### **Related Poster Presentations:**

**Badgley BD, Harwood VJ** (2008) The Importance of Submerged Aquatic Vegetation as a Potential Habitat for Persistent Strains of *Enterococcus spp.* *Annual Meeting of the American Society for Microbiology*, Boston, MA.

**Badgley BD, Harwood VJ** (2009) Investigating the Importance of Sediment and Submerged Aquatic Vegetation as Environmental Reservoirs for Water Quality Indicator Bacteria. *Annual Meeting of the American Society for Microbiology*, Philadelphia, PA.

**Katherine Benko**  
Colorado School of Mines

*Treatment of Co-Produced Water for Beneficial Use in the Western US using Novel  
Integrated Membrane Systems*

Expected Graduation Date: May 2009  
Advisor: Jorg Drewes, Ph.D.

**Katie Benko, Colorado School of Mines  
Ph.D. Program Progress Report**

**NWRI Student Fellowship Progress Report September 2007 to September 2008  
Beneficial Use of Produced Water in the Western US Using Novel Integrated  
Membrane Systems**

**1.0 Research Focus**

The objective of this research is to evaluate the suitability of ceramic ultrafiltration membranes as a pretreatment technology for desalination processes for produced water. Ceramic membranes are robust, chemically and thermally resistant, can produce high flux rates, and have high mechanical strength. In this study, ceramic membranes are compared to polymeric membranes as pretreatment for desalination technologies such as reverse osmosis and electrodialysis. This work aims to understand the contaminant rejection characteristics of ceramic membranes and the optimal hydrodynamic conditions for operating these membranes. The effects of pre-coagulation are also investigated to enhance contaminant rejection and decrease flux decline.

**2.0 Evaluation of operating parameters for ceramic membranes**

An experimental design was implemented to evaluate the impact of operating parameters on ceramic membrane performance. The parameters of interest are membrane configuration (# channels which relates to hydrodynamic conditions within the membrane channel), coagulation dose, cross flow velocity, trans-membrane pressure on membrane performance, and backwash. A half factorial experimental design was executed to evaluate these parameters.

Three response variables investigated:

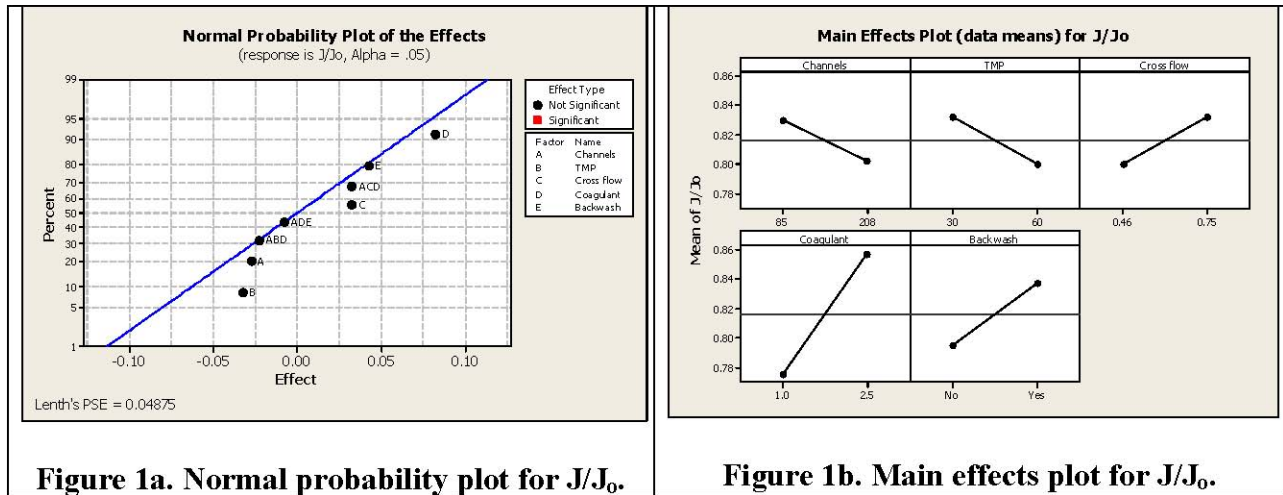
1.  $J/J_0$  after 15 gallons have been filtered
2. Absolute value of flux after 15 gallons have been filtered
3. Pure water permeability of fouled membrane after run

**3.0 Data Analysis**

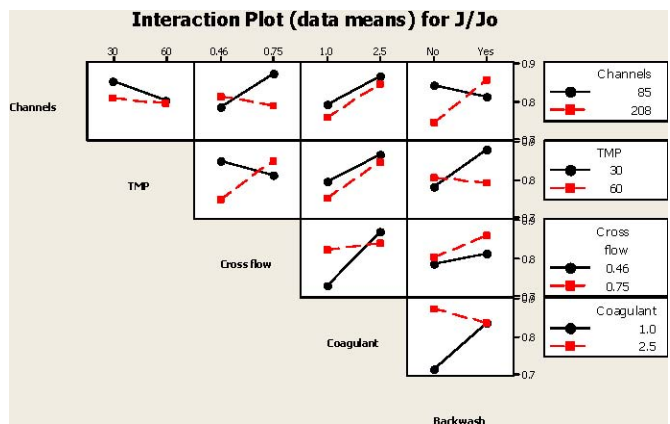
The following types of plots were generated to show the individual and interaction effects of each experimental factor: Normal probability plot of effects – negligible effects are normally distributed with a mean of zero and will fall along a straight line, significant effects will have nonzero means and will not lie along the straight line. Interactions plot – describes the interactions between different experimental factors Main effects plot – describes the effect of individual experiment factors

**4.0 Results**

The following graphs are from the data analysis done with the normalized flux response variable, Figure 1. Figure 1a shows which factors generated a significantly different response from the others. Figure 1b shows the influence of each factor individually on the normalized flux.



Only by using an experimental design is it possible to determine the effects of varying two experimental factors together to determine the interaction between two factors, Figure 2.



**Future Work**

Future work will be conducted to further revise the levels of the experimental factors to help elucidate the interactions between the factors. The transmembrane pressure used in the experimental design was too dominant to distinguish a difference in the response from the other factors.

Field work is also planned to take the test unit to the Raton Basin in Southern Colorado to test actual produced water from a coal bed methane well.

Ronald B. Linsky Fellowship for Outstanding Water Research

**Douglas F. Call**  
Penn State University

*Accelerating Microbial Fuel Cells to Full scale Application:  
An Investigation into Scalable Membranes for Use as Cathodes*

*Expected Graduation Date: May 2011  
Advisor: Bruce Logan, Ph.D.  
Ronald B. Linsky Fellow*

**NWRI Fellowship Progress Report – April 2009**  
**Douglas F. Call, Penn State University**  
**Ph.D. Program**

During the 2008 – 2009 academic year, I continued my studies as a PhD candidate in the field of Environmental Engineering at Penn State University. In May of 2008, I received my master's degree in Environmental Engineering and during the summer of 2008, I continued research towards my doctoral degree. As part of an ongoing collaboration between Penn State and the Ecole Centrale de Lyon in France, I moved to France in August 2008 to conduct part of my doctoral research related to microbial fuel cells (MFCs) and microbial electrolysis cells (MECs). The researchers at the Ecole Centrale have extensive experience in microbial community analysis and genomics, and I am applying many of their techniques and tools to study the microbial communities of MFCs and MECs. The work completed in France will be part of my final dissertation and I will return to Penn State in the summer of 2009.

Since the last progress report, I have published several articles and presented at many conferences throughout the world. I published or I am in the process of submitting the following articles during the 2008 – 2009 academic year:

- Call, D.; Logan, B. E., Hydrogen production in a single chamber microbial electrolysis cell lacking a membrane. *Environ. Sci. Technol.* **2008**, *42*, (9), 3401-3406.
- Call, D. F.; Merrill, M. D.; Logan, B. E., High surface area stainless steel brushes as cathodes in microbial electrolysis cells. *Environ. Sci. Technol.* **2009**, *43*, (6), 2179-2183.
- Cheng, S.; Xing, D.; Call, D. F.; Logan, B. E., Direct biological conversion of electrical current into methane by electromethanogenesis. *Environ. Sci. Technol.* **2009**. In press.
- Call, D. F.; Wagner, R. C.; Logan, B. E. Hydrogen production by *Geobacter* species and a mixed consortium in a microbial electrolysis cell. **2009**. In preparation.
- Logan, B. E.; Call, D.; Cheng, S.; Hamelers, H. V. M.; Sleutels, T. H. J. A.; Jeremiasse, A. W.; Rozendal, R. A., Microbial electrolysis cells for high yield hydrogen gas production from organic matter. *Environ. Sci. Technol.* **2008**, *42*, (23), 8630-8640

In May of 2008, our lab hosted the first International Microbial Fuel Cell Symposium at Penn State, and I acted as a student co-chair to help organize the event. I also presented the work from my master's thesis at the symposium. In September of 2008, I presented at the International Water Association (IWA) 6th World Water Congress in Vienna, Austria and in October of 2008, I presented work on MECs at the H2Expo in Hamburg, Germany. I also attended and presented at a conference dedicated to MFCs in France called the Electrochemically Active Biofilms Conference.

In order to further advance my understanding of a microbial identification tool known as Fluorescent In-Situ Hybridization (FISH), I attended a one week course at the Technical University of Munich (TUM) in Munich, Germany. At that course, I learned many of the newest FISH techniques, and I will apply these methods to study the microbial communities of MFCs.

I am very grateful for receiving the Ronald B. Linsky fellowship for a second year as it has allowed me to present at conferences worldwide and to attend the FISH course in Germany. Each of these experiences has enhanced my academic career by providing me with confidence in presenting my research and by teaching me new techniques and tools to advance my doctoral research. Without the support of NWRI, I would not have been able to participate in these events, and I appreciate the continued support.

**Christina C. Davis**  
Virginia Tech

*Simultaneous Prediction of Contaminant Removal and Particle Destabilization During  
Coagulation*

*Expected Graduation Date: May 2009*  
*Advisor: Marc Edwards, Ph.D.*

## NWRI Fellowship Progress Report

**Project Title:** Simultaneous Prediction of Contaminant Removal and Particle Destabilization During Coagulation

**Principal Investigator:** Christina C. Davis

**Date:** March 31, 2009

### Tasks Completed & Key Results:

The experimental plan tests the effects of natural organic matter (NOM) and various ions (aqueous silica, bicarbonate, sulfate, and calcium) on ferric chloride coagulation (Table 1). The plan includes both single-sorbate and dual-sorbate experiments. Measured response variables are sorption density, zeta potential, total organic carbon (TOC) removal, and UV<sub>254</sub> Absorbance removal.

