National
Water Research
Institute

NWRI FELLOWSHIP PROGRAM

2011 Fellowship Progress Reports

April 26, 2011

About NWRI

A 501c3 nonprofit organization, the National Water Research Institute (NWRI) was founded in 1991 by a group of California water agencies in partnership with the Joan Irvine Smith and Athalie R. Clarke Foundation to promote the protection, maintenance, and restoration of water supplies and to protect public health and improve the environment.

NWRI's member agencies include:

- Inland Empire Utilities Agency (**www.ieua.org**)
- Irvine Ranch Water District (**www.irwd.com**)
- Los Angeles Department of Water and Power (**www.ladwp.com**)
- Orange County Sanitation District (**www.ocsd.com**)
- Orange County Water District (**www.ocwd.com**)
- West Basin Municipal Water District (**www.westbasin.org**)

For more information, please contact:

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NWRI-AMTA Fellowship for Membrane Technology

NWRI-Southern California Salinity Coalition Fellowship

1. About the NWRI Fellowship Program

For over 15 years, the National Water Research Institute (NWRI) has awarded fellowship funding to graduate students conducting leading-edge research in water science and policy. The purpose of these fellowships is threefold: to 1) support graduate students; 2) highlight talent and innovations at U.S. universities; and 3) encourage students to pursue careers in water.

Our program helps fund an average of 6-10 students a year at universities across the U.S. Fellowships range from $2,500 to $10,000 per student per year. Research areas include, but are not limited to, engineering, physical and chemical sciences, biological sciences, health sciences, political sciences, economics, and planning and public policy that are related to water and/or water resources.

Fellowship recipients are selected by the NWRI Fellowship Committee based on the strength of the application, which consists of a letter on inquiry, resume, research project proposal, and advisor's recommendation letter.

Members of the NWRI Fellowship Committee include:

- *Chair:* JoAnn Silverstein, Ph.D., P.E., University of Colorado, Boulder
- Joseph A. Cotruvo, Ph.D., Joseph Cotruvo & Associates, LLC (Washington, DC)
- Douglas R. Lloyd, Ph.D., University of Texas at Austin
- Bruce A. Macler, Ph.D., U.S. Environmental Protection Agency (San Francisco, CA)
- Mohsen Mehran, Ph.D., Rubicon Engineering (Irvine, CA)
- Jeffrey J. Mosher, National Water Research Institute (Fountain Valley, CA)
- Charles I. Noss, Sc.D., U.S. Environmental Protection Agency (Durham, NC)
- Mark A. Thompson, Schlumberger Water Services (Denver, CO)
- Ian C. Watson, PE, American Membrane Technology Association (Stuart, FL)

The NWRI Fellowship Program is funded in part through partnerships with organizations like the American Membrane Technology Association, Southern California Salinity Coalition, and NWRI Corporate Associates. An endowment fund was also established to support the Ronald B. Linsky Fellowship for Outstanding Water Research, which is a special fellowship awarded every 2 years to an innovative, multi-disciplinary research project within the water sciences.

More information about the NWRI Fellowship Program can be found on the NWRI website at www.nwri-usa.org/fellowship.htm.

2. NWRI Fellowship Program Sponsors

The NWRI Fellowship Program is sponsored by the NWRI Corporate Associates, whose membership fees are used to fund NWRI Fellowships. NWRI is thankful for the support of the following 2010-2011 NWRI Corporate Associates:

BLACK & VEATCH

Black & Veatch Corporation is a leading global engineering, consulting, and construction company with more than 100 offices worldwide.
www.bv.com

carollo engineers

Carollo Engineers the largest firm in the United States that is solely dedicated to water related engineering.
www.carollo.com

CDM

CDM is a consulting, engineering, construction and operations firm with over 120 offices worldwide.
www.cdm.com

CH2MHILL

CH2M Hill is a global leader in consulting, design, design-build, operations, and program management.
www.ch2m.com

Kennedy/Jenks Consultants provides expertise in water,
wastewater, environmental management, industrial facilities,
transformational infrastructure, and more.
www.kennedyjenks.com

Malcolm Pirnie, the Water Division of ARCADIS, has more than
a century-long history of consulting with a concentration
on water and the environment.
www.pirnie.com

MWH is the global leader of the wet infrastructure sector, ranging
from water supply and treatment to the design and construction
of hydropower and renewable energy facilities.
www.mwhglobal.com

United Water, which is part of the SUEZ ENVIRONNEMENT group, is a leader
in the water services industry, operating 226 municipal water systems.
www.unitedwater.com

3. NWRI Fellowship Program Community Partners

Funding for the NWRI Fellowship Program is also provided by water industry organizations, who are involved in selecting and following up with fellowship recipients and their research. NWRI is thankful for the support of the following 2010-2011 NWRI Fellowship Program community partners:

The **American Membrane Technology Association** consists of organizations and individuals from the United States who are interested in solving water supply and quality issues through the widespread application of membrane technology.
www.amtaorg.com

The **Southern California Salinity Coalition** was established in 2002 by a group of Southern California water and wastewater agencies to better manage salinity in our water supplies.
www.socalsalinity.org

4. Donors to the Ronald B. Linsky Fellowship Endowment Fund

NWRI established an endowment fund to support the NWRI Ronald B. Linsky Fellowship for Outstanding Water Research. We are thankful for the support of the following donors who have made the Linsky Fellowship possible:

- The Joan Irvine Smith/Athalie R. Clarke Foundation
- Mrs. Patricia Linsky
- Peter and Elsa Ching
- Dr. and Mrs. Harvey Collins
- Dr. William Blomquist
- Mr. Blake Anderson and Rev. Giovanna Piazza
- Dr. Chittaranjan and Sasmita Ray
- Dr. Jack Wang and Family
- Dr. and Mrs. James Moncur
- Dr. and Mrs. Richard Sakaji
- Mrs. Sandy White
- Dr. and Mrs. David Hsu
- Dr. Stephen Lyon
- Dr. and Mrs. H.S. Muralidhara
- Mr. and Mrs. Jeffrey J. Mosher
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- Ms. Nancy R. Bushnell
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- EOA, Inc.
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- Mr. and Mrs. Jean Stern
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- Dr. and Mrs. George Tchobanoglous
- Mr. Stewart Suchman
- Mr. and Mrs. John Shearer
- Mr. Michael Wehner
- Mr. Larry McKenney
- Mr. Daniel Cozad
- Dr. Philip Singer
- Dr. Joseph Cotruvo
- Ms. Vicki Elmer
- Mr. Kenneth Ishida
- Mr. and Mrs. Thomas Gielow
- Mr. James Zukin
- Mr. Larry Gallup
- Dr. Menachem Elimelech

5. 2011 NWRI Fellowship Progress Reports

Students who receive fellowship funding from NWRI must demonstrate measurable progress in their research. Therefore, they are required to provide short progress reports to NWRI in the fall and spring of each academic year that they are funded.

The following progress reports were provided by the 10 graduate students receiving NWRI Fellowship Program funding for academic year 2010-2011.

NATIONAL WATER RESEARCH INSTITUTE
NWRI Fellowship Program

2011 Progress Report

NWRI Ronald B. Linsky Fellowship
for Outstanding Water Research

(2010-Present)

Julie C. Padowski
Soil and Water Science Major
University of Florida

Graduation Date: 2011
Advisor: Dr. James W. Jawitz

A Combined Hydrological and Managerial Approach to Evaluating Urban Water Vulnerability

To combine hydrological and managerial analysis approaches to evaluate water vulnerability in urban areas of the U.S. The ultimate goal of this research is to determine the most effective strategies used by urban water managers to improve the resiliency of water supplies and reduce vulnerability.

NWRI Ronald B. Linsky Fellowship 2010-2011 Progress Report- April 2011
Julie Padowski, University of Florida

A Combined Hydrological and Managerial Approach to Evaluating Urban Water Vulnerability

Report Overview

This document outlines the progress made towards the completion of my dissertation project since the last report in December 2010. During this period, a water utility survey was approved by the University Review Board and is currently being distributed to four hundred water utilities across the nation. Preliminary results from this survey are being used to augment the water availability study. In addition, the development of a predictive model for identifying regions where water supply management issues may occur, and cases in which coordinated resource management may alleviate problems, has been started.

Water Utility Survey Implementation

Reports from the water industry and other water-related research programs suggest that water utilities are increasingly communicating and engaging in partnerships with other groups when making water supply management decisions. To date, there have been few published studies that have evaluated the degree to which these collaborations are taking place, and the extent to which these activities improve water supply management. As part of this dissertation project, a survey tool was constructed for measuring the extent to which U.S. urban water utilities utilize participatory engagement (collaboration) strategies when managing water supplies. Results from this survey will establish a baseline understanding of (1) the level of participation among these utilities and (2) the role of participatory engagement in defining urban water supply management strategies. To accomplish this, four hundred water utilities were selected for participation, and individual email contact information was collected from each utility. When email information was not available online, utilities were contacted by phone to obtain email addresses for the appropriate survey respondent. Online links to the survey were distributed via email beginning in late-February. The study currently on-going, and will remain open until May 2011.

