National
Water Research
Institute

NWRI FELLOWSHIP PROGRAM

2011-2012 Fellowship Progress Reports

February 2012

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:

Jeff Mosher
Executive Director
National Water Research Institute
18700 Ward Street
P.O. Box 8096
Fountain Valley, California 92728-8096 USA
Phone: (714) 378-3278
Fax: (714) 378-3375
jmosher@nwri-usa.org
www.nwri-usa.org

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1. About the NWRI Fellowship Program

For over 16 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 based on the strength of the application, which consists of a letter of inquiry, resume, research project proposal, transcripts, and advisor's recommendation letter.

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 2011-2012 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, which are involved in selecting and following up with fellowship recipients and their research. NWRI is thankful for the support of the following 2011-2012 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
- Mr. John T. Andrew
- Ms. Dawn Jorgensen
- Ms. Karen Cowan
- Dr. Shahid Chaudhry
- Dr. William Cooper
- Mr. William R. Mills
- Mr. Leonard Dueker
- Dr. Charles P. Gerba
- Ms. Nancy R. Bushnell
- Mr. Terry and Mrs. Jan Debay
- EOA, Inc.
- RBF Consulting
- McCormick, Kidman & Behrens, LLP
- Dr. Kara Nelson
- Mr. and Mrs. Jean Stern
- Miss Kendra Colyar
- 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
- Dr. James Barnard
- Mr. Larry Russell
- Dr. Douglas Call

5. 2011-2012 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 six graduate students receiving NWRI Fellowship Program funding for academic year 2011-2012.

NATIONAL WATER RESEARCH INSTITUTE
NWRI Fellowship Program

2011-2012 Progress Report

NWRI Fellowship
(Fall 2010-Fall 2011)

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).

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 goal is to determine whether coalbed methane (CBM) produced water can be effectively pretreated for desalination, thus providing water quality suitable for use as an alternative water resource. Progress since April 2011 into advanced natural organic matter characterization techniques to predict reversible and irreversible membrane fouling phenomena unique to coal-derived organic matter includes: (i) water quality assessment, (ii) water quality trends, (iii) NOM signature identification, and (iv) experimentation into preventing downstream fouling of desalination membranes.

Inorganic and organic water quality characteristics of coalbed methane (CBM) produced water discovered from this research and how those qualities impact beneficial use opportunities and treatment were published in Environmental Science and Technology in July (Dahm, et al., 2011)[1]. Produced water originating from coal seams carries attributes from the coal depositional environment. Database water composition is dominated by sodium bicarbonate and sodium chloride type waters with total dissolved solids concentrations of 150 to 39,260 mg/L. Constituents commonly exceeding standards for drinking, livestock, and irrigation water applications were total dissolved solids (TDS), sodium adsorption ratio (SAR), temperature, iron, and fluoride. Chemical trends in the basins are linked to the type of coal deposits, the rank of the coal deposits, and the proximity of the well to fresh water recharge. These water composition trends based on basin geology, hydrogeology, and methane generation pathway are relevant to predicting water quality compositions for beneficial use applications in CBM-producing basins worldwide.

A second publication, evaluating trends in water quality and water composition in an effort to anticipate problematic constituents for treatment, is in preparation (Dahm, et al, 2011)[2]. A figure in preparation for this publication is included as Figure 1 in this report. Figure 1 describes the impact of coal depositional environment on inorganic water composition. Waters with brackish or marine influence demonstrate different trends in dominant ions then continental or limnic depositional environments. The presence of chloride in marine basins presents an issue for beneficial use. Conversely sodium bicarbonate type water compositions in continental deposits commonly exhibit lower TDS concentrations and the best water compositions for use.

[1] Composite Geochemical Database for Coalbed Methane Produced Water Quality in the Rocky Mountain Region. Katharine G. Dahm, Katie L. Guerra, Pei Xu and ,Jorg E. Drewes. Environmental Science & Technology 2011 45 (18), 7655-7663

[2] Water Quality Trends in Coalbed Methane Produced Water. Katharine G. Dahm, Katie L. Guerra, Junko Munakata-Marr and, Jorg E. Drewes. In preparation for Water Research 2011