To date, all single-sorbate experiments have been completed. Dual-sorbate experiments have also been completed with the exception of Set No. 2. Set No. 2 experiments will be undertaken in April.

*Table 1: Experimental Conditions for Single- and Dual-Sorbate Experiments*

Experiment No.	pH	Initial TOC (mg/L)	Initial SiO <sub>2</sub> (mg/L)	Initial HCO <sub>3</sub> <sup>-</sup> (mg/L)	Initial SO <sub>4</sub> <sup>2-</sup> (mg/L)	Initial Ca <sup>2+</sup> (mg/L)
<b>Single-Sorbate Experiments</b>						
Set 1 (SS01 – SS06)	5.5, 6.5, 7.5	2, 12				
Set 2 (SS07 – SS12)	5.5, 6.5, 7.5		10, 50			
Set 3 (SS13 – SS18)	5.5, 6.5, 7.5			45, 400		
Set 4 (SS19 – SS24)	5.5, 6.5, 7.5				15, 250	
<b>Dual-Sorbate Experiments</b>						
Set 1 (DS01 – DS12)	5.5, 6.5, 7.5	2, 12	10, 50			
Set 2 (DS13 – DS24)	5.5, 6.5, 7.5	2, 12		45, 400		
Set 3 (DS25 – DS30)	5.5, 6.5, 7.5	2, 12				40
Set 4 (DS31 – DS42)	5.5, 6.5, 7.5		10, 50	45, 400		
Set 5 (DS43 – DS48)	5.5, 6.5, 7.5		10, 50			40
Set 6 (DS49 – DS54)	5.5, 6.5, 7.5			45, 400		40

An overview of results from the single- and dual-sorbate tests with inorganic ions was provided in the October 2008 progress report. Data analysis is currently underway for the following conditions: single-sorbate TOC experiments (initial TOC=2 mg/L) at pH 7.5; single-sorbate TOC experiments (initial TOC=12 mg/L) at all pHs; dual-sorbate experiments (initial TOC=2 mg/L and silica) at pH 7.5; and dual-sorbate experiments (initial TOC=12 mg/L and silica). Key findings for the remaining experiments with organic carbon and silica are summarized below:

- Silica sorption to ferric flocs increased with increasing pH and initial silica concentration. As hypothesized, coprecipitation of silica with ferric iron led to sorption densities greater than the equivalent of a monolayer (~0.25 mol Si/mol Fe) in samples at pH 6.5 and 7.5. At pH

5.5, silica sorption densities greater than a monolayer were observed in the sample at high initial silica concentration (50 mg/L as SiO<sub>2</sub>).

- The average removal of UV-254 Absorbance, an indicator of NOM concentration, was greater than or equal to approximately 88 percent under the following conditions: (1) single-sorbate TOC experiments (initial TOC=2 mg/L) at pHs 5.5 and 6.5; (2) dual-sorbate experiments with low TOC (initial TOC=2 mg/L) and low silica (10 mg/L as SiO<sub>2</sub>) at pHs 5.5 and 6.5; and (3) dual-sorbate experiment with low TOC (initial TOC=2 mg/L) and high silica (50 mg/L as SiO<sub>2</sub>) at pH 5.5. However, at high silica (50 mg/L as SiO<sub>2</sub>) and pH 6.5, UV-254 Absorbance was reduced to 63 percent.

The high silica/pH 6.5 condition corresponded to the highest silica sorption densities, ranging from 0.41 to 0.64 mol Si/mol Fe, depending upon reaction time. Very negative zeta potentials (-15 to -24 mV) were also observed under these conditions. Though not common, silica levels of 50 mg/L as SiO<sub>2</sub> and higher do occur in some natural waters. These results indicate that silica at these levels can interfere with NOM removal and particle destabilization, even at pH 6.5. Once analyzed, the results at pH 7.5 are expected to indicate even greater interference attributable to silica. These data support the hypothesis that the effects of silica and other common ions need to be incorporated into a comprehensive model for coagulation.

- Zeta potential decreases with increasing pH, then with increasing silica concentration. At pH 6.5, zeta potentials were negative for all low TOC samples (initial TOC=2 mg/L, with and without added silica). Fe controls at both pH 5.5 and 6.5 are above +20 mV.

#### **Future Work:**

The remaining data for TOC and silica experiments will be analyzed. Dual-sorbate experiments with NOM and bicarbonate will also be executed. When all data are collected and analyzed, they will serve as a calibration data set for refining the preliminary surface complexation model (SCM) developed earlier in this research.

Once the model is calibrated to the data from the single- and dual-sorbate experiments, it will be assessed for accuracy. If this step reveals conditions under which the model does not perform well, additional experiments will be performed with three or more sorbates. These experiments will be designed to provide calibration data for the critical regions where the model predictions must be improved. Upon completion of this iterative process, model validation will be performed using jar test data for actual source waters.

**Anne C. Eischeid**  
Duke University

*Fundamental Mechanisms in the Extreme UV Resistance of Adenoviruses*

Expected Graduation Date: Spring 2010  
Advisor: Karl Linden, Ph.D.

**April 2009 Progress Report**  
**Anne C. Eischeid**  
**Duke University**

Project Title: Fundamental Mechanisms in the Extreme UV Resistance of Adenovirus

Specific Aim 1 and Specific Aim 4

The goals of these two aims were to assess DNA damage of LP and MP UV-treated adenoviruses using QPCR and to carry out cell infectivity assays on the irradiated viruses. The proposed work for both aims has been completed for 5 doses each of low pressure (LP) and medium pressure (MP) UV and was presented at the NWRI Graduate Fellowship Research Conference in April 2008. A manuscript describing this work has been published: Eischeid, Anne C., Meyer, J.N., and Linden, Karl G. 2009. UV disinfection of adenovirus: Molecular indications of DNA damage efficiency. *Applied and Environmental Microbiology*. 75 (1): 23-28.

Specific Aim 2: Assess protein damage of UV-treated adenoviruses: SDS-PAGE

Two sets of experiments have been carried out to assess protein damage in LP and MP UV treated adenoviruses. The hypothesis for this part of the project was that MP UV would be better at damaging proteins than LP UV. Proteins from treated adenoviruses were precipitated and run on SDS-PAGE gels; the major adenoviral proteins were quantified from gel images and amounts of proteins from treated samples were determined relative to an untreated control. In the first set of experiments using UV doses up to  $186 \text{ mJ/cm}^2$ , there was little difference between LP and MP UV lamps in levels of protein. A second set of experiments using higher UV doses shows that MP UV is more effective than LP UV at causing protein damage, though LP UV was more effective than expected. The SDS-PAGE data are now complete and a manuscript is in preparation for publication in a peer-reviewed journal.

Specific Aim 3: Assess capsid integrity of UV-treated adenovirus

Flow cytometry experiments did not prove fruitful and instead, transmission electron microscopy (TEM) has been carried out to assess integrity of the viral particles after UV treatment. Electron micrographs of adenoviruses irradiated with high doses of LP and MP UV ( $300 \text{ mJ/cm}^2$ ) show that in both cases, the viral particles are enlarged, misshapen and aggregated. From these images, it has been determined that TEM is a preferable method of examining the integrity of UV-treated adenoviruses, and completion of this study in the next two months will include collection of TEM images at lower UV doses like those used in disinfection.

NWRI-AMTA Fellowship for Membrane Technology

**Manish Kumar**

University Of Illinois at Urbana-Champaign

*Biomimetic Membranes for Water Treatment*

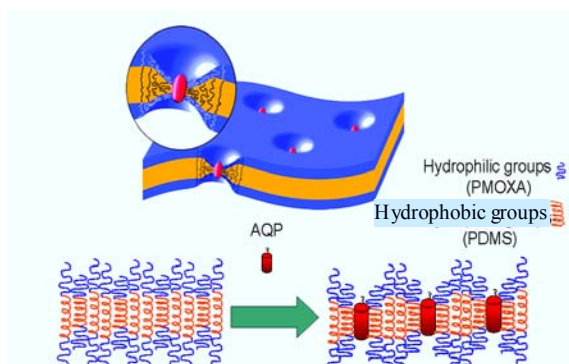
Expected Graduation Date: May 2010

Advisor: Mark Clark, Ph.D.

## AQUAPORIN BASED MEMBRANES FOR WATER TREATMENT

Manish Kumar, University of Illinois at Urbana Champaign

**Research Objective and Hypothesis.** *The objective of my dissertation research is to study and eventually develop biomimetic polymeric membranes for removal of dissolved contaminants from drinking water conceptualized in Figure 1. Membranes developed by inserting biological channel proteins such as aquaporins (AQPs) into suitable polymers will have much higher efficiencies when compared to currently available membranes because of unique mechanisms for water transport and solute transport or exclusion.*



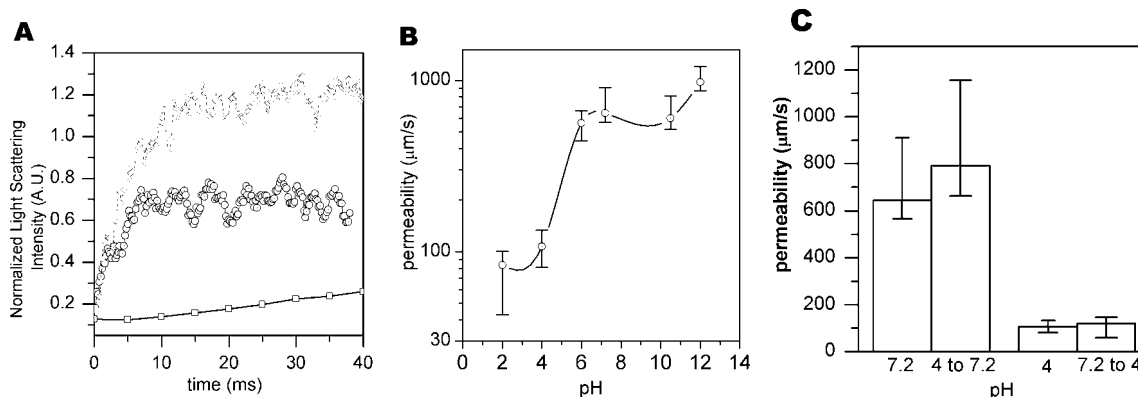
**Figure 1: Conceptual model of an AQP based membrane**