Urban Water Availability and Vulnerability in the United States

Water scarcity concerns have grown over the last decade, in developing nations as well as in developed countries like the U.S.. Nationally, this issue was highlighted by a “State of the [Water] Industry” report published by the American Water Works Association in 2008, which concluded that source water availability was the number one concern of water managers in North America. This portion of the project was designed to increase our understanding of this urban water problem by examining differences in water availability and water management across the nation. A major goal of this research was to identify and characterize the water supply system for each urban area in the U.S., based on a selected set of criteria. A quantitative metric was then designed to measure the availability of fresh water resources for each urban area in the U.S. in the context of the current management system. Results from this water availability study are being combined with survey results to create a predictive model for identifying where water availability issues may create conflict, and where it may foster collaborative opportunities for water utilities under various scenarios. This analysis is ongoing, and results are expected to be submitted for peer-review in 2011.

NATIONAL WATER RESEARCH INSTITUTE
NWRI Fellowship Program

2011 Progress Report

NWRI Fellowship
(2010-Present)

Katharine G. Dahm
Environmental Science and Engineering Major
Colorado School of Mines

Graduation Date: May 2012
Advisor: Dr. Jörg Drewes

Evaluation of Coal Derived Organic Fouling of Desalination Membranes by Coalbed Methane Produced Water

To evaluate whether coalbed methane produced water can be desalinated by high-pressure membranes (specifically using advanced natural organic matter characterization techniques to predict reversible and irreversible membrane fouling phenomena unique to coal-derived organic matter).

NWRI Progress Report
April 1st, 2011
Evaluation of Coal Derived Organic Fouling of Desalination Membranes by Coalbed Methane Produced Water

Principal Investigator: **Katharine G. Dahm**

As a doctoral candidate in Environmental Science and Engineering at the Colorado School of Mines, my research is aimed at evaluating whether coalbed methane (CBM) produced water can be effectively pretreated for desalinated by high-pressure membranes to be utilized as an alternative water resource. CBM is an unconventional gas resource that involves the disposal of large volumes of co-produced, saline water; this water can potentially be used to augment local water supplies if properly treated. This research will specifically make use of advanced natural organic matter characterization techniques to predict reversible and irreversible membrane fouling phenomena unique to coal-derived organic matter.

Progress since fellowship award on October 6th, 2010 by Objective, towards the research into advanced natural organic matter characterization techniques to predict reversible and irreversible membrane fouling phenomena unique to coal-derived organic matter

[Objective A] Characteristics of organic matter present in CBM produced water

CBM produced water occurs from the coal seam itself due to screen location and higher effective conductivity. Confined aquifer systems produce older waters trapped within the geologic strata during formation. Natural geologic conditions coupled with human impacts, such as surface mining, allow recharge from shallow groundwater sources and meteoric water. Characteristics of organic matter present in produced water were based upon comparison of the water sources to five known systems as listed below:

i. Groundwater Comparison: Brackish Groundwater Characteristics
ii. Formation Water Comparison: Deep Aged Ocean Water Characteristics
iii. Coal-Derived Comparison: Extracts Dissolved from Coal Characteristics
iv. CBM Well Production Additive Comparison: Coal Formation Fracturing Polymer Characteristics
v. Naturally Occurring Discrete Organics Comparison: BTEX Compounds

By utilizing 3-D fluorescence spectroscopy to determine organic carbon concentrations and dominant fractions, coal derived organic matter (iii above) was found to be most similar to CBM produced water signatures (see Figure 1). Advance characterization was conducted by analysis using size exclusion chromatography (SEC) with online dissolved organic carbon (DOC) and ultra-violet absorbance (UVA) detection. CBM produced water was characterized as low molecular weight, humic substance type organic matter. Identification and fingerprinting of organic matter using this advanced characterization methodology will be the basis for refining interactions with desalination membranes.

[Objective B] Dominant contributor to DOC and interaction with inorganic solutes

The dominant characteristics of DOC from the CBM water appear to originate from coal-water interactions (see Figue 1). This was determined by comparing chemical characteristics found utilizing 3-D fluorescence spectroscopy on field samples from Objective A with samples created in the laboratory utilizing coal core samples taken from CBM production wells. Much of the spectra closely compared between lab extractions with sample signatures determined through Objective A. Coal was prepped and dissolved into saline solution over six week intervals to observe the organic fingerprint. To determine interactions with inorganic solutes a variety of microcosm experiments were conducted to analyze the impact of salinity, pH, and trace metals at concentrations observed in CBM produced water samples taken across four producing basins in the western United States. Complexation of metals and organic matter will dictate the size, active concentration, and dominate chemical identity of dissolved organic matter. The type, size and functional groups associated with the organic matter will dictate fouling potential and type of fouling (reversible or irreversible) that is likely to occur during treatment. Membrane experiments are designed to replicate interactions observed between coal-derived organic matter and inorganic solutes. It should also be noted that the experimental data and results from objective B have been accepted for presentation at the Fourth IWA Specialty Conference on Natural Organic Matter in July of 2011.

[Upcoming Research] Objective C. CBM produced water membrane fouling experiments

The goal of the final research stage is to determine how characteristics of organic matter and effects of complexation constrain the application of nanofiltration (NF) and reverse osmosis (RO) membranes for use in desalination of CMM produce water. Results from objective B experimentation will be used to determine the range of organic matter characteristics, size and concentration. These ranges from different sources will then be used in follow-up experimentation on membrane fouling. Natural organic matter from CBM production is expected to be aged and of low molecular weight. Low molecular weight organic matter has potential to cause irreversible fouling in desalination membranes Ultrafiltration (UF) membranes are utilized to pre-treat for downstream desalination membrane processes. Removal of irreversible membrane foulants in the pre-treatment stage will improve downstream desalination membrane life and reduce NF and RO membrane fouling. Membrane technologies are not yet proven as applicable treatment options for produced water and information is critical on the fouling propensities of coal-type organic matter on membranes. This research will make use of advanced natural organic matter characterization techniques to predict reversible and irreversible membrane fouling phenomena unique to coal-derived organic matter present in CBM produced water.

NATIONAL WATER RESEARCH INSTITUTE
NWRI Fellowship Program

2011 Progress Report

NWRI Fellowship
(2010-Present)

Bruce K. Daniels
Hydroclimatology Major
University of California, Santa Cruz

Graduation Date: June 2012
Advisor: Dr. Lisa Sloan

Impacts on the Terrestrial Water Cycle from Climate Change of Precipitation Magnitude, Pattern, Timing, and Intensity

To scientifically verify if precipitation decreases predicted for the California climate could produce severe impacts to recharge for groundwater and stream baseflow supplies. This research will also quantify the impacts from predicted climate changes to precipitation properties, such as rainfall intensity, patterns, and timing.

NWRI Fellowship Progress Report

by Bruce Daniels
April 1st 2011

As background information on my project, my research proposal was "Impacts on the Terrestrial Water Cycle from Climate Change of Precipitation Magnitude, Pattern, Timing, and Intensity". This work proposed to employ numerical hydrological models for actual watershed and groundwater basin locations built using the the USGS GSFLOW software. The historical climate records for a location would serve as its initial climate baseline. Testing would consist of modifications of a single climate input factor at a time and this precipitation characteristic could vary across a range of values. The hydrological outputs corresponding to that precipitation change would be examined to compute the changes in hydrology. The change in a hydrology output relative to the change in the precipitation input would yield the sensitivity metric for that relationship.

Much of the research progress consists of software programs written in the Java programming language that provide access and processing of models and their datasets. First, routines have been coded that loads model input data, performs mathematical operations such as "increase by 0.5%", and then stores the data back out. Similarly code has been produced to load model output data. Next, code has been created to compute data for the difference between pairs of input or output datasets. These differences can be either absolute such as just (x' – x), or else relative such as (x' – x) / x. Finally, sensitivity is computed by additional code which divides the relative difference of outputs by the relative difference of the input. An example of such a sensitivity calculation produced by my code is shown in Illustration 1: "Sensitivity of Hydrologic Components to Change of Precipitation Quantity by ± 0.5%".

Hundreds of model instances are needed for the thorough sensitivity investigation of each site location. Software has been written to automatically create the model instances for each sensitivity test. Code has also been produced to repeat the creation of such sensitivity tests across a wide range of important values, or even multiple ranges of values. This code also generates execution scripts which can be used to repeatedly invoke the GSFLOW program to perform and calculate each of these test models as background computational tasks. Finally, code has been created to access, extract and collate the set of data results from the executions of all these models. An example of such a sensitivity test repeated across a range of values that has been generated and executed by my code is shown in Illustration 2: "Sensitivity to Precipitation Amount Across a Range of Temperatures".

Finally, all the computational code above along with some other capabilities such as data plotting graphics (see Illustration 3) has been encapsulated in a graphical user interface application. This application provides easy access to all the computational capabilities and helps someone to be much more capable and productive in their research work.