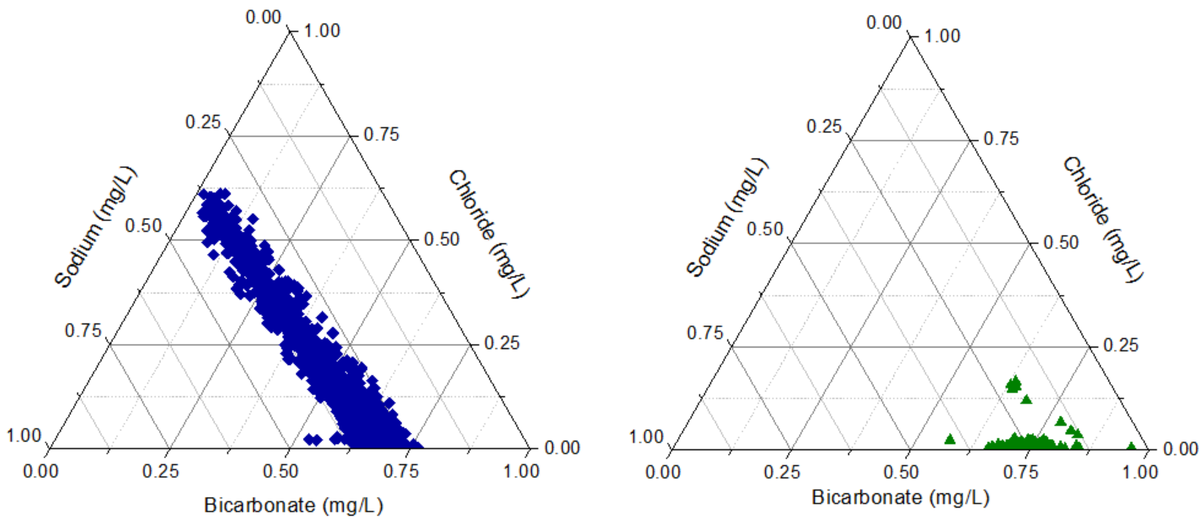


Figure 1.Ternary distribution of sodium-chloride-bicarbonate by coal depositional environment (left) brackish or marine, (right) continental or limnic

The continental basin evaluated in this research exhibited the most promising water quality for reuse based on inorganic water composition. Methane in this basin is generated from biogenic methanogenesis. The production of methane from this biogenic pathway results in slightly higher organic carbon concentrations in this basin. Organic carbon in this particular basin exhibited a unique organic signature when imaged with 3-D fluorescence spectroscopy. Utilizing spectra collected from wellhead samples and ultrafiltration membrane pretreated water provides a database of information for assessing NOM rejection and potential impact on desalination membranes. The following approach will be applied to complete this research:

- Determine if the organic signature for coalbed methane produce water is unique
- Determine inorganic interferences on UV and fluorescence spectra
- Role of iron in treatment and membrane fouling
- Assess organic matter rejection in membrane treatment

To determine variations in the 3D florescence spectra images experts in the field of fluorescence spectroscopy including George Aiken and Brett Poulin at the US Geological Survey are being consulted. This collaboration has resulted in interesting insight into inorganic constituent effects on the fluorescence spectra and ways to apply the spectra as an indication of treatment to aid in the completion of this study.

NATIONAL WATER RESEARCH INSTITUTE
NWRI Fellowship Program

2011-2012 Progress Report

NWRI Fellowship
(Fall 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 Program - Progress Report
October 2011

Policy Designs to Address Water Reallocations During Societal Transitions

Project Overview

This research 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 legal framework in the Western United States uses the prior appropriation doctrine (first in time, first in right) to allocate water. While the prior appropriation doctrine is deeply embedded in water law, over time, the prior appropriation doctrine has been conditioned by various provisions (e.g. beneficial use, duty of water). The interviews that have been conducted so far have addressed how human behavior and interactions relate to current water law and how variations and changes in society and ecology affect legal water institutions. This report outlines the progress that has been made in this research since the last progress report in April 2011.

Progress

Since my last progress report in April, I have conducted 15 more interviews with water managers, hydrologists, and various stakeholders for a total of 44 interviews. I have also been collecting primary documents related to my case study, such as the Draft Environmental Impact Statement for the Southern Nevada Water Authority's Groundwater Development Project and the resulting public comments. In addition, the Nevada State Engineer's water hearings on the Southern Nevada Water Authority's groundwater applications have begun. I have been listening and recording the hearings for later analysis.

Preliminary Research Findings

One common factor of all three case studies is the attempt to integrate environmental needs in water law. In all three case studies, interviewees have recognized that current water law inadequately protects against environmental impacts. Participants in the three case studies are using various methods (e.g. cooperative settlement agreements, water banks, and litigation) to more clearly define how and to what extent the environment should be considered. Interviewees have also shown that groundwater law is less defined than surface water law, and "sustainable yield" in terms of groundwater allocation can be interpreted differently. This research will attempt to understand how people make sense of the ambiguities of particular aspects of water law and how they work within the current rules to deal with water conflict.