**Background.** *As the pressures on fresh water sources increase around the world, humanity is looking towards developing lower quality water sources(1). Reverse Osmosis (RO) is becoming the preferred method to remove salts and other contaminants from these more difficult-to-treat water sources. However, one limitation of desalting membranes such as Nanofiltration and RO is the high energy consumption leading to questions about long term sustainability. My research is inspired by efficient solute-rejecting membranes that are found in biological systems where productivities of certain membranes, such as those present in human renal proximal tubules, exceed by orders of magnitude the productivity of any current commercial membranes. Nature overcomes the large diffusion limitation in cellular membranes by the use of membrane-channel proteins called aquaporins (AQPs). Suitable synthetic membrane incorporating AQPs or AQP-like water channels could be the ultimate step in producing the next generation of desalting and contaminant removal membranes. We are focusing on the science and engineering of such membranes and membrane based systems*

**Current Progress.** *We have made significant progress in our endeavor in the first two years of this project. Additional research areas have also cropped up with expanding collaborations. These are briefly described in the bulleted list below*

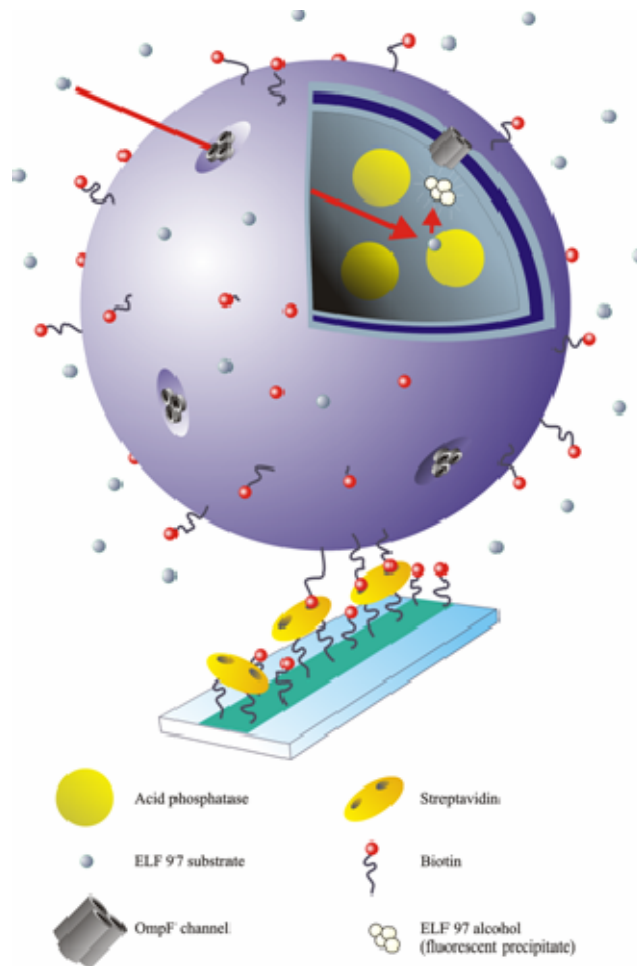
- *Proof of concept for activity of Aquaporins in synthetic polymers.* We have shown that Aquaporins purified from Escherichia Coli known as Aquaporin Z (AqpZ) can be inserted into a synthetic polymer and still maintain activity. This was achieved by design of polymers that mimic the amphiphilic lipid bilayer that forms the natural environment of Aquaporins. We have also shown that incorporation of these proteins into the polymer increases the permeability of the polymer by up to 800 times (4). This is the first time that this was demonstrated and these results have been published in the prestigious *Proceedings of the National Academy of Sciences (USA)*.
- *pH gating in Aquaporin Z.* While conducting experiments with Aquaporin-based membranes under different operating conditions expected in a desalination membrane we have

discovered that low pH conditions these membranes have low permeability and this decrease is reversible (Figure 2). However, pH gating, the phenomenon of the AqpZ closing at a low pH has not been reported before. In a manuscript currently in preparation, we describe this phenomenon and its relevance to bacterial physiology and survival under acid and osmotic shock conditions. This unexpected discovery is important from the public health perspective as infectious bacteria ingested into the human digestive system undergoes osmotic and acid challenges similar to that demonstrated in our experiments and the combined response of aquaporins and other channels under such conditions are critical to their infectivity.



**Figure 2.** *AqpZ-ABA vesicles have a lower permeability at acidic pH and this effect is reversible. (A) Normalized light scattering response from a representative osmotic shock experiment on vesicles prepared at pH 4, 7.2, and 12. Procedure described in Kumar et al (4) (B) A significant increase in permeability (as seen by clear difference in error range) is seen between pH 4 and 6 indicating closure of AqpZ. Permeability was calculated from the initial exponential rise in the light scattering response. (C) AqpZ closure is reversible. AqpZ-ABA vesicles were tested at one pH, recovered, resuspended at the other pH, and tested again.*

- *Development of Flat sheet membranes.* We are continuing to work on a templating approach to create an AqpZ rich flat membrane. A flat configuration is important for water treatment membranes as this is the most commonly used configuration (in the form of spiral wound modules). We have had some success in utilizing this approach and have observed film sizes as large as 24 mm x 16 mm. We are working to optimize the synthesis procedure further to obtain larger films so that the membranes could be tested in conventional water treatment lab equipment.
- *Use of biomimetic membrane vesicles as nanoreactors.* In collaborative work with the University of Basel we have developed a system to immobilize nanometer sized biomimetic vesicles with channel proteins inserted into the membrane wall on glass slides. The immobilization was achieved by using the interaction of the biological molecules Biotin and Streptavidin. This has allowed us to construct nanoreactors where enzymes are trapped within the nanoreactors while substrate travels to it through the protein inserted into the membrane to initiate a reaction which can be followed using fluorescence microscopy. This approach is illustrated in Figure 2. This work could have relevance to creating reactive surfaces with enzymes that degrade environmental pollutants in water and further work is continuing in collaboration with the U.S. Army. This work has been submitted for publication to the nanotechnology journal *Small*.



**Figure 3. Schematic representation of the immobilization of nonreactor system on glass surface. Acid phosphatase was encapsulated in the membrane channel (OmpF) bearing biotinylated vesicles and immobilized on the surface of the glass structured with streptavidin.**

We expect accelerated progress in the upcoming year and look forward to NWRI's support on this project.

### References

1. P. Harrison, F. Pearce, *AAAS Atlas of Population and Environment*. (American Association for the Advancement of Science, 2001), pp. 215.
2. M. Kumar, S. S. Adham, W. Pearce, paper presented at the American Water Works Association Annual Conference, Orlando, Florida, 2004.
3. D. Furukawa, (2002).
4. M. Kumar, M. Grzelakowski, J. Zilles, M. Clark, W. Meier, *Proc Natl Acad Sci U S A* **104**, 20719 (Dec 26, 2007).

NWRI-SCSC Fellowship

**Nancy Lin**  
UCLA

*Development of Fouling/scaling-Resistant Surface Nano-Structured Polyamide RO/NF  
Membranes*

Expected Graduation Date: June 2010  
Advisor: Yoram Cohen, Ph.D.

# Development of Fouling/Scaling-Resistant Surface Nano-structured Polyamide RO/NF Membranes

Nancy Lin

Chemical and Biomolecular Engineering Department  
University of California Los Angeles

## Project Objectives

The goal of the proposed research is to gain fundamental knowledge of mineral salt surface crystallization processes on Reverse Osmosis membranes. A systematic approach will be developed to evaluate the effect of aromatic polyamide membrane surface roughness on gypsum crystal growth. It involves the development of surrogate surfaces that mimic the surface chemistry and topology of the aromatic polyamide RO membrane and extensive modifications of the surrogate surfaces to study the kinetics of mineral salt scale formation. The understanding of mineral salt scale formation kinetics would help in optimizing the graft-polymerization process for nanostructured RO membrane surfaces. The effectiveness of the nanostructured RO membranes would be demonstrated with respect gypsum scale and organic matter resistance. Comparison between commercial membranes and surface nanostructured RO membranes would show that with such graft polymerization process, one can significantly improved membrane performance. The knowledge gained from the proposed research will help to predict membrane performance and create more resilient RO membranes that are either easier to clean, or to have less tendency to scale.

## Research Result Summary

### *Effect of Surface Chemistry and Topography on Scale Formation*

The effect of membrane surface roughness on gypsum crystallization was studied using aromatic polyamide (AP) surfaces applied on a quartz crystal microbalance. The total surface mass density at the end of the minimal 48-hr (or longer) crystallization experiment is shown in Figure 1. The resulting increase in surface mass density in the order of increasing surface roughness magnitude was AP1 (RMS 1.2 nm) < AP2 (RMS 2.8 nm) < AP3 (RMS 65nm) < AP4 (RMS 94 nm). The observed gypsum crystal induction time for AP4 surface is approximately 40 hours. These experimental results were presented in the Second Annual NWRI Fellowship and Research Conference. A journal publication based on this study is in preparation.