Sensitivity Test for Sagehen Basin (1980-1996)

Zone	Flow	Plus	Minus	Diff	RelDiff	Sensitivity
Surface	**Precip**	4.69E+8	4.64E+8	4.66E+6	1.00%	**1.00**
	PlantET	2.98E+7	2.98E+7	2.93E+4	0.10%	**0.10**
	SnowET	2.63E+7	2.63E+7	1.11E+2	0.00%	**0.00**
	SurfaceET	0.00E+0	0.00E+0	0.00E+0	------	------
	Runoff	1.19E+6	1.12E+6	7.61E+4	6.59%	**6.59**
	RunoffOut	0.00E+0	0.00E+0	0.00E+0	------	------
	Infiltration	4.11E+8	4.07E+8	4.56E+6	1.11%	**1.11**
Soil	**Exfiltration**	9.04E+7	8.97E+7	6.67E+5	0.74%	**0.74**
	SoilET	2.37E+8	2.36E+8	1.53E+6	0.65%	**0.65**
	Interflow	1.35E+8	1.33E+8	2.34E+6	1.75%	**1.75**
	InterflowOut	0.00E+0	0.00E+0	0.00E+0	------	------
	Percolation	1.29E+8	1.28E+8	1.35E+6	1.05%	**1.05**
Unsaturated	**UnsatET**	0.00E+0	0.00E+0	0.00E+0	------	------
	Recharge	1.27E+8	1.25E+8	1.49E+6	1.18%	**1.18**
Saturated	**SatET**	0.00E+0	0.00E+0	0.00E+0	------	------
	GwFlowOut	3.80E+6	3.80E+6	1.43E+3	0.04%	**0.04**
	BaseFlow	7.98E+7	7.94E+7	3.60E+5	0.45%	**0.45**
Water Body	**WtrBodyPrecip**	0.00E+0	0.00E+0	0.00E+0	------	------
	Leakage	3.87E+7	3.87E+7	-4.35E+4	-0.11%	**-0.11**
	WtrBodyET	0.00E+0	0.00E+0	0.00E+0	------	------
	StreamFlow	1.77E+8	1.75E+8	2.82E+6	1.60%	**1.60**

Illustration 1: Sensitivity of Hydrologic Components to Change of Precipitation Quantity by ± 0.5%.

	Tests for Sensitivity to Change of Precipitation Amount									
Temps at	**+14 ˚F**	**+12 ˚F**	**+10 ˚F**	**+8 ˚F**	**+6 ˚F**	**+4 ˚F**	**+2 ˚F**	**+0 ˚F**	**-2 ˚F**	**-4 ˚F**
Precip	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
PlantET	0.12	0.11	0.11	0.11	0.11	0.11	0.10	0.10	0.10	0.09
SnowET	0.70	0.80	0.67	0.57	0.50	0.29	0.07	0.00	-0.17	-0.14
SurfaceET	---	---	---	---	---	---	---	---	---	---
Runoff	4.27	5.19	5.18	4.34	4.73	3.62	5.94	6.59	4.70	1.38
RunoffOut	---	---	---	---	---	---	---	---	---	---
Infiltration	1.08	1.06	1.05	1.04	1.04	1.07	1.09	1.11	1.13	1.11
Exfiltration	0.71	0.76	0.75	0.75	0.73	0.74	0.74	0.74	0.80	0.80
SoilET	0.49	0.46	0.45	0.44	0.50	0.56	0.64	0.65	0.57	0.57
Interflow	1.99	1.92	1.84	1.76	1.63	1.67	1.65	1.75	1.87	1.79
InterflowOut	---	---	---	---	---	---	---	---	---	---
Percolation	1.16	1.15	1.12	1.11	1.05	1.04	1.03	1.05	1.15	1.14
UnsatET	---	---	---	---	---	---	---	---	---	---
Recharge	1.32	1.29	1.25	1.24	1.17	1.16	1.15	1.18	1.30	1.27
SatET	---	---	---	---	---	---	---	---	---	---
GwFlowOut	0.03	0.03	0.03	0.03	0.03	0.03	0.04	0.04	0.04	0.04
BaseFlow	0.44	0.50	0.49	0.46	0.44	0.45	0.46	0.45	0.47	0.50
WtrBodyPrecip	---	---	---	---	---	---	---	---	---	---
Leakage	-0.01	0.08	0.10	-0.03	-0.10	-0.12	-0.10	-0.11	-0.12	-0.04
WtrBodyET	---	---	---	---	---	---	---	---	---	---
StreamFlow	1.81	1.79	1.73	1.69	1.61	1.59	1.59	1.60	1.69	1.63

Illustration 2: Sensitivity to Precipitation Amount Across a Range of Temperatures

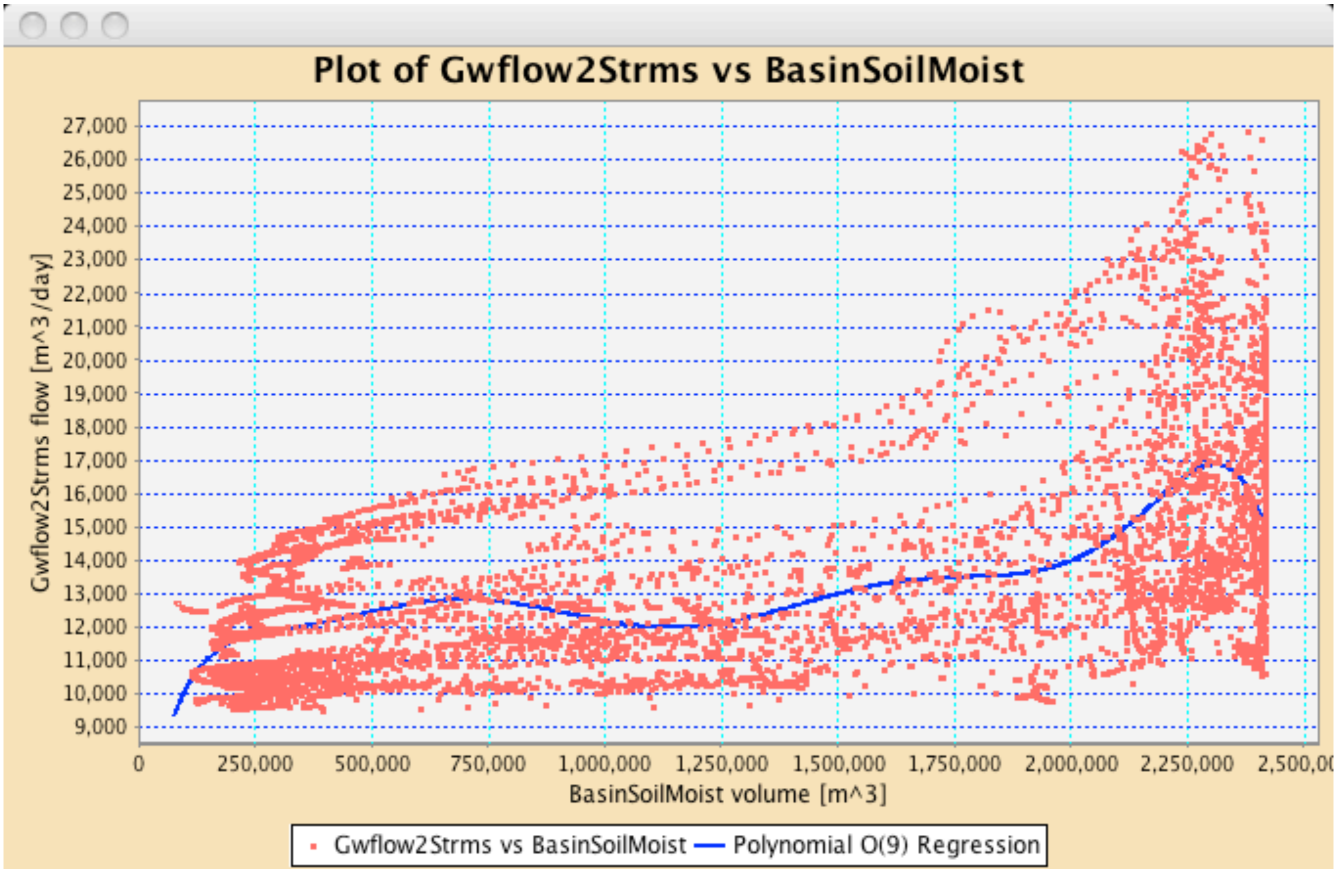

Illustration 3: Plot of Groundwater Flow to Streams versus the Soil Moisture

NATIONAL WATER RESEARCH INSTITUTE
NWRI Fellowship Program

2011 Progress Report

NWRI Fellowship
(2008-Present)

Hector Garcia
Environmental and Water Resources
Engineering Major
University of Texas at Austin

Graduation Date: May 2011
Advisor: Dr. Desmond Lawler

Enzyme-Enhanced Membrane Bioreactors: Upgrading Wastewater Treatment for Reuse

To combine the use of membrane bioreactors and enzymes to enhance the degradation of target compounds, such as pharmaceutical care products and endocrine disrupting compounds.

April 1, 2011

Jeffrey J. Mosher
Executive Director
National Water Research Institute

Progress Report – Hector Garcia

The following report describes the activities that have been performed since October 2010 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 sixth months include: i) resubmission of an article to the journal Water Research; ii) evaluation of the mechanisms and kinetics of the laccase oxidation of the ACE mediator; and iii) confirmation of the high stability of the ABTS mediator and evaluation of the ABTS oxidation rate.

i) Resubmission of an article to Water Research:

On November 2010 we received the comments from the reviewers of the paper originally submitted in August 2010. The comments from the reviewers strengthened the paper considerably. The paper was resubmitted and accepted for publication in January 2011. The citation for the article is presented below. The paper acknowledges the National Water Research Institute for the fellowship provided.