So far, this research has also shown that people relate differently to institutions that have different structures but were created for a similar overall purpose. For example, both water banks and water conservancy districts keep water within a local area but the different structure of the two mechanisms lead to different rules that influence how people choose to use them. Utah and Wyoming both have an irrigation duty of water, but it is enforced differently. Several interviewees have explained that the difference affects how irrigators choose to irrigate their land.

Future Work

In the next several months, I will transcribe my interviews and then code and categorize the data from the interviews and collected documents to uncover descriptions, patterns, and descriptive relationships among categories. Careful analyses are required to fully understand how people use and develop the rules behind water law to meet a variety of water needs. The support from the NWRI Fellowship has been greatly appreciated, and it has allowed my research to proceed in a timely manner.

NATIONAL WATER RESEARCH INSTITUTE
NWRI Fellowship Program

2011-2012 Progress Report

NWRI Fellowship
(Fall 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 (April, 2011—September, 2011)

October 1, 2011

Joshua T. Wray
MCB PhD student
Arizona State University

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

Project Status: Wastewater treatment plants have utilized membrane bioreactors for wastewater processing for years. However, it was only until recently that membrane photobioreactors started to surface (Castaing et al., 2011; Su et al., 2011; Zhang et al., 2010) as a means to grow algae or other photoautotrophic organisms in a continual or semi-continuous process that can easily be coupled with traditional wastewater treatment to provide tertiary treatment. Such technology is desirable because algae have been known to produce a wide array of valuable oils and pigments as well as a high percentage of dry weight as starch or protein. However, before such technology can be realized, there are many questions yet to be answered, including identification of optimal physical parameters like pore size, membrane length and diameter as well as process variables backwash intervals and timing and cleaning protocols for membrane longevity. The focus of this project is to determine the feasibility of growing algae using a microfiltration membrane photobioreactor for the removal of nitrogen and phosphorous from waste streams.

Many of the studies to date involving membrane photobioreactors have looked at using ultra filtration membranes (Zhang et al., 2010) which has a pore size in the nanometer range and is commonly used in wastewater treatment for polishing today. Many commercial membrane bioreactors are available in this size range, but few if any exist for microfiltration applications. This is unfortunate in that such small pore size does not suit the process parameters needed for tertiary treatment of wastewater. First of all, traditional membrane bioreactors are intended to smaller particles like bacteria with a diameter for two microns or less. This is not necessary for algae culture where most algae are typically five or more microns. A higher pore size means less energy will be expended filtering since water can pass through with less resistance. Flow rate will be improved and backwash and cleaning time should be much less as well. All of these factors should keep the cost of microfiltration (MF) low and allow low cost mass algae cultivation in conjunction with wastewater treatment.

While the potential for MF membranes for mass algae culture is only starting to be realized (Castaing et al., 2011), there are many other critical factors to be considered. One focus in this project is filter direction. The water can be filtered from the inside of the filter fiber to the outside or outside to inside. Most of the studies to date have focused on inside-out filtering, in which the concentrated algae biomass slurry is held on the inside of the membrane fiber. This will likely increase energy usage for the process because the surface area of the filter is not maximized, and the liquid inside will be more viscous and harder to pump. Outside-in filtration would have a much larger filter surface area than inside-out. For this reason, my design has provided for outside-in filtering. With this setup, treated water can be pulled from the process without needing to shut down the process, thereby reducing downtime.

Besides the commercial scale use of membranes for treatment of wastewater, there is also a growing demand for a research-grade small and portable plug-and-play type devices capable of filtering and reducing the volume of small batches of culture. Such a device would have to be capable of fitting in a narrow tank or column, which is typical for many photobioreactors in use today. As a research associate for Arizona State University's Laboratory for Algae Research and Biotechnology (LARB), there are many times such a device would be utilized, especially as the new test bed facility comes online.

The first six months of this project has been devoted to finding the necessary suppliers and procurement of much of the supplies and equipment needed for this prototype plug-and-play system. This was mostly completed during the first six months of the project. The deliverable for the following six months has been developing the prototype and preparing it for testing. This has been an on-going effort. Many membrane companies do not offer membrane bioreactors with the appropriate specs for this project and custom building such membranes is out of the budget range for this project. Therefore, the system has been fabricated from scratch. This has been a challenging and ongoing process; however preliminary results have led to improved design modifications. After the final flaws are taken out of the system, numbers will be generated comparing permeate flux at different vacuum levels, pore sizes and different cultures to access the feasibility of continuous MF of algal cultures using an outside-in approach.