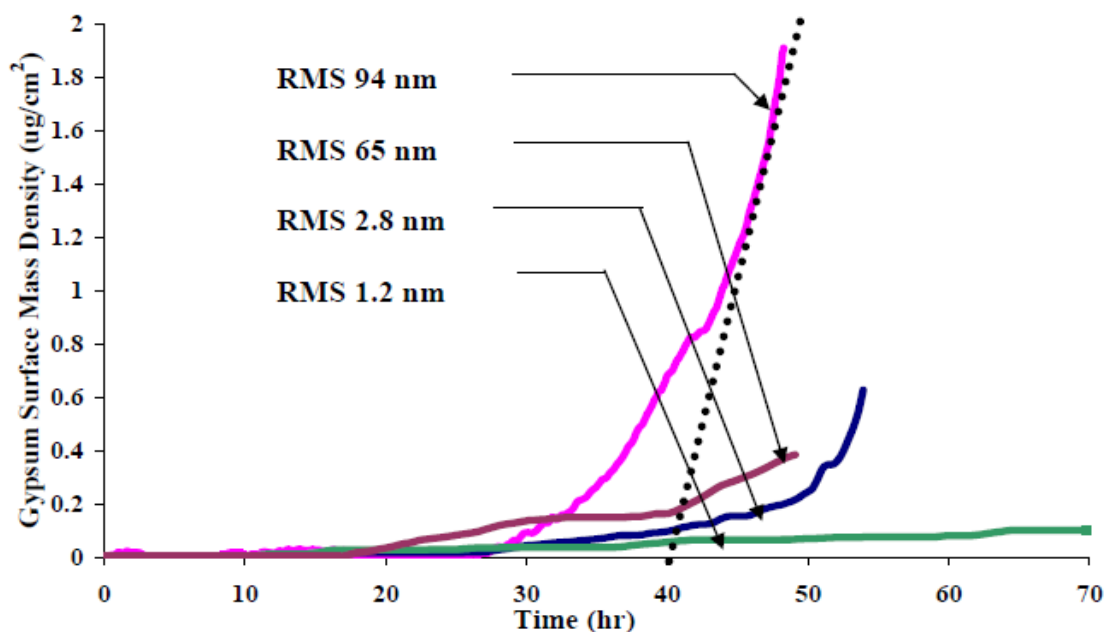
### *Surface Nano-Structuring of RO Membranes via Graft-Polymerization*

In the present study, a novel atmospheric pressure plasma-induced graft polymerization method has been developed for surface nanostructuring of RO membranes with a highly dense, covalently-bound permselective grafted polymer layer. The chemical and physical features of the grafted polymer film were adjusted by altering the monomer chemistry as well as the reaction conditions, to achieve unique “architectures” for low fouling/scaling RO membranes. Three monomers (negatively and positively charged) were selected to investigate the effectiveness of the grafted polymer brush layer. Graft polymerization parameters, such as monomer concentration, reaction temperature and treatment time of atmospheric pressure plasma, were used to optimize surface nanostructured RO membranes. Performance of those unique membranes with respect to gypsum surface scaling is displayed in the following diagrams. Figure 2 shows the commercial RO membrane with the highest flux decline percentage,

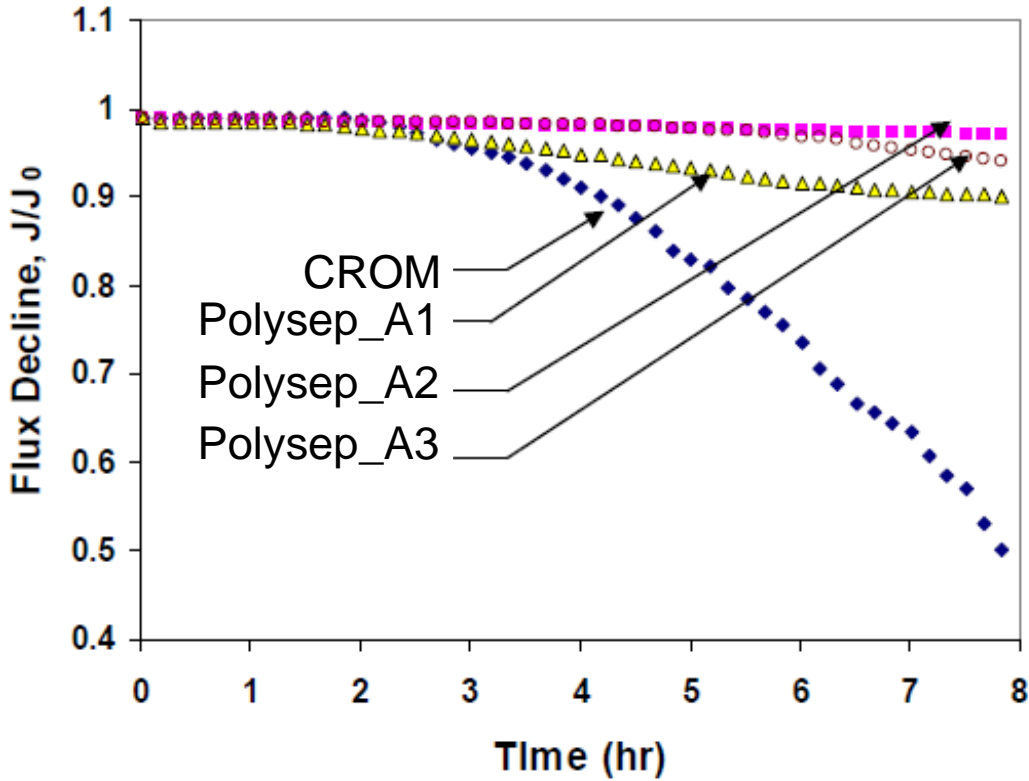
compared to three RO membranes nanostructured with charged monomer A. All three surface nanostructured membranes synthesized in our laboratories show considerably less flux decline.

The effectiveness of scale mitigation is further examined with the RO membranes nanostructured with charged monomer B. Gypsum was used as the model scalant, and the crystal surface coverage was analyzed after 8 hours of experimental time. The nanostructured membranes have significantly improved the performance with respect to gypsum scales for both charged monomers (Figure 3).

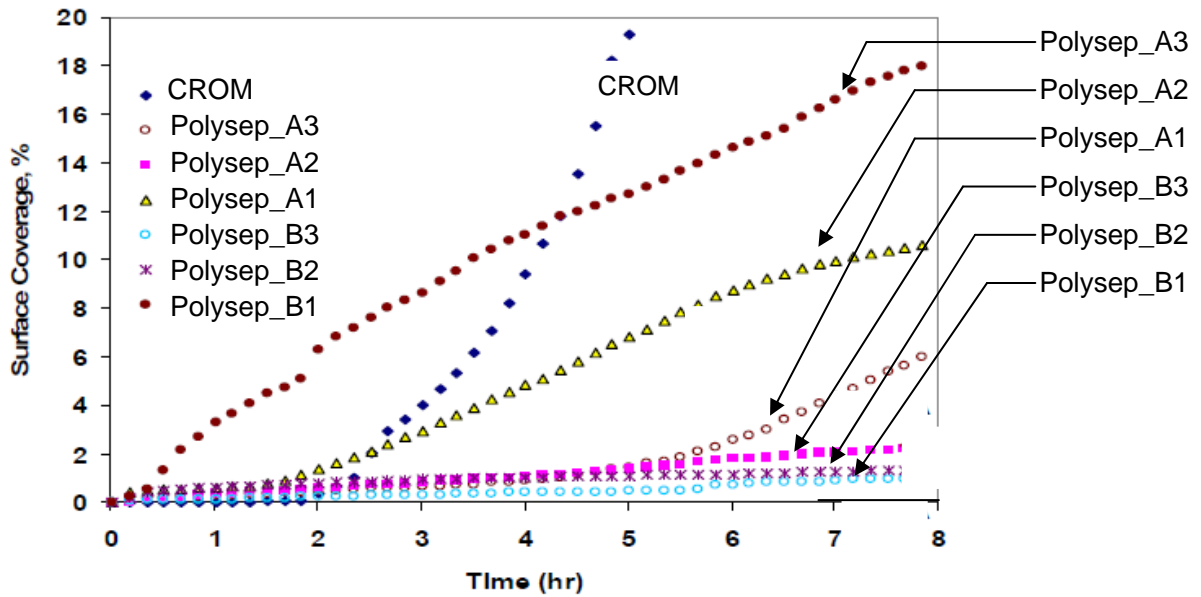
Surface nanostructuring of RO membranes is ongoing; the next step would be expanding the current process into a large scale process. Tuning the nanostructured RO membranes performance with other monomers is currently in progress. Anticipated results would demonstrate the effect of surface chemistry on membrane scaling and biofouling. The ultimate goal is to create a more resilient RO membrane that can be scaled to commercial membrane production and help decrease the cost of RO desalination.



**Figure 1.** Gypsum surface mass density from the surface crystallization experiment over time for all four aromatic polyamide surfaces. The dash-line represents the estimation of observed induction time.



**Figure 2.** Flux decline with respect to gypsum scaling experiment; CROM- commercial RO membrane; Polysep\_A1, Polysep\_A2 and Polysep\_A3 correspond to the nanostructured RO membranes with charged monomer A with increasing monomer concentration.



**Figure 3.** Surface crystal coverage after scaling experiment; CROM- commercial RO membrane; Polysep\_A1, Polysep\_A2 and Polysep\_A3 correspond to the nanostructured RO membranes with charged monomer A with increasing monomer concentration; Polysep\_B1, Polysep\_B2 and Polysep\_B3 correspond to the nanostructured RO membranes with charged monomer B with increasing monomer concentration.



**Luke MacDonald**  
Princeton University

*Phosphate and Arsenic Sequestration on Iron Oxides: The Influence of Iron Reducing Bacteria on P and As Detention and Release Rates*

Expected Graduation Date: Spring 2009  
Advisor: Peter Jaffe, Ph.D.

**Luke MacDonald**  
**Civil and Environmental Engineering**  
**Princeton University (Princeton, NJ)**

**Phosphate and arsenic sequestration on iron oxides: The influence of iron reducing bacteria on phosphate and arsenic detention and release rates**

**Progress Report**

Since the last report in October 2008, this research has focused on evaluating the efficacy of iron oxides in trapping phosphate and arsenate in conditions closely related to nature. Previous experiments focused on iron reduction in batch systems using *geobacter sulfurreducens* and pure goethite ( $\text{FeOOH}_{(s)}$ ). The resulting capture of phosphate and arsenate under iron reducing conditions in these systems demonstrate proof of principle of arsenate and phosphate in highly controlled and simplified systems. The logical extension of these early experiments is to test the same principle in more realistic conditions. Towards that end, greenhouse mesocosms were begun where iron oxides were amended to the soil to test for arsenate capture.

Plants are currently in the growth stages and establishing roots within the soil profile. The presence of roots can drive both iron oxidation and reduction through competing mechanisms. Oxygen from root hairs oxidized ferrous iron and causes the precipitation of iron oxides on the root surface, which may serve to trap arsenate and phosphate. In anoxic zones, further from the root hair, organic carbon exuded by roots drives iron reduction which, as shown in the early stages of the NWRI funded research, can serve to trap phosphate and arsenate. To test whether plants can help sequester arsenate and phosphate on iron oxides the greenhouse mesocosms were arranged as Figure 1 shows.

Preliminary results show a slight effect of phosphate capture in iron amended mesocosms. As plants and soil redox conditions become established greater differences between low and high iron mesocosms will arise. The earlier goethite and *geobacter* experiments, which indicate that phosphate can be captured under iron reducing conditions, will then serve to help explain the results.