Garcia, H. A., Hoffman, C. M., Kinney, K. A., and Lawler, D. F. (2010) Laccase-catalyzed oxidation of oxybenzone in municipal wastewater primary effluent. Water research, 45(5), 1921-1932.

ii) Evaluation of the mechanisms and kinetics of the laccase oxidation of the ACE mediator

Previous results demonstrated that laccase cannot directly oxidize a representative PPCP such as oxybenzone. The addition of low molecular weight mediators expanded the oxidative ability of laccase through the formation of mediator free radicals. The oxidation of oxybenzone was achieved by using two different mediators: ABTS and ACE. Due to the chemical diversity of PPCPs, it is highly suspected that several PPCPs would require the addition of mediators to be successfully oxidized. That is, mediators play a fundamental role in this process. Consequently, a better understanding of the mechanism and kinetics of the laccase-oxidation of mediators is essential and would allow making improvements in the design of the laccase-mediator system for the removal of emerging contaminants such as PPCPs.

The evaluation of the laccase oxidation mechanism of the ACE mediator led to a very important confirmation of this research. Laccase oxidation of suitable substrates produces free radicals that can undergo extensive coupling, either with each other or with other compounds. In these experiments, it was observed that after the ACE free radicals were produced they reacted through coupling reactions producing compounds with larger molecular weights. Therefore, the removal of target emerging contaminants such as PPCPs by the laccase-mediator system occurs through the formation of mediator free radicals that undergo coupling reactions, transforming (oxidizing) the target contaminants into oxidation byproducts. When using the laccase-mediator system for removing target emerging contaminants, it would be desirable to promote radical coupling reactions between the mediator free radicals and the target compounds. That is, the ultimate goal would be to design a laccase-mediator system that produces a high concentration of mediator radicals, avoiding mediator radical coupling with each other, so most of the oxidative power of the mediator radicals can be used to oxidize the target compounds.

The laccase oxidation of the mediator ACE followed the Michaelis-Menten equation kinetics. The extent of the mediator ACE oxidation can be predicted as a function of time for a given set of experimental conditions such as ACE initial concentration, laccase initial activity, temperature, pH, and solution composition. A municipal wastewater primary effluent matrix decreased the laccase oxidation rate of the mediator ACE. Primary effluent solutions contain several organic and inorganic constituents that inhibit the activity of the laccase towards the substrate (ACE mediator). Higher retention times will be required in primary effluent solutions to achieve the same degree of laccase oxidation of the ACE mediator than in ultrapure water buffered solutions. Experiments that involved the laccase-mediator systems can be better designed by knowing how fast the mediators are oxidized (*i.e.,* how fast the free radicals are produced).

iii) Confirmation of the high stability of the ABTS mediator and evaluation of the ABTS oxidation rate

Experiments in this section were performed to confirm the relatively high stability of the ABTS radical produced by the laccase oxidation of ABTS, and to evaluate the rate at which the ABTS radicals are produced for a specific set of experimental conditions. Laccase oxidation of the ABTS mediator produced very stable ABTS free radicals with respect to self-coupling and decay reactions. ABTS free radicals did not couple with each other or decay, so the entire ABTS free radicals were available to react with the target contaminants. The high stability of the ABTS radicals compared to the ACE radicals might explain the better performance of the ABTS mediator compared to the ACE mediator for removing the target compounds in the laccase-mediator system.

Please contact me with any questions you may have. Once again, thank you for this fellowship, which has enabled me to perform my research.

Best Regards,

Hector Garcia

NATIONAL WATER RESEARCH INSTITUTE
NWRI Fellowship Program

2011 Progress Report

NWRI Fellowship
(2010-Present)

Lisa Welsh
Human Dimensions in Ecosystem
Science and Management Major
Utah State University

Graduation Date: 2012
Advisor: Dr. Johanna Endter-Wada

Water Policy Designs to Address Societal Transitions

To examine the foundational rules for allocating scarce water supplies and address current debates on how to meet the challenges of providing water in changing societal contexts efficiently, equitably, and effectively.

Lisa Welsh, Utah State University
NWRI Fellowship (2010-2012) Progress Report
April 1, 2011

Policy Designs to Address Water Reallocations During Societal Transitions

Introduction

My dissertation project uses three distinct case studies to illustrate how societal transitions are making people confront the rules by which we allocate and reallocate water. The first case study (water technologies in the Bear River Basin of Utah, Idaho, and Wyoming) analyzes certain technological changes and associated human behaviors that strive to increase the efficiency of water use. The second case study (water banking policy in Cache County, Utah) examines the use of water banks, leasing, and transfers as tools for increasing institutional flexibility by providing short-term and long-term ways to move water between different uses. The third case study (Las Vegas transfer of Snake Valley water) examines conflicts over water in a rapidly urbanizing metropolis and the challenges of meeting urban and rural as well as human and ecological water needs.

The significance of this research is that it focuses on the foundational principles and rules for the allocation and reallocation of scarce water resources that must necessarily balance public and private interests as well as human and environmental needs. With expected growth in the world's population and economy, the same amount of water must supply more needs. Taking into account climate change projections and water-related environmental stressess, even less water might be available for human uses (Spencer and Altman, 2010). People will need to decide how to serve a multitude of water needs. My case studies address various approaches to allocating and reallocating water.

My research project uses a case study approach. A case study approach is appropriate in this research, because analyzing policy designs responding to societal transitions requires geographic and temporal contextualization. Case studies address qualitative variables, individual actors, decision-making processes, historical and social contexts, and path dependencies (George and Bennett, 2005), which are all essential elements in understanding how water policy works in reality. Many rules have been used to allocate water, and the specific rules that particular locations choose depend partly on precedents that can be generalized but partly on unique and specific situations (Honadle, 1999). The case studies I have chosen illustrate some of the recent approaches to allocating and reallocating water. In each case study, I will examine the rationales behind the policies that have been chosen.

Within each case study, I am using a variety of data-gathering strategies, namely key-informant interviews, observation, and document analysis. For each case study, I am currently conducting key-informant interviews to obtain a diversity of opinion and knowledge. Key-informants have been selected based on geographic location, job position, reputation, and specific knowledge. I am also using snowball sampling and building my interviewee list with recommendations from key-informants. I have constructed a list of 20-25 questions for each case study based on my research objectives. For consistency, I am asking a set of approximately ten questions of all interviewees. I am selecting from the other 10-15 questions for each interview based on the interviewees' specific expertise and background. With permission, I am recording interviews using a digital sound recorder. I am also taking detailed field notes about my observations.

For all case studies, I am also relying on primary and secondary documents. Primary, archival documents allow me to reconstruct the policy processes in the case studies by studying information produced by the legislative process, including the procedural histories and legal agreements made in each case study. I am also examining secondary, contemporary public accounts of the case studies by searching for newspaper and other media accounts of the cases as they have unfolded over time. These public accounts are important because they help situate issues and define contexts within which policymakers operate (George and Bennett, 2005).

Research Objectives

The overarching objective of my research is to understand how new policies for dealing with water reallocation challenges can be designed to work within the context of existing water institutions to meet the parameters of efficiency, equity, and effectiveness. My primary research objectives are to:

- document the various rules embedded in policies used to allocate and reallocate water;
- contribute to a better understanding of how water policy designs can integrate the technical and social aspects of water management;
- analyze debates over using market mechanisms as the means to reallocate water;
- investigate how environmental and lower economic-valued uses of water get balanced with more economically powerful uses of water.

Progress

Since receiving the NWRI Fellowship award, I have taken my comprehensive exams and have advanced to Ph.D. candidacy. My dissertation proposal has been defended to my committee and has been approved. I have also completed and received IRB (Institutional Review Board) certification for my project. IRB certification is necessary whenever conducting research with human subjects. Completing my IRB application required that I had my interview protocols complete. I have also received a National Science Foundation Doctoral Dissertation Improvement Grant for further research funding for my numerous research trips.

Due to the funding support from NWRI, I have been able to conduct 29 interviews throughout Utah, Idaho, Wyoming, and Nevada to address each of my three case studies. For case study #1 (water technologies in the Bear River Basin of Utah, Idaho, and Wyoming), I have had the opportunity to interview water managers, hydrologists, and irrigators throughout the Bear River Basin. These interviews have addressed how metering, monitoring, and modeling technologies have affected water allocation throughout the Bear River Basin. For case study #2 (water banking policy in Cache County, Utah), I have interviewed the water manager of Cache County to understand the rationale behind a proposed water banking policy in Utah. I have also visited Idaho's Legislative Library to collect the legislative history of Idaho's water banking policy as one comparison study. For case study #3 (Las Vegas transfer of Snake Valley water), I have interviewed the state engineer of Nevada, who will be making a decision on Las Vegas's water right applications in Snake Valley, as well as different stakeholders in the Snake Valley region, such as local ranchers and Native Americans. These interviews have addressed how people are debating the rules of water allocation in Snake Valley.