Degree Status/Other Projects: I am entering my fourth year as a Molecular and Cellular Biology PhD student at Arizona State University (ASU). I am in the process of finishing my dissertation prospectus and defending it while working in the LARB on projects collecting data that will support my dissertation. I am very excited about the possibility of integrating my membrane photobioreactor into other projects I am involved with. I currently am working on two carbon capture projects and one wastewater project as a research associate at ASU's LARB facility. One of the projects is concerned with utilizing flue gas from Intel's fabrication plant to grow algae and capture carbon dioxide. As the plug-and-play membrane design enters its final stages, I will likely test the design in harvesting algae from the Intel reactors. Automation of the device would make the timely harvesting and addition of nutrients much more user-friendly as a lot of work is involved in present harvesting techniques. Likewise, the plug-and-play membrane module would be very helpful in the EPA-sponsored P3 project I am involved in to create a suitable algal growth media from digested agricultural wastewaters. This would especially be useful in the continuous batch mode where harvest and nutrient addition is needed on a daily basis.

I would like to once again thank the National Water Research Institute and all the sponsors for giving me the opportunity to work on this project with the support of this fellowship. The project has been a continual learning experience for me and I think it complements and helps bring together the other work I am doing.

References:

Castaing JB, Masse A, Sechet V, Sabiri NE, Pontie M, Haure J, Jaouen P. Immersed hollow fibres microfiltration (MF) for removing undesirable micro-algae and protecting semi-closed aquaculture basins. Desalination 2011;276(1-3):386-396.

Su ZF, Li X, Hu HY, Wu YH, Noguchi T. Culture of Scenedesmus sp LX1 in the modified effluent of a wastewater treatment plant of an electric factory by photo-membrane bioreactor. Bioresource Technology 2011;102(17):7627-7632.

Zhang XZ, Hu Q, Sommerfeld M, Puruhito E, Chen YS. Harvesting algal biomass for biofuels using ultrafiltration membranes. Bioresource Technology 2010;101(14):5297-5304.

NATIONAL WATER RESEARCH INSTITUTE
NWRI Fellowship Program

2011-2012 Progress Report

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

Yaolin Liu
Civil and Environmental Engineering Major
University of Maryland

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, September 30, 2011

Yaolin Liu
Civil and Environmental Engineering Department,
The University of Maryland

Tasks Completed & Key Results

This report summarized the progress of our current study on the proposed project of Biofouling in Forward Osmosis: Mechanisms and Fouling Control. In the past six months, we focused on studying the factors affecting biofouling behavior in the FO processes, including solution chemistry, bacteria concentration, and membrane surface characteristics. The results obtained from the following experiments are presented here. For detailed information regarding methods and materials as well as experimental setup please refer to our previously submitted progress report.

(1) Bacteria attachment/detachment experiments under different solution conditions.

- Under same experimental conditions, the change of bacteria concentration in feed solution only shows effects on the total bacterial coverage of membrane surface, but no obvious effects on deposition rate. The deposition rate obtained for cell concentrations of 10^4 Colony Forming Unit (CFU)/ml, 10^5 CFU/ml, and 10^6 CFU/ml are 5.56 µm/s, 7.8 µm/s, and 6.79 µm/s, respectively.
- Although pH may affect bacteria surface charge, it did not have significant effects on the bacteria deposition rate for the CTA membrane. The isoelectric point of the bacteria is around 5.6, thus the surface of bacteria should be close to neutral at pH 5.6 and negatively charged at pH 7. The deposition rate at pH 7 and 5.6 is 9.96 µm/s and 8.16 µm/s, respectively.
- Our results also showed that ionic strength does not affect bacteria deposition. We changed ionic strength in feed solutions by adjusting NaCl concentrations from 100 mM to 1 mM. The obtained deposition rate is 7.8 µm/s and 8.55 µm/s for 100 mM and 1 mM, respectively.

(2) Bacteria attachment/detachment experiments with different membrane materials. We tested three types of membrane materials—cellulous triacetate (CTA) FO membrane, polyamide (PA) FO membrane and dopamine coated CTA membrane. As shown in Fig. 1, the PA membrane has relatively higher deposition rate and lower removal efficiency by physical rinsing than CTA membrane. Fig. 2 shows that surface modification by dopamine coating can dramatically slow down bacteria deposition rate. Note that the two sets of experiments were running with different permeate