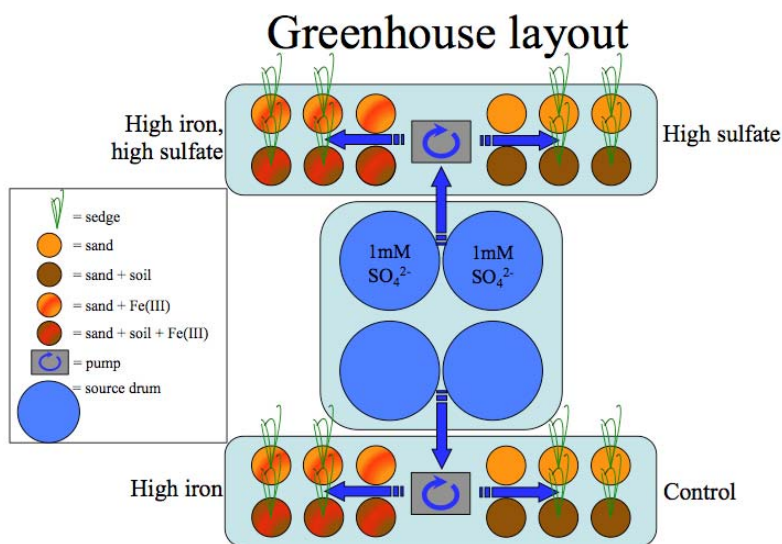


Figure 1: Greenhouse layout showing the soil and porewater treatments given to planted mesocosms. This setup tests whether plant driven redox conditions like iron reduction and sulfate reduction leads to arsenate or phosphate sequestration.

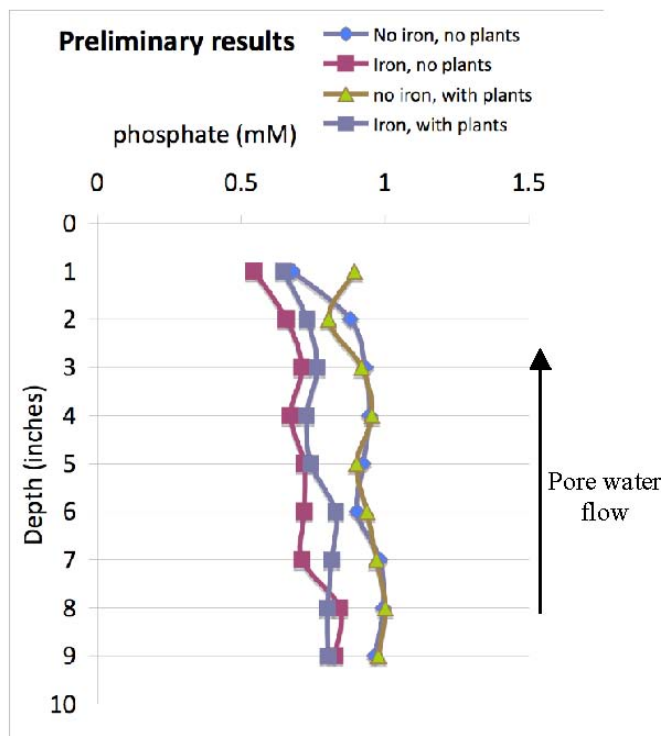


Figure 2: Baseline study monitoring porewater phosphate concentrations as redox conditions and plant roots are established. Iron amendments show a slight effect of phosphate capture. As the system matures, we expect more phosphate retention in planted mesocosms and greater difference between iron amended mesocosms and mesocosms without iron.



**Figure 3: Photo showing greenhouse mesocosms**

**Christie A. Chatterley**  
University of Colorado Boulder

*Development Of UV-Led Irradiation System For Disinfecting Water In Rural  
Communities*

Expected Graduation Date: May 2010  
Advisor: Karl Linden, Ph.D.

**NWRI Fellowship**  
**Christie A. Chatterley, University of Colorado, Boulder**  
**Spring 2009 Progress Report**

## **Introduction**

UV disinfection is a well-established disinfection technology that has been used in centralized water and wastewater facilities in developed countries for decades. UV radiation inactivates bacteria, viruses, and protozoa, with the benefits of no taste and odor issues, no known disinfection byproducts (DBPs), no danger of overdosing, relatively fast treatment rates compared to sand and ceramic filters, and low-maintenance. Over the last ten years, small UV systems have become available, including commercially available systems such as Sterilight and the low-cost, locally manufactured UV-Tube system that have become an appropriate treatment option for developing communities in a number of countries including Mexico, Rwanda, Sri Lanka, and India (Reygadas et al., 2006).

UV disinfection can be an improvement over other treatment options, such as chemical disinfection, for many applications, but there are sustainability issues that arise from current low-pressure lamp systems. They use toxic mercury as the UV radiation source and typically only last for around one year (8,000-10,000 hours) at which time communities are faced with a number of issues: finding and paying for replacement lamps, transporting these fragile glass and filament tubes, and disposing of mercury contained in the used lamp in areas that do not always have a toxic waste disposal system (US EPA, 2006).

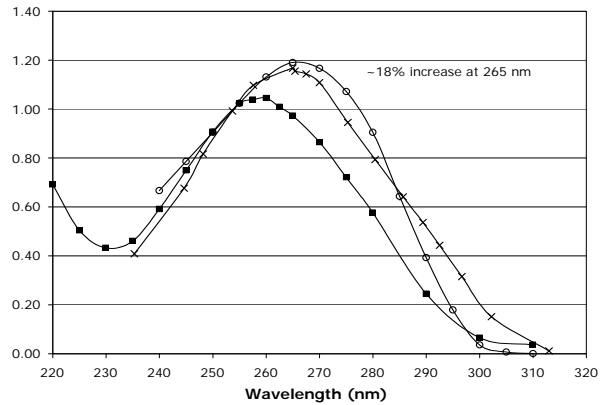
UV light emitting diodes (LEDs) may provide solutions to many of the sustainability issues of UV mercury lamps. They are small (5-9 mm diameter), and do not contain glass, filament or mercury, aiding their transport and disposal (Bettles et al., 2007). Warm-up time is not required for LEDs, saving energy and allowing for intermittent use and quick recovery from a power failure—important characteristics for rural applications especially. LEDs are replacing a number of light sources currently utilized today including traffic lights and household lights. LEDs have an excellent track record for lowering system costs through energy savings, lower maintenance, and longer replacement intervals. The average electrical-to-germicidal efficiency of low-pressure UV mercury tube lamps is 35-38% (US EPA, 2006). Visible LEDs can operate at 75% efficiency for ten years (100,000 hours) (Bettles et al., 2007). Currently, the efficiencies of UV-LEDs are less than 1% with lifetimes of around 1,000 hours (Bettles et al., 2007; Gaska, 2007). Although research of this technology is still in its infancy, improvements to UV-LEDs are expected to occur rapidly following visible LED source trajectories, resulting in a high efficiency, low power input.

## **Research Objectives**

The objective of this project is to evaluate the efficacy of Ultraviolet Light Emitting Diode (UV-LED) technology for the development of point-of-use (POU) water disinfection systems to improve public health in rural communities in a sustainable, environmentally responsible manner. There are a number of POU technologies available, but the application of UV-LEDs as a disinfection source will provide an additional technology to the POU toolbox that will enable

longer-life disinfection systems with low user input and very low energy cost compared to current low-pressure mercury lamps. This will improve public health by increasing system reliability and decreasing maintenance needs. Specifically, this research seeks to evaluate the use of UV-LEDs at 265 nm for inactivation of *E. coli* in water through meeting the following objectives:

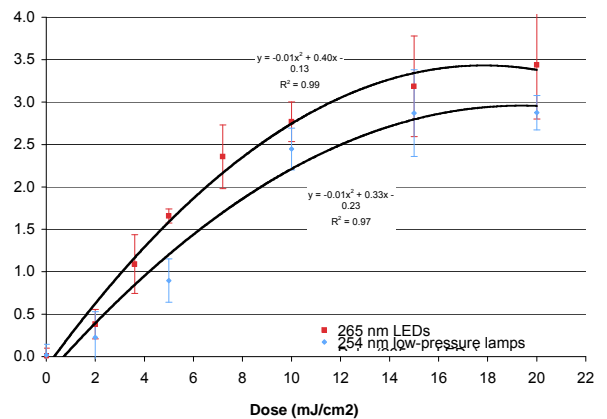
- Determine if UV-LEDs at 265 nm are more efficient than low-pressure lamps (254 nm) for inactivation of *E. coli* (based on the action spectra of *E. coli* (Figure 1))
- Build and evaluate a point-of-use UV-LED prototype
- Determine if UV-LEDs are a feasible option for water treatment



**Figure 1.** Action Spectra for DNA ( $\nu$ ) and *E. coli* DIN Standard (O) and ISF Standard (x)

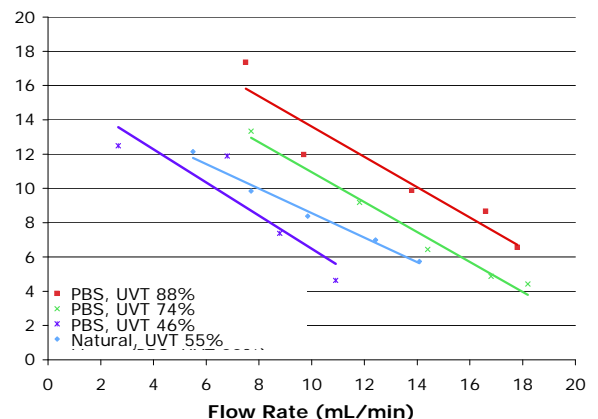
### Progress

The efficiency of UV-LEDs at 265 nm and low-pressure (LP) lamps at 254 nm have been evaluated and compared. The UV-LEDs appear to have a slightly increased efficiency, but the results are not statistically significant within a confidence interval of 95% (Figure 2). However, they are an effective option for water disinfection from a technical standpoint. They are currently limited by cost, power output, and lifetime, but these are expected to rapidly improve in the next three years according to two UV-LED manufacturers.



**Figure 2.** Comparison of UV-LEDs (265 nm) and LP lamps (254 nm) for *E. coli* inactivation

A prototype consisting of ten UV-LEDs at 265 nm (1.2 watts total) was also evaluated using *E. coli* as an indicator organism (Figure 3). The dose provided by the prototype was calculated using the dose response curves created through bench-scale testing (Figure 2). Three UV transmittance (UVT) values, 46%, 74%, and 88%, were tested in *E. coli* spiked phosphate buffer solution (PBS). UVT was increased by adding sodium thiosulfate. Tests were also conducted on *E. coli* spiked natural water with a UVT of 55%. Flow rates were varied from 3 to 18 mL/min. A dose of 12 is required for >3-log reduction of *E. coli*. This can be reached using a



**Figure 3.** Dose provided by a ten LED prototype for various flow rates and UVT

flow rate of 8 mL/min for water with 75% UVT (commercial systems are typically rated down to 75% UVT).