Future Work

I have several more interviews planned for the next several months. I will continue to interview irrigators throughout the Bear River Basin, as well as other diverse users and interests of Bear River Basin water. I have planned three other visits to the Legislative Libraries of Colorado, Kansas, and Texas. These trips will allow me to collect the legislative history of each state's water banking policy. I am planning to compare the policy designs from each state with the water banking policy that is currently being designed and debated in Utah. The policies of Idaho, Colorado, Texas, and Kansas were chosen because they each use different water bank structures and were identified by Cache County as possible examples upon which Utah’s proposed water bank could be modeled. I will also be interviewing more stakeholders in the Snake Valley case study, including decision-makers and opponents as well as proponents for the water transfer.

Continued funding from NWRI will also allow me to attend a regional tour of the Snake Valley area to learn about the hydrology, geology, and biology of the groundwater flow system. This tour will enable me to become better acquainted with the Snake Valley area so that I can more deeply understand all of the issues that are being debated with the proposed water transfer. I am also planning on attending the American Water Resources Association's annual meeting in November to present preliminary results of my research. I have been very grateful to receive a NWRI Fellowship. The Fellowship has enabled my research to proceed, and I am on track to graduate in summer 2012.

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NATIONAL WATER RESEARCH INSTITUTE
NWRI Fellowship Program

2011 Progress Report

NWRI Fellowship
(2010-Present)

Joshua T. Wray
Molecular and Cellular Biology Major
Arizona State University

Graduation Date: Spring 2013
Advisor: Dr. Milton Sommerfeld

Nitrate and Phosphorous Removal from Waste Streams Using a Microalgae-Based Membrane Bioreactor with Improved Anti-Fouling Design

To examine whether a new microalgae-based membrane bioreactor can be used to remove nitrate and phosphates from waste streams in a cost-effective manner, making nutrient recycling economically viable, as well as reducing impacts on water supplies of communities downstream.

Progress Report (October, 2010 –April, 2011)

April 1, 2011

Joshua T. Wray
5717 S Rowen
Mesa, AZ 85212

Project Name: Nitrate and Phosphorous Removal from Waste Streams Using Microalgae-Based Membrane Bioreactor with Improved Anti-Fouling Design

Project Status:

The inspiration for this project was a logical extension of technology already being used today in industrial wastewater treatment applications. Many membrane technologies, both microfiltration (MF) and ultra filtration (UF) exist for separation of secondary treated wastewater from the sludge in a high throughput manner, but relatively few studies exist examining in detail the feasibility of using MF hollow fiber membrane materials specifically for the use of removing algae from tertiary treated wastewater. Most of the available data on the use of membranes for bioremediation with microalgae uses UF membranes that have much smaller pore sizes than is necessary for biomass removal. Additionally, the inside- out direction of filtration of many projects involving algae filtration is problematic as solid algae are difficult to remove from the inside of small hollow fiber material. The membrane I'm creating is aimed at resolving these problems so that operators can utilize membrane technology to effectively and efficiently separate microalgae from tertiary-treated wastewater.

The design for the proposed system will alleviate the aforementioned problems by increasing the pore size to at least 0.1 micron, which is at least 10 times the size of membranes used in other algae studies. This is expected to decrease the amount of energy inputs to the system as well as reducing the downtime needed for backwashing. Additionally, the system will offer improved antifouling design due to material selection, pore and fiber size, outside-in filtering, and air flow around the fibers.

Traditional membrane bioreactors utilized in industrial wastewater systems are submerged in a microbial broth and a vacuum system draws out the treated wastewater. While this has been proposed for algal photo bioreactors, the typically thin tank size and shape prohibits the use of membranes directly in the bioreactors. Such a device would also likely prohibit the passage of light thorough the algal culture. The main difference between a floc-forming bacterial culture vs. an algae culture is that the algae need light to grow. There is potentially a possibility of using a small amount of hollow fibers deep within a photobioreactor, however, right now I am focusing on a plug-and-play type module filter that can separate algae and treated wastewater on a continual basis.

The initial schedule for this project has been modified slightly due to changes in funding allocations as well as availability of some components of the system. The project is now anticipated to continue over two years, so the first year will be dedicated to basic system design and construction, which has just been initiated. The second year will involve extensive testing and optimization to find the best possible combination for a given wastewater system. Procurement of supplies needed for construction is 90% complete. The procurement of the filter media itself for initial testing took the longest due to a 1 month lead-time and then shipping from a supplier in China. However, most of the components are now in place to begin fabrication and testing of the device.

Once fabrication is complete, I want to generate data on the efficiency of this device in terms of cost and throughput rate during the end of the first year and continuing throughout the second year. The initial testing will be conducted on PVC with an ID/OD of 1.5/2.5 mm and pore size of both 0.1 and 0.2 micron; however, I would like to investigate larger sizes if commercially available. Additionally, I will be testing the system with several types of algae typically used in wastewater bioremediation, which vary in size from a few microns to up to 20 to 30 micron. This will make the base system customizable for different applications. I can foresee this technology as pivotal for wastewater treatment and bioremediation as well as production of microalgae for high value products.

Overall, the project is on track. I have had time to review additional articles and refine my design while waiting for materials to arrive. With the next installment, I plan to purchase additional filter media made from different materials with custom pore sizes for removal of specific organisms, and set up a semi-automated control system that pulls culture from a photobioreactor on a continual basis and separates the treated water. I plan to have some preliminary data on the basic design PVC and 0.1 and 0.2 micron pore sizes by the end of year one and additional data on specific organisms and the efficiency of the device in year 2.

Degree Status/Other Projects:

As a third year Molecular and Cellular Biology (MCB) PhD student at Arizona State University, I am currently working on developing my dissertation prospectus. This will include the topics of CO_2 capture and wastewater bioremediation using microalgae, which my NWRI membrane bioreactor project will contribute towards. I have been involved with two CO_2 capture projects in the past 6 months that have added to my knowledge of how waste flue gas can be utilized to grow algae while potentially utilizing waste nutrient streams. I, along with a team of two other graduate students, were selected as winners of ASU's Edson Student Entrepreneur Initiative program for which we received $15K to test the idea of using agricultural wastewater for production of algae for use as an organic fertilizer. Finally, I may have the opportunity to work on a project that incorporates algae, industrial flue gas capture, and wastewater bioremediation at a local power plant and wastewater treatment facility as discussions are ongoing.

As far as my coursework, I am in academic good standing, have finished my comprehensive exam and should have my prospectus completed by mid-summer. I recently presented the work I am doing on one of the carbon capture projects to both my MCB Colloquium class and MCB retreat and received a lot of interest. One project is in collaboration with Intel Corporation, where I actually travel to the Intel site and collect samples on a daily basis to explore the feasibility of growing algae from Intel carbon emissions. Intel and other companies are interested in curbing their carbon emissions to meet the new, tighter emissions standards, so the data I'm collecting is not only useful for my dissertation but also potentially quite important to industry.

Last July, along with two other graduate students, I started to investigate the use of dairy wastewater as a nutrient medium to grow algae biomass to be sold as an organic fertilizer in the home garden market. We have had very encouraging results from our fertilizer experiments, which includes both indoor plant growth experiments in a controlled greenhouse setting as well as outdoor test plots, testing our fertilizer formulations in real world conditions. We learned a lot about the breakdown of manure and wastewater, which compliments my work on the NWRI project. Likewise, the development of a membrane bioreactor designed for algae and the tertiary treatment of wastewater will enhance our Edson project as well. Besides fertilizer data, we are also collecting production and operating cost data on our new low-cost photobioreactor production system. This project was all made possible by the ASU Edson Student Entrepreneur Initiative, which gives seed money, business coaching, and office space to students with ideas so they can make them a reality. This has given us the opportunity to test our ideas along with very valuable experience in business development.

Finally, in addition to my work on CO_2 mitigation, our Edson entrepreneurial venture, and the NWRI project, I am excited that in the future I may get to work on a collaboration between a municipal wastewater treatment facility and a coal-fired power plant. Especially exciting for my dissertation work would be the ability to be able to explore the cellular implications to using wastewater and waste flue gas as nutrient streams to grow algae.

NATIONAL WATER RESEARCH INSTITUTE
NWRI Fellowship Program

2011 Progress Report

NWRI Fellowship
(2008-Present)

Thomas Zearley
Environmental Engineering Major
University of Colorado at Boulder

Graduation Date: Fall 2011
Advisor: Dr. R. Scott Summers

The Influence of Adsorption and Attenuation on the Biodegradation of Trace Micropollutants

To develop a low-cost method for removing micropollutants in water using biologically activated carbon that can remove emerging contaminants like endocrine disrupting compounds at levels as small as parts per trillion.

Adsorption Facilitated Degradation of Trace Micropollutants in Biological Drinking Water Systems

NWRI Progress Report
Tom L Zearley
April 1, 2011

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

Education & degree requirements

All of my coursework has been completed and I passed my comprehensive exam in December. I plan defending my dissertation in December 2011.

Compound Selection

Compounds were selected based on environmental occurrence and relevance in surface waters in the United States. Instrumental detection limitations were also taken into consideration. The compounds selected also cover a range of adsorption affinities and predicted biodegrability. A matrix was created summarizing the biodegradation and adsorption predicted behaviors of the compounds (Table 1). All of the compounds were spiked in at a constant concentration for 9 months with influent concentrations <500 ng/L.

Table 1. Adsorption and potential biodegradation of compounds.

		Adsorption		
		Weak	Partial	Strong
Biodegradability	Rapid	Acetaminophen Malaoxon	Warfarin	Tributyl phosphate
	Possibly	Caffeine Cotinine Dimethoate Methomyl Trimethoprim	2,4–D Aldicarb Carbamazepine Carbaryl Clofibric acid Metolachlor Prometon	Bisphenol A Chlorpyrifos Diazinon Gemfibrozil Ibuprofen MIB Molinate Naproxen
	Recalcitrant	Iopromide Sulfamethoxazole	Atrazine Diuron Simazine	Acetochlor Diclofenac Erythromycin Ethinylestradiol Progesterone Triclosan

Bench-scale biological filters

Currently, four columns with GAC media with varying adsorption capacities remaining, two columns with sand media, and a slow sand filter are running on dechlorinated tap water with additional organic matter as their primary substrate. The organic matter was extracted from a local lake using a reverse osmosis system.

The columns have been operating for approximately 9 months and 29 of 35 compounds showed bioremoval potential at a long EBCT and a long acclimation period as is the case in the slow sand filter. Higher removal rates were observed with an increase contact time in the biofilter. The adsorption capacity of GAC in biofilters can also increase removal rates. These biodegradation-adsorption behaviors in GAC biofilters can also be classified into groups depending on compound characteristics. Many of the results will be presented at the Annual Conference and Exhibition (ACE) of the American Water Works Association in June, 2011.

Retained biodegradation capacity after absence of exposure

Results for the retained capacity were reported in the previous progress report. The results were presented at the Water Quality and Technology Conference for the American Water Works Association in November, 2010.

Journal Submissions
I am currently preparing my results for submission to peer-reviewed journals.

Table 2. Timeline of tasks to be completed

Task	**Completed**
Literature Review	Yes
Adsorption only & biodegradation/bioacclimiation only	May 2011
Combined adsorption & biodegradation	May 2011
Dissertation write up	Dec 2011

Presentations

Zearley, T.L., Summers, R.S., 2010, "Micropollutant Removal in Drinking Water Biofilters: Critical Issues" Presented at International Water Associations – Leading Edge Technology Conference, June 1, 2010, Phoenix, AZ.

Zearley, T.L., Summers, R.S., 2010 "Trace Micropollutant Removal by Granular Activated Carbon and Biofilters" Presented at CA-NV AWWA – 90th Anniversary Fall Conference, October 6, 2010, Sacramento, CA.

Zearley, T.L., Summers, R.S., 2010 "Retained Removal Capacity of Biofilters for Trace Micropollutants Degradation during Episodic Influent Events" Presented at AWWA-Water Quality and Technology Conference, November 17, 2010, Savannah, GA.

Zearley, T.L., Summers, R.S., 2011 "Emerging Contaminates Removal in Drinking Water Biofilters" Presented to Utah Water Quality Alliance: Biological Filtration Workshop, January 20, 2011, Salt Lake City, UT.

NATIONAL WATER RESEARCH INSTITUTE
NWRI Fellowship Program

2011 Progress Report

NWRI-AMTA Fellowship for Membrane Technology
(2010-Present)

Yaolin Liu
Civil and Environmental Engineering Major
George Washington University

Graduation Date: 2014
Advisor: Dr. Baoxia Mi

Biofouling of Forward Osmosis Membranes: Mechanisms and Fouling Control

To develop a better quantification of concentration polarization in the membrane channel of realistic reverse osmosis processes.

Direct Observation of Bacteria Attachment and Detachment in Forward Osmosis Process

Progress Report for NWRI-AMTA Fellowship for Membrane Technology, March 31, 2011
Yaolin Liu
Civil and Environmental Engineering Department,
The George Washington University

1. Summary

This report presents the progress of our current study on the proposed project of Biofouling in Forward Osmosis: Mechanisms and Fouling Control. As a first step, we built a non–intrusive microscopic direct observation setup to conduct real-time monitoring of bacteria deposition on membrane surfaces in a cross-flow forward osmosis (FO) membrane process; and then investigated the application of this technique on characterizing initial microbial cell deposition and release onto/from the FO membrane surface at various conditions. A flat sheet cellulose triacetate (CTA) FO membrane provided by Hydration Technologies, Inc. (Albany, OR) is tested in this study. *Escherichia coli* (*E. coli*) K12 MG1655 tagged with a plasmid coding for green fluorescence protein is used as the model bacteria. The results that we obtained so far demonstrate that direct microscopic observation is a useful tool to study initial bacteria deposition on FO membrane surfaces. The initial microbial deposition rate is relatively slow and 74-100% cells deposited on the FO membrane surface can be easily removed by simultaneously increasing crow-flow rate and stopping permeate flux which indicates a weak bond between bacteria and membrane surface. Measurements of force interactions between bacterium and membrane surfaces will help understand the mechanisms of the initial attachment and detachment of bacteria on/from membrane surfaces. Long term membrane biofouling examination and biofilm characterization is also required to fully understand FO membrane biofouling mechanisms, which is critical towards developing anti- biofouling strategies in FO process.

2. Introduction

FO is an osmotic process in which water flow through the membrane is solely driven by the osmotic pressure difference between solutions. FO is considered as a potentially sustainable alternative to conventional membrane processes, which may offer the advantages such as high rejection rate of a wide range of contaminants, less energy consumption, low membrane fouling propensities due to the lack of hydraulic pressure rate [1, 2, 3]. Membrane fouling is a major obstacle for the application of virtually every membrane process, and among the various types of membrane fouling, biofouling is inherently more complicated because microorganisms will grow, multiply, and relocate on membrane surfaces after the initial deposition [4]. Non–intrusive direct observation technique has been proved to be a reliable method to study the development of biofouling in RO and NF membrane processes [5, 6, 7]. To the best of our knowledge, however, biofouling in FO process has not been systematically studied yet. Therefore, it is important to develop an applicable method to investigate and understand the biofouling behavior of the FO membranes in order to develop effective fouling control strategies.

3. Materials and Methods

3.1. FO Membrane and Direct Observation Experimental Setup

A flat sheet FO membrane provided by Hydration Technologies, Inc. (Albany, OR) was used in this study. According to the manufacturer, the FO membrane is made of cellulose triacetate (CTA) has an asymmetric structure with a dense active surface layer and a more porous support layer. In this study, all of the direct observation experiments were conducted with the active layer facing the feed solution side. A cross-flow FO direct microscopic observation system was employed in this study to monitor the microbial cell deposition and release on/from membrane surface (shown in Figure 1). The membrane cell was specially designed and built with a glass window (16 mm × 38 mm) in the middle of the upper plate to enable real-time monitoring by an Olympus BX51 microscope (Olympus, Japan). The system closely resembles the cross-flow FO membrane system used in our previous study [3].

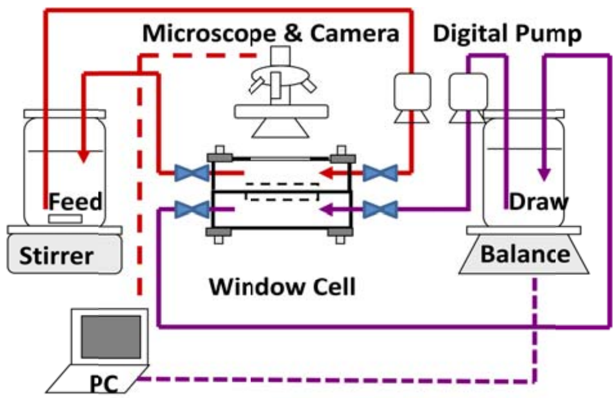

Figure 1. Schematic diagram of the direct observation FO system.

3.2. Microbial Cell Suspension

The model bacteria used in this study is *E. coli* K12 MG1655, which was provided by Prof. Kai Loon Chen from Johns Hopkins University. *E. coli* K12 MG1655 is tagged with a plasmid coding for green fluorescence protein to allow visualization via microscope. *E.coli* colonies were cultured in LB broth and cleaned with in 154 mM NaCl solution for three times before use. To make the feed solution for direct observation experiment, the cleaned bacteria cell suspension was diluted in synthetic wastewater solution [8] to a targeted concentration of 1×10^5 colony forming unit (CFU)/mL. All the chemicals and reagents used in the experiments are of analytical grade. DI water was used in all the experiments for solution preparation.

3.3. Direct Observation Experiments

FO direct observation experiments were conducted in the following steps: (1) sterilize the membrane system following the cleaning procedures developed by Moshe and Menachem [8]; (2) insert a new membrane sample into the membrane cell with active layer facing the glass window on upper plate; (3) stabilize the system with the microbial suspension on the feed solution side and 100 mM NaCl on the draw solution side for 30 minutes; (4) switch the draw solution to 4 M NaCl and start experiment with a cross-flow rate of 100 mL/min; (5) take images at a fixed spot on the membrane surface every 1 minute in the first 10 minutes of the experiment and then every five minutes after that; and (6) after 60 minutes of deposition experiment, switch the draw solution to 100 mM NaCl and increase the cross-flow rate to 1000 mL/min and take image every 1 minute.