### **Future Work**

This research will be defended in a master's thesis on May 6, 2009, after which time it will be used for continuing work through a PhD. This will include evaluation of UV-LED technology for a point-of-use water treatment option through field work in Iquitos, Peru (Fall, 2009). Lab based research will resume in Spring 2010 and reflect the information attained in Peru.

### **Presentations**

WEF Disinfection 2009 Conference – Podium Presentation  
Feb 28 – Mar 3, 2009

**UV-LED Irradiation Technology for Point-of-Use Water Disinfection** □

UCI/UNESCO Water Scarcity Conference – Podium Presentation  
Dec 1-5, 2008

**UV-LEDs for Point-of-Use Water Disinfection in Developing Communities**

University of Colorado Energy Initiative Research Symposium – Poster Presentation  
Nov 17, 2008

**UV-LEDs for Point-of-Use Water Disinfection in Developing Communities**

**Hector A. Garcia**  
University of Texas at Austin

*Enzyme-Enhanced Membrane Bioreactors:  
Upgrading Wastewater Treatment For Reuse*

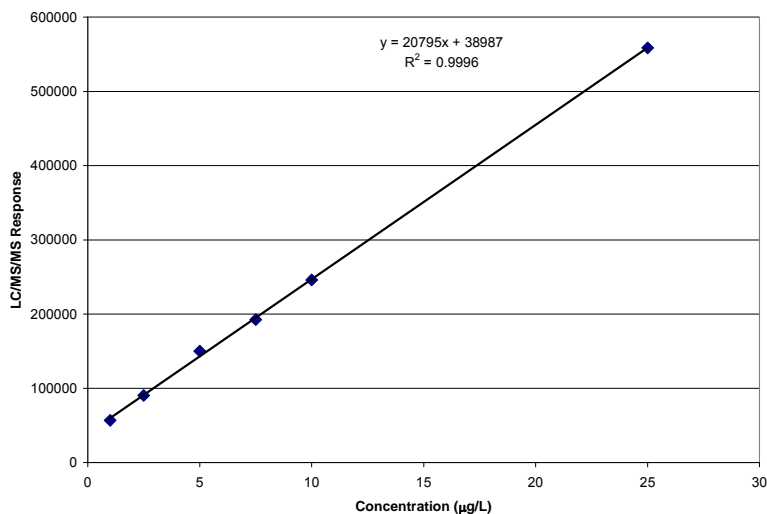
Expected Graduation Date: May 2011  
Advisor: Desmond Lawler, Ph.D.

**Progress Report – Hector A.Garcia**  
**University of Texas at Austin**

The following report describes the activities that have been performed since August 2008 regarding my research project on the use of enzymes for enhancing the removal of pharmaceuticals and personal care products (PPCPs) from water and wastewater sources. The main activities carried out during the last seven months include: i) setting up analytical techniques for measuring PPCPs in water at environmental relevant concentrations, ii) setting up analytical techniques for measuring enzyme concentrations (activities) in water, iii) performing removal efficiency experiments of certain PPCPs in water by oxidoreductase enzymes, iv) performing other activities such as application to the AMTA 2009 conference, and preparation of my dissertation proposal.

The analysis of PPCPs was performed using liquid chromatography/tandem mass spectrometry as in Vanderford *et al.*, (2003). A Finnigan Surveyor MS pump and an autosampler Surveyor (Thermo Electron Corporation) were used for all the analyses. The analytes were separated using a Shimadzu 150x4.6 mm C18 column with a 5  $\mu\text{m}$  particle size. A binary gradient consisting of methanol and water at a flow rate of 700  $\mu\text{L}/\text{min}$  was used. Mass spectrometry was performed using a TSQuantum mass spectrometer (Thermo Electron Corp.). All compounds were measured using electrospray ionization in the positive or negative mode. The analytical techniques for measuring four PPCPs [carbamazepine (antiepileptic drug), sulfamethoxazole (antibiotic), oxybenzone (sunscreen), and triclosan (antimicrobial)] were set up. The analytical techniques for measuring the first three were developed using positive electrospray ionization, so their detection limits were approximately 0.5  $\mu\text{g}/\text{L}$ . On the other hand, triclosan was set up using negative electrospray ionization, so the detection limit was not as good as in the positive mode, approximately 0.5  $\text{mg}/\text{L}$ . The detection limits noted do not consider any previous sample concentration step such as solid phase extraction (SPE). Pre-concentrating the samples will allow reaching lower detection limits (in the  $\text{ng}/\text{L}$  order). Figure 1 is a representative standard curve performed for oxybenzone for a concentration range between 1  $\mu\text{g}/\text{L}$  and 25  $\mu\text{g}/\text{L}$ . The regression analysis for the standard curve for oxybenzone (as with the other compounds) exhibited a  $R^2$  value equal to 0.9996 demonstrating the excellent response of the analytical instrument.

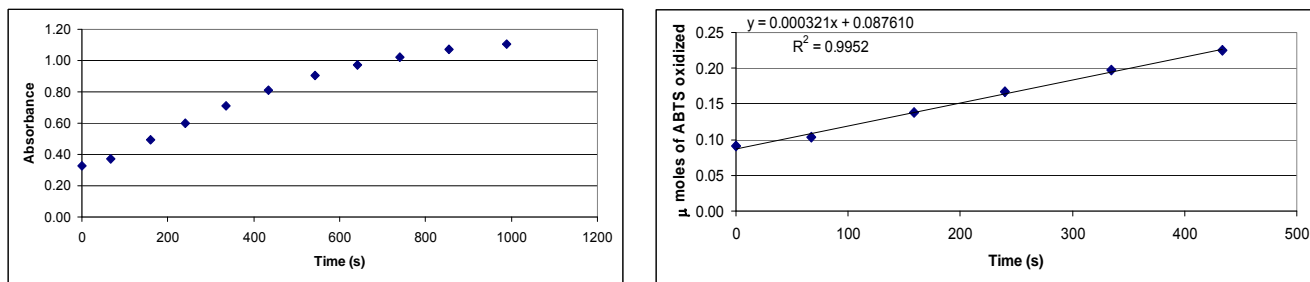
The analytical technique for measuring oxidoreductase enzyme activities, particularly laccase, was also developed. A colorimetric assay was used to analyze the activity of the laccase enzyme as in Auriol *et al.*, (2007). The oxidation of a well known enzyme substrate 2,2'-azino-bis(3-ethylbenzthiazoline-6-sulphonic acid) (ABTS) to a well defined product ( $\text{ABTS}^+$ ) at an initial concentration of 5.0 mM in a 0.1 M oxygen-saturated sodium acetate buffer (pH = 5.0) by the laccase enzyme was measured at 37°C. The disappearance of ABTS (and formation of  $\text{ABTS}^+$ ) was determined using a spectrophotometer at a wavelength equal to 420 nm. The extinction coefficient is equal to  $3.6 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ . One unit (U) of enzyme activity is defined as the amount of enzyme that catalyzes the oxidation of 1  $\mu\text{mol}$  of ABTS per minute at 37°C.



**Figure 1** – Oxybenzone calibration curve for a concentration range between 1 and 25 µg/L

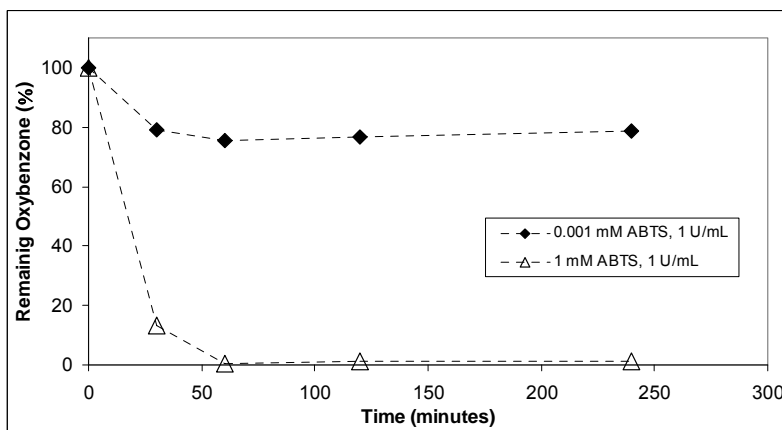
Laccase enzyme was purchased at an enzyme activity (assured by the provider) of at least 20 U/mg (one enzyme unit (U) as previously defined). For measuring the enzyme activity, initial solutions containing a theoretical enzyme activity of 35 U/mL (1.75 mg/mL) were prepared. Since the enzyme oxidation of the ABTS substrate to ABTS<sup>+</sup> is extremely fast, the enzyme needs to be diluted to measure the ABTS oxidation in a reasonable period of time. Figure 2 shows the experimental results for determining the enzyme activity of a solution. The solution was prepared at an initial enzyme concentration of 1.784 mg/mL corresponding to a theoretical initial activity of 35.68 U/mL. The following dilutions were performed to the initial solution [(1/50) + (1/35) + (1/10.9)], and the ABTS oxidation to ABTS<sup>+</sup> of the diluted solution was performed. The left side of Figure 2 shows the absorbance of the sample as a function of time, and the right side shows the calculated values of µmoles of ABTS oxidized to ABTS<sup>+</sup> as a function of time. The slope of this curve represents the µmoles of ABTS oxidized per second. Since one unit (U) of enzyme activity is defined as the amount of enzyme that catalyzes the oxidation of 1 µmol of ABTS per minute, the results of the right side of Figure 2 show that the diluted solution has an enzyme activity (slope) of 0.01926 U (that is, the slope equal to 0.000321 µmol/sec \* 60 sec/min = 0.01926 U). After accounting for the dilutions, the measured enzyme activity completely agrees with the enzyme activity reported by the enzyme provider of 35.68 U/mL. These results mean that the colorimetric analytical method is an excellent measure of the enzyme activity.

Several experiments were performed utilizing laccase enzyme in batch reactors and analyzing the oxidation of PPCPs (disappearance of the parent compounds) as a function of time. The experiments were conducted in glass amber batch reactors containing 35 mL, at an initial PPCP concentration of 1,000 µg/L, in a 0.1M sodium phosphate buffer at a pH equal to 7. The initial laccase activity was equal to 1 U/mL (units as previously defined). ABTS was used as a mediator for enhancing the oxidation power of the laccase enzyme at concentrations ranging from 0.001 mM to 1 mM. The reactors were placed in a constant temperature water bath (orbital shaking water bath) at 23°C.



**Figure 2** – Left Side: UV absorbance at 420 nm as a function of time. The substrate ABTS is oxidized to  $\text{ABTS}^+$  by the enzyme at an initial  $[\text{ABTS}] = 5.0 \text{ mM}$  in 0.1M sodium acetate at  $37^\circ\text{C}$ . Right side:  $\mu\text{moles}$  of ABTS consumed (or  $\text{ABTS}^+$ ) generated as a function of time (extinction coefficient =  $3.6 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ ).

The first set of experiments consisted of analyzing the oxidation of oxybenzone by laccase with and without the addition of the mediator ABTS. Experiments performed with no mediator addition (not shown) exhibited almost no removal of the target compound. On the other hand, as shown in Figure 3, the addition of ABTS to the reaction mixture yielded almost complete removal of oxybenzone after 4 hours treatment for optimized mediator and enzyme additions. ABTS concentrations higher than 0.001 mM were required to completely oxidize oxybenzone. Lower ABTS concentrations were ineffective in removing the parent compound. The results of these experiments suggested that removal increases with increasing mediator concentration. Although the free enzyme without mediator was not able to oxidize the target PPCP, the use of mediator compounds such as ABTS clearly enabled the oxidation of the target compound.



**Figure 3** – Oxybenzone oxidation by laccase enzyme. The enzyme activities and the mediator concentrations are described in the graph.

Therefore, the preliminary evidence summarized here indicate that the oxidoreductase enzymes enhance the oxidation of recalcitrant aromatic compounds such as PPCPs. The major results and conclusions for this research so far are as follows:

1. The analytical procedures described in the literature for measuring relevant environmental concentrations in water and wastewater sources of PPCPs can be successfully performed in our laboratories.

2. Analytical methods for measuring oxidoreductase enzyme activity were successfully implemented in our laboratories.
3. Even though oxidoreductase enzyme (laccase) without the addition of a mediator such as ABTS was not able to oxidize oxybenzone, the addition of ABTS allowed the complete oxidation of oxybenzone.
4. The higher the mediator concentration, the higher the removal efficiency of the parent compound for the same enzyme activity.

Other activities that have been performed during the last 7 months period include: i) the submission of a paper to be presented at the AMTA 2009 conference to be held in Austin, Texas in July 2009, ii) the scheduling of my dissertation proposal examination for April 3<sup>rd</sup>, 2009, and iii) the submission of a proposal on this topic to the National Science Foundation. While the proposal was officially submitted by my advisors, Drs. Lawler and Kinney, I was instrumental in its preparation; this effort represents an attempt to leverage the generous Fellowship from NWRI for complete funding of the research.

Please, contact me with any questions that you might have, and once again thank you for this fellowship which has enabled me to perform my research.

Best Regards

Hector Garcia

# NWRI-AMTA Fellowship for Membrane Technology

**Evan Hatakeyama**  
University of Colorado at Boulder

*Development Of A Novel Polymer Membrane  
with Uniform, Sub-1-Nanometer Pores For Desalination*

Expected Graduation Date: May 2010  
Advisor: Douglas Gin, Ph.D. and Richard Nobel, Ph.D.

## Progress Report 4/09

### Development of a novel polymer membrane with uniform, sub-1-nanometer pores for desalination

Evan Hatakeyama, University of Colorado at Boulder  
Ph.D. Program

Currently, our lab has developed a membrane based on lyotropic liquid crystals (LLCs). When mixed with water, LLCs self-assemble into ordered, phase-separated assemblies containing uniform aqueous domains. Effectively, these aqueous domains act as uniform pores that allow the transport of water. Polymerizable LLCs can be polymerized to retain the nanoscaled pores in the form of a robust polymer membrane. Previous work in our research lab has shown that nanofiltration (NF)/reverse osmosis (RO) type separations can be performed with these membranes. This previous research was “proof of concept” work and I have proposed several studies that need to be done to better understand the capability of this novel polymer membrane.

#### *Development of methods for fabricating supported thin films of the LLC material.*

The goal is to be able to produce a membrane that has a active barrier layer thickness of 1  $\mu\text{m}$  or less. Initial experiments to fabricate thin films of the LLC polymer membrane have had limited success. LLC phases need a specific amount of water, in this case 12 – 18 wt%, in order to form the desired pore structure. The proposed method was to add a measured excess of water and then allow the water to evaporate until the desired water content range was met. The water evaporation was measured by using an appropriate scale. The resulting film would be one to two orders of magnitude thinner than our previous films. We were able to create a few films that were 1/10 the thickness (3  $\mu\text{m}$  compared to 35  $\mu\text{m}$ ), however, there were issues delaminating the membrane for testing. Even thinner membranes were attempted but several issues from uneven evaporation, scale sensitivity, and material handling prevented any successful samples. Currently we are rethinking this process.

#### *LLC monomer design for pore size control*

Currently, the focus of our research has been developing new LLC monomers to see if we control the effective pore size of our membranes. We are developing a gemini imidazolium LLC monomer to replace our 1<sup>st</sup> generation gemini phosphonium LLC monomer. There are two other systems that are currently being characterized to see if they are suitable as membranes. Also, the new LLC monomers that we are currently researching are cheaper and simpler to synthesis and process than our current system. While the current LLC monomer has provided good initial results, it is not a very commercially viable material. Several of the future studies will be conducted on these new systems.

#### *Chlorine degradation and biological fouling studies*

These studies are currently limited because we cannot produce thin films of this material at this time. Once thinner membranes with higher fluxes can be achieved, we will examine their resistance to chlorine degradation and biological fouling. As reported earlier, these materials

exhibit resistance to both chlorine degradation and protein fouling; however, more definitive studies need to be done.

The additional aid from the NWRI – AMTA fellowship has enriched the research significantly. The fellowship has double our equipment to perform dead end filtration experiments to characterize the transport properties of commercial membranes and our novel polymer membranes. During the summer, I plan on testing several new generations of LLC polymer membranes that are cheaper and easier to make. The additional dead end filtration cells will greatly expand my capacity to do research.

Also, the fellowship has given me the opportunity to travel and present my work partially funded by NWRI and AMTA to the American Chemical Society (ACS) division of polymer chemistry conference titled “Advances in Materials and Processes for Polymeric Membrane Mediated Water Purification”. At the conference, I presented past and current work on LLC-based polymer membranes for desalination.

Immediately, my research goals are to develop new LLC monomers and fabricate polymer membranes for basic transport characterization. Ideally, these new systems will provide NF/RO type separations and can directly replace our current system. Concurrently, I will be examining other methods of fabricating thinner films of our LLC polymer to increase the overall flux. This is crucial to the commercial viability of the membrane and we are currently collaborating to find new ideas.

**Hee Suk Lee**  
University of North Carolina at Chapel Hill

*Development Of Rapid Detection Method Of Somatic Coliphage As Viral Indicator Of  
Source Water*

Expected Graduation Date: December 2009  
Advisor: Mark Sobsey, Ph.D.

**Hee Suk Lee, University of North Carolina, Chapel Hill**  
**Ph.D. Program Progress Report**

**Development of Rapid Detection Methods for Somatic Coliphages as Fecal Viral Indicators of Source Water Quality**

I began a doctoral degree program in the Department of Environmental Sciences and Engineering at the University of North Carolina at Chapel Hill in June, 2006. Since I received the NWRI fellowship, I have made consistent academic and research progress. After passing my written doctoral qualifying exam in June 2008, I passed my preliminary oral exam, which consisted of a defense of my research proposal in late January, 2009. With NWRI's Graduate Research Fellowship support, I am planning on graduating in December 2009.

**The two main goals of my work are:**

- 1. Determine if somatic coliphages are a useful indicator of the presence of human viruses in surface water.**
- 2. Develop rapid detection methods for somatic coliphages, based on identifying the most persistent and prevalent taxonomic groups.**

My research began with experiments evaluating the survival in water of somatic coliphage strains isolated from wastewater to determine the most prevalent and persistent taxonomic family of somatic coliphages over time. Also, survival over time was evaluated in surface water for positive control strains of somatic coliphage representing four taxonomic groups. On the basis of survival tests, I selected *Microviridae* and *Siphoviridae* as possible candidate families of somatic coliphages for use as indicators because they survived longer than representative of the other two taxonomic groups. The *Microviridae* family was found to be the most persistent family isolated from wastewater when measured by a multiplex conventional PCR method using family-specific primers. Therefore, based on survival tests, the *Microviridae* family was identified as the candidate somatic coliphage taxonomic group for developing a rapid detection method.

I have made substantial progress on the development of rapid detection methods for *Microviridae* in the past several months. The approaches for development of rapid detection methods are 1) a molecular detection method based on real-time PCR and 2) an immunological screening method, such as a 60-second particle immuno-agglutination assay. Rapid real-time PCR for the *Microviridae* family was optimized by using positive control strains. This rapid detection method is now being applied to isolates from wastewater for evaluation of its performance.

For rapid immuno-screening methods, we have produced polyclonal antibodies for four different somatic coliphage families. We are testing the specificities and sensitivities of these antibodies using several methods such as ELISA, dot blotting, and Western blotting. If these antibodies are group-specific and sensitive enough to detect somatic coliphage families, a rapid

immuno-agglutination assay can be developed, evaluated and applied for rapid detection of somatic coliphages.

In conclusion, the results of this study to date suggest that the *Microviridae* family is a promising candidate somatic coliphage group for use as a virus indicator, based on studies of somatic coliphage persistence and their relative abundance and their persistence over time in survival studies. Developing new and rapid detection methods will assist future studies to evaluate somatic coliphages as viral indicators for water quality assessment. These rapid detection methods will make rapid water quality assessment possible if somatic coliphages are verified as reliable indicators of viral contamination in environmental waters.

The research findings of this project will be presented in a presentation at the International Water Association (IWA) 15<sup>th</sup> International Symposium on Health-Related Water Microbiology in May 2009.

I appreciate NWRI's continued support of my doctoral work.

Sincerely,

Hee Suk Lee

NWRI-AMTA Fellowship for Membrane Technology

**Shane Walker**  
University of Texas at Austin

*Improving The Recovery Of Reverse Osmosis Desalination By Electrodialysis*

Expected Graduation Date: May 2010  
Advisor: Desmond Lawler, Ph.D.