4. Results

Images were taken in 1-5 minutes intervals during the 60-min bacteria deposition and subsequent cleaning experiment and saved in a Tagged-Image File Format (TIFF). The images were edited by image processing software [9] to minimize background noise impact and obtain the attached bacteria cell density. Images taken at 2 and 60 minutes of deposition and 2 and 10 minutes of rising are shown in Figure 2(a-d). The attached cell density is plotted as a function of time in Figure 2(e). As demonstrated in these images (Figure 2(a-d)), the total amount of deposited bacteria and the rate of deposition, however, are relatively low. Most of the membrane surface is still not covered after one hour of deposition; and the rinsing after deposition experiment removed most of the deposited cells from membrane surface. As shown in the Figure (e), microbial cell deposition during the first 10 minutes was relatively quick and the cell density appeared to be linear with time. Rinsing effectively removes microbial cells from the membrane surface, about 74% of bacteria are removed in 1 minute rinsing, and almost all the deposited bacteria are removed from membrane surface after ten minutes rinsing. Initial bacteria cell deposition rate k_d is determined by equation (1), where cell density N is normalized with the cell concentration in feed solution N_0, which is 2.4 μm/s.

$$k_d = \frac{\Delta N}{\Delta T}\frac{1}{N_0} \tag{1}$$

A weak bond between the deposited microbial cell and FO membrane surface can be concluded from these results.

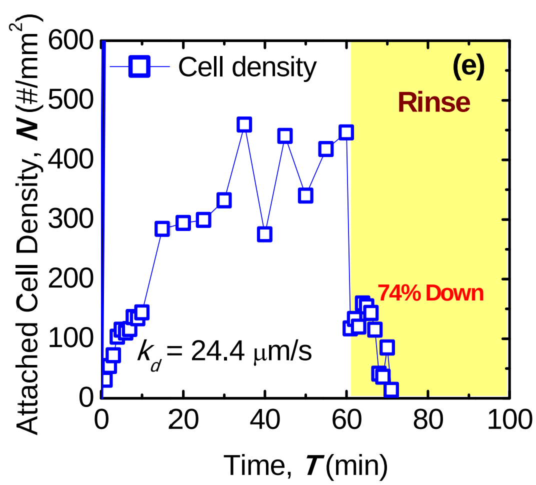

Figure 2. Images of *E. coli* deposition/release onto/from FO membrane surfaces taken during direct observation experiments. (a) at 2 minutes of deposition, (b) at 60 minutes of deposition, (c) at 2 minutes of rinsing, and (d) at 10 minutes of rinsing. (e) the deposition rate and cleaning efficiency of *E. Coli* in FO membrane process. Images were

taken with a 10× objective lens by CCD camera with a resolution of 1600×1200 pixels. The membrane area shown in the image is 0.25 mm^2.

5. Preliminary conclusions and future work

The preliminary results demonstrate that the direct microscopic observation method is a useful tool to investigate the initial bacterial deposition and release in cross-flow FO membrane process. Microbial cell deposition is relatively slow and can be easily removed by increasing cross-flow rate. Our following work on measurements of force interactions between bacterium and membrane surfaces will help explain the underlying mechanisms of bacteria initial attachment and detachment on/from the FO membrane surfaces. Long term membrane biofouling examination and biofilm characterization will also be conducted to fully understand FO membrane biofouling mechanisms, which is critical towards developing anti-biofouling strategies in FO process. As immediate next step, we are planning to perform the following experiments: (1) Bacteria attachment/detachment experiments under a range of solution conditions (e.g., total ionic strength, divalent cation concentration, and pH) to better understand the influence of solution chemistry on bacteria attachment/detachment on/from membrane surfaces; (2) Bacteria attachment/detachment experiments with different membrane material to test the impact of membrane materials on bacteria deposition rate; (3) try to develop a method to directly measure the force interactions between a live bacterium and the membrane surface; (4) long term biofouling experiments under constant driving force to monitor membrane flux decline with biofouling; (5) using available methods to characterize biofilm formation in long-term biofouling experiments.

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NATIONAL WATER RESEARCH INSTITUTE
NWRI Fellowship Program

2011 Progress Report

NWRI-AMTA Fellowship for Membrane Technology
(2010-Present)

Alberto Tiraferri
Environmental Engineering Major
Yale University

Graduation Date: 2014
Advisor: Dr. Menachem Elimelech

Nanocomposite Polymeric Membranes for Enhanced Water and Energy Production in Membrane-Based Separation Processes

To develop robust nanocomposite membranes to enhance the performance and expedite the implementation of advanced membrane-based water and energy production technologies.

NWRI Fellowship Progress Report

Alberto Tiraferri, Yale University

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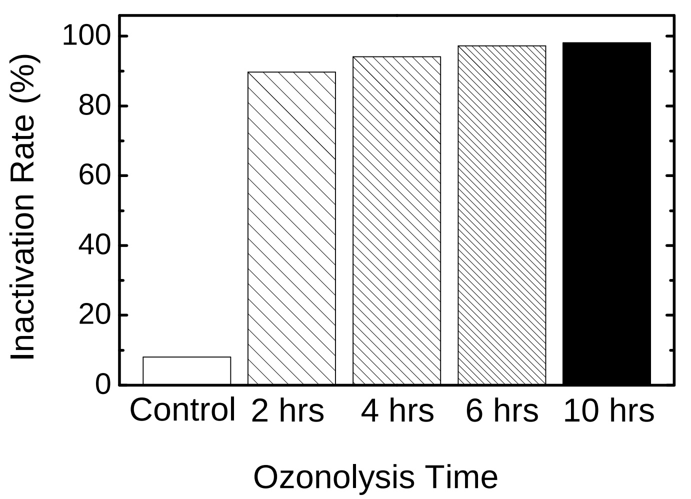
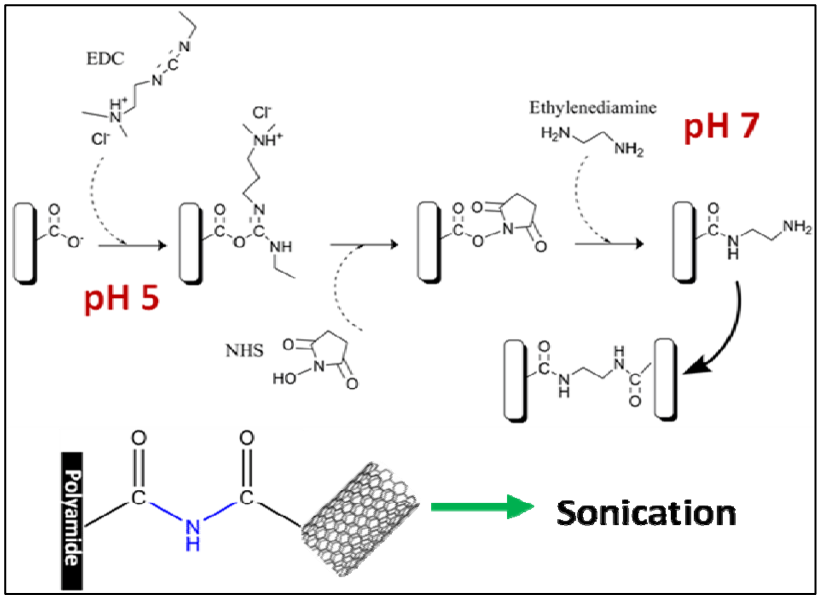
April 1, 2011

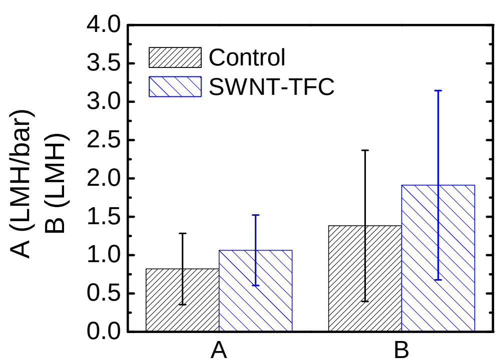
Specific, desired properties are imparted to water purification membranes by irreversibly binding nanoparticles to the membrane surface. In particular, short carboxylated single-walled carbon nanotubes (SWNTs) are covalently bound to thin film composite (TFC) membranes via amide bond with the innate carboxylic groups of the polyamide film. This process will create a non-depleting cytotoxic membrane surface, which is expected to delay biofouling during membrane operation.

The SWNTs are customized in order to maximize dispersability in aqueous solution and to enhance their antimicrobial properties. Short and highly functiolized nanotubes are preferred. Therefore, the SWNTs are initially purified in HCl solution at 70°C for 6 hours and cleared of the amorphous carbon, which is burnt at high temperature. This purification is followed by an ozonolysis step, whereby the SWNTs are placed in a UV-ozone chamber for various times. Here, the strongly oxidant atmosphere attacks the nanotube walls creating defects, separating and shortening the nanomaterials, and generating negatively charged carboxylic groups at their walls through ozonide mediators. The SWNTs are then characterized using thermogravimetric analysis (TGA), XPS, Raman backscaterrting spectroscopy, and TEM. The characterization confirms the larger extent of defetcs and functionalization for the ozonolyzed SWNTs. The antimicrobial properties of the functionalized nanotubes are evaluated by filtering a fluorescent *E.coli* suspension in bacterial isotonic solution trhough a SWNTs mat. After 1 hour of incubation at 37˚C, the dead and the live cells on the mats are stained and imaged using a fluoresce microscope. An almost complete inactivation of cells is observed for the ozonolyzed SWNTs mats, as shown in the figure above.



The reaction between SWNTs and TFC membrane is performed by exploiting the carboxylic functional groups of both the nanomaterials and the polyamide film surface (figure on the right). The membrane carboxylic groups are initially contacted with a EDC-NHS solution at pH 5, thus converting into reactive semi-stable esters. Subsequently, a pH 7.5 solution of ethylene diamine is used to translate the esters into stable amide bonds. A suspension of ~40 mg/L SWNTs in HEPES buffer at pH 7.5 is probe sonizated for 2 hours to enhance dispersion and debundling of the nanomaterials. The sonicated suspension is contacted to the amide-rich membrane surface for at least 2 hours under continuous stirring and at an applied pressure of 50 psi to facilitate contact of the nanotubes with the membrane surface. The reaction is stopped by discarding the unreacted solution from the surface and pipetting a high alkaline (pH 11) solution onto the membrane, to restore the unreacted carboxylic groups. The modified membrane is tested for water permeability, A, and NaCl permeability, B, in a dead-end filtration cell, at an applied pressure of 400 psi and using a 20 mM NaCl feed solution. After testing, the SWNT-membrane is bath sonicated in two cycles of 7 minutes each, to remove all the loosely bound SWNTs from the surface. The transport parameters, A and B, of the SWNT-membranes are observed to increase slightly (~20-30%) compared to the control, due to contact of polyamide with ethylene diamine during reaction (figure on the left).





The modified membrane before and after sonication is characterized using contact angle measurements with deionized water, SEM imaging, Raman backscattering spectroscopy, tapping mode AFM, and TGA. The characterization confirms the presence of heterogeneously sized and dispersed SWNTs and SWNTs bundles/aggregates bound to the membrane surface. The wettability of the membrane is not significantly affected by modification. Nevertheless, roughness characteristics are observed to change due to the presence of the nanomaterials, with a generally higher roughness while maintaining a similar overall roughness factor compared the control unmodified polyamide surfaces. Thee films modified with SWNTs demonstrate enhanced cytotoxic properties in comparison with the unmodified polyamide thin. Tests are carried out by contacting *E.coli* bacterial cells (~10^8 cell/mL) with the membrane active layer for 1 hour in isotonic solution (0.9% NaCl) at 27˚C. Following the contacting period the cells are resuspended using sonication, and the resulting suspension is plated in order to count colony-forming units. SEM images of the bacteria on the surface of the control and of the SWNT-modified membranes at the end of the cytotoxic test show different cell morphology for the two samples, confirming the enhanced antimicrobial properties of the surface in the presence of nanomaterials.

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Water Desalination by Reverse Osmosis with Nanostructured Polymers

To develop a new class of high-performance reverse osmosis (RO) membranes and conduct a pilot demonstration of advanced surface nano-structured RO membranes to produce water of potable quality.

Water Desalination by Reverse Osmosis with Nanostructured Polymers

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April 1, 2011
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Project Objectives

Effective use of RO/NF membranes in brackish desalination and water reuse applications requires effective suppression of membrane fouling and mineral scaling. Traditional strategies for producing membranes of low fouling propensity have relied on alteration of membrane surface chemistry and topography by addition of a permselective polymer thin film, coated or graft polymerized, that would act both as a separation layer and a physical boundary to reduce adsorption of foulants. In the present study, the recently developed atmospheric pressure plasma-induced graft polymerization (APPIGP) method was utilized to generate a high surface density of active surface sites on a polyamide membrane for subsequent graft polymerization using a suitable water soluble vinyl monomer. Surface structuring via graft polymerization was then employed, with three different water soluble monomers, to form a brush layer of polymeric chains that are terminally and covalently attached to the polyamide surface of an optimized (with respect to flux and salt rejection) of a thin-film composite (TFC) polyamide (PA) membrane. The chemical and physical features of the resulting surface nano-structured (SNS) TFC-PA was tuned by the selected vinyl monomer chemistry as well as the reaction conditions to achieve the desired surface architecture to reduce fouling and scaling, while achieving the target membrane performance with respect to flux and rejection. The presence of grafted polymeric brush layer is confirmed by Fourier Transform Infrared (FTIR) Spectroscopy. Graft polymerization kinetics will be determined, with respect to the change in grafted polymer layer thickness with reaction time and initial monomer concentration. Also, the change in surface energy (a measure of the degree of surface hydrophilicity/hydrophobicity) is quantified via contact angle measurements. Furthermore, the surface nano-structured RO/NF membrane performance was evaluated by examining the membrane mineral salt scaling and biofouling propensities. Membranes effectiveness in retarding organic fouling was assessed via flux decline studies with model proteins and polysaccharides solutions. Reduction in membrane mineral scaling propensity was quantified from both flux decline studies (using salt solutions supersaturated with respect to calcium sulfate) and via direct observations of the evolution of mineral scaling on the membrane surface in an optically transparent high pressure RO cell.

Experimental Procedure

Our experimental process is composed of three different steps. The first being surrogate surface preparation, followed by plasma surface activation, and lastly graft polymerization. In the end, we achieve synthesizing nano-structured polyamide thin-composite films.

In the first step of the process we make surrogate surfaces through silicon-polyethyleneamine-polyamide (Si-PEI-PA) wafer preparation. The silicon wafers are first thoroughly cleaned in a piranha bath. After the silicon surfaces are rid of all organics, PEI is then coated onto the silicon surface and cast spun. Next, MPDA (m-phenylenediamine) is placed on the silicon-PEI surface, absorbs, and is cast spun. Immediately after MPDA is cast spun, TMC (tri-methylene chloride) is placed onto the surface and absorbed. During this point interfacial polymerization is taking place. Any remaining TMC is then spun off the surface. At the end of this process, a Si-PEI-PA substrate is produced. This surrogate surface is then used to carry out graft polymerization.

The next step of the process is plasma surface activation. The process begins with a neutral gas that is bombarded by electrons in a plasma generating device. Upon collision, the energy of the electron is transferred to the neutral species which causes excitation and the creation of radicals and metastable species. These species are then directed through the plasma generating device towards an inorganic or organic substrate that is positioned a distance from the exit region. The excited species activate the substrate surface species, transferring kinetic energy, and thus create activated species on the substrate surface. These activated species can be in the form of radicals or peroxides.

The last step in this process is graft polymerization. In this step, the activated surface is immersed in a monomer/solvent solution with heat. Two different monomers were tested: acrylamide, and vinylpyrrlidone. The monomers in solution diffuse to the substrate surface where they covalently bond to the activated surface. Propagation of the chemically grafted chain occurs until termination or chain transfer. The result is a thin, dense layer of grafted chains which are chemically and thermally stable.

Research Progress

We have characterized our surfaces using ATR-FTIR (Attenuated Total Reflectance – Fourier Transform InfraRed spectroscopy) analysis. This analysis shows the absorbance as a function of the wavenumber. We can see that polyacrylamide is formed with the presence of C=O (carbonyl) and C-N and N-H (amide) peaks. Furthermore, the bond signal strength increase for both the carbonyl group and amide groups for the polyacrylamide samples.

The AFM images show distinct surface topography of surface features under different grafting conditions. The brush layer structured surface can be control by reaction conditions. It is shown that polymer grafting increase the features observed with AFM analysis. In the case of AA-SNS-PA-TFC membranes, the RMS surface roughness are much lower than the PA substrate. The features of AA-SNS-PA-TFC membranes are much larger than PA (2.5 nm, compared to 27 nm-scale).

Water contact angle measurements are used to characterize the hydrophilicity of the membrane surface. The water contact angle data of polyacrylamide and polyvinylpyrrolidone show that there is a significant decrease in contact angle when polymers are grafted onto the surrogate surface. There is also an observed decrease in contact angle with increasing time and monomer concentration. Surface energy data is calculated from contact angle measurements. There is a significant increase, 25%, in surface energy by grafting polymers onto the surrogate surfaces. This shows increase of surface energy.

Biofouling test done on a mini plate and frame RO unit showed that PAAm-SNS-PA-TFC membranes have good biofouling resistance with respect to BSA and alginic acid. This membrane performed just as well as LFC1 membrane.

Gypsum scaling test performed on the same mini plate and frame RO unit demonstrated that PAAm-SNS-PA-TFC membranes exhibit a reduction in the number of nucleation sites compared to LFC1 commercial membrane, thus lowering the rate of nucleation and flux decline. At the end of experiment, 8 hours, we observed a reduction in the mineral scaling due to the grafted polymer brush layers on the surface.

Conclusion

Atmospheric pressure plasma induced graft polymerization is an effective approach to increasing the surface energy of polyamide surfaces. The properties of the polymer grafted layer can be engineered to reduce fouling and mineral scaling propensity. Lastly, water contact angle data shows that there is an increase in hydrophilicity with increasing reaction time and initial monomer concentration.

Continued Research

Research will be done to identify additional monomers as candidates for RO membrane brush layers. Criteria for suitable monomers include: water soluble, low polymerization temperature, specific chemical functionality of resulting polymer that is fouling/scaling resistant, and highly hydrophilic. Additionally, further characterization needs to be done to determine the thickness of the grafted layers in order to determine grafting kinetics.