## **Shane Walker, University of Texas at Austin Ph.D. Program Progress Report**

### ***Laboratory Experimentation***

A batch-recycle electrodialysis experimental apparatus similar to other works (Choi et al. 2003; Moon et al. 2004; Ortiz et al. 2005) was assembled with accoutrements for precisely monitoring hydraulic, electrical, and chemical behavior. Laboratory-scale gear pumps are used to circulate each of the three process streams: diluate (D), concentrate (C), and electrode rinse (R), and the flow rate (Q) through each stream is monitored continuously; the flow rate of the concentrate and diluate streams were controlled by electronic liquid flow-controllers. The reservoirs are magnetically-stirred one-liter Erlenmeyer flasks and operate as approximately ideal continuous-flow, stirred-tank reactors (CFSTRs) which are monitored continuously for pH, conductivity ( $\kappa$ ), and temperature (T). The mass of the diluate and concentrate reservoirs are monitored continuously to account for water and electrolyte transfer. Pressure (P) is monitored at the inlet and outlet of the electrodialyzer for each of the process streams in order to characterize the headloss through each stream, as well as the average trans-membrane pressures.

Experiments have been performed using simple sodium chloride solutions and more complicated synthetic solutions simulating brackish RO concentrate wastes from Maricopa County, Arizona, Cameron County, Texas, and Martin County, Florida. Real concentrate waste was collected recently from the RO plant in Cameron County, Texas, which future ED experiments will utilize.

### ***Mathematical Modeling***

A mathematical model has been developed to simulate the results of single-pass electrodialysis operation, and another model utilizes the single-pass model to simulate the batch-recycle experimentation. The single-pass model is a one-dimensional, theoretical and empirical treatment that captures the principal electrochemical transport phenomena within the electrodialyzer: (1) convection of ions along the flowpath, (2) electromigration of ions, (3) electro-osmosis of water, and (4) osmosis of water.

The electrodialyzer is treated as an electrolytic cell, and the model calculates the electrical current density, through a discrete element along the flow path. Analytical expressions for the parameters incorporated in this model are borrowed from fundamental electrochemical texts (Bard and Faulkner 2001; Newman and Thomas-Alyea 2004). The resistance of the stack at a point along the flowpath is modeled as the summation of resistances of each membrane and ionic solution. The resistances of AEMs and CEMs are taken from published analyses (Strathmann 2004; Tanaka 2007), and the resistances of the solutions are functions of chemical composition (Landolt and Börnstein 1960). Preliminary results from the single-pass model show mathematical similarity to the batch-recycle results, and future work will refine the model.

### ***Preliminary Conclusions***

Based on the experimental and mathematical results, several conclusions can be drawn. First, it is expected that electrodialysis is technically feasible for treating BWRO concentrate waste (6-18 g/L). Second, the rate of mass transport in the electrodialyzer is essentially proportional to the square root of the velocity between the membranes. Thus, an optimization tradeoff exists between improved mass transport and mean hydraulic residence time (capital cost) and increased pumping power (minor operating cost). Third, the electrical energy consumption (major operating cost) is proportional to the applied voltage and the equivalent concentration removed. Subsequent experimentation and modeling will investigate the feasibility of more aggressive operation of this treatment process.

## **References**

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University of Colorado at Boulder

*Influence of Adsorption and Attenuation of The Biodegradation of Trace Micropollutants*

Expected Graduation Date: September 2011  
Advisor: R. Scott Summers, Ph.D.

# **The Influence of Adsorption and Attenuation of the Biodegradation of Trace Micropollutants**

## **NWRI Progress Report**

**Tom Zearly**

**April 24, 2009**

### **Project Overview**

This project evaluates the capacity of an adsorbent such as granular activated carbon (GAC) to attenuate a pulse input of trace micropollutants allowing for biodegradation by attached microorganisms. The project is divided into 3 phases: 1) Adsorption only of micropollutants, 2) biodegradation only of micropollutants, and 3) adsorption and biodegradation of micropollutants.

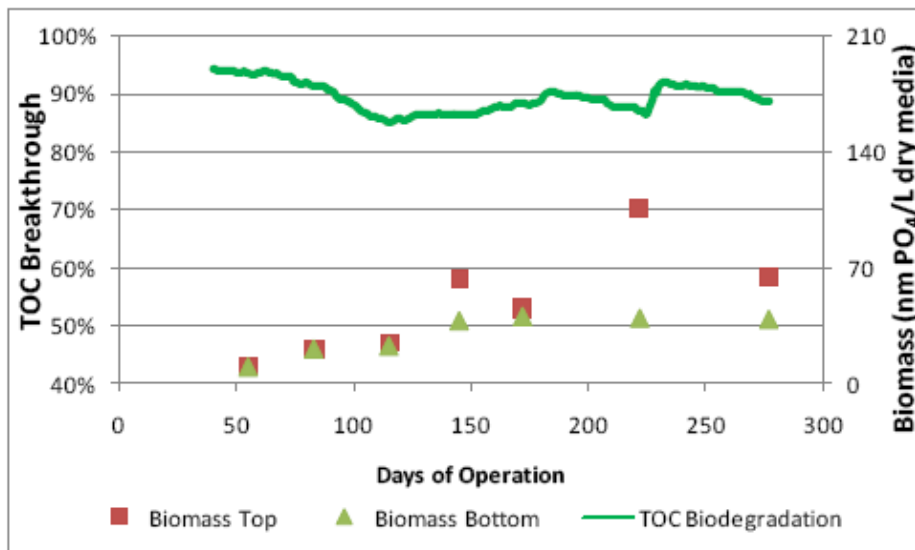
### **Project Progress**

#### *Literature Review*

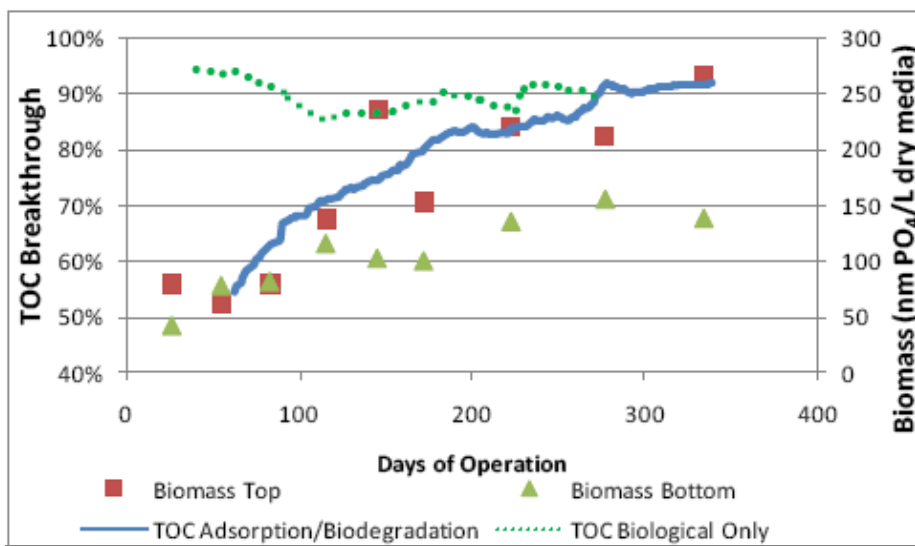
My literature review is mostly complete. The literature review covered biofiltration specifically looking at the development and sustaining of biofilms attached to granular media in drinking water filters. The last part of the literature review to be completed is the biodegradation of micropollutants.

#### *Biomass growth and development at demonstration and pilot scale treatment plants*

Over the last year, I monitored the biomass development in 5 filters at a utility in Alabama. Three of the columns were GAC (biodegradation and adsorption) and two columns were anthracite media (biodegradation only). In addition to biomass measurements, a host of other water quality parameters including micropollutants were monitored. Biodegradation of total organic carbon (TOC) reached steady state value of 10-15% in the anthracite (no adsorption) media after 100 days (Figure 1). Biomass measurements taken at the top and bottom of the filter showed that after steady state TOC removal was achieved the top had 30% higher biomass than the bottom. In the GAC filter, the TOC removal started significantly higher than the anthracite media because of GAC's adsorption capacity (Figure 2). Over the course of the year, the adsorption capacity was exhausted and the GAC column reached the same TOC removal as the biological degradation only column. I am currently analyzing relationships between biomass, removal of (TOC), chlorination scheme, and micropollutants.



**Figure 1. Biological TOC breakthrough in an anthracite media filter along with biomass measurements of the top and bottom of the filter.**



**Figure 2. Adsorption and biodegradation of TOC in a GAC media filter along with biomass measurements of the top and bottom of the filter. Once the GAC adsorption capacity is reached, TOC removal is by biodegradation (green dashed) only.**

*Micropollutant removal in 1-year acclimated biofilters under steady-state and pulse input* After the 1-year study period in Alabama, the GAC media and anthracite media was shipped to the University of Colorado for further study. The columns are currently acclimating to the new feed water. In May, the columns will be fed a constant feed of 20 different micropollutants at low levels for two months. Removal in the anthracite column (biodegradation only) and GAC column (adsorption/biodegradation) will be monitored. After the steady-state feed the micropollutant concentrations will be significantly increased for short period (~5 days). The columns will then be monitored for two to three months to observe the ability of the biomass on the GAC media to attenuate and then biodegrade the micropollutants.

*Attenuation and biodegradation of a range of exhausted biologically active GAC*

Starting in May, a utility in Northern California will ship GAC media that has been in service for 1, 4, and 18 years. In addition to the partially exhausted GAC columns, a column of fresh GAC and another column of sand will be operated for a year under steady state loading of a mixture of micropollutants. The 18 year old GAC's adsorption capacity will be mostly exhausted and the performance will represent biological removal with the potential for attenuation. The other three GAC columns will provide an assessment of GAC age on performance, and will represent the spectrum of adsorption only (fresh) to mostly biological removal (4 year old). The sand column running concurrently with the same feed water will represent biodegradation only.

*The affects of primary substrate on biomass growth and micropollutant at full scale treatment plant*

Since the beginning of the year, I have been working with another doctoral student on examining the use of different primary substrates to promote biomass growth and subsequent micropollutant removal. My contribution to the project is analyzing the biomass growth in the filters.

**Table 1. Timeline of tasks to be completed**

<b>Task</b>	<b>Completed</b>
Literature Review	Jun 2009
Adsorption only & biodegradation/bioacclimation only	Jan 2010
Combined adsorption & biodegradation	Feb 2011
Dissertation write up	Aug 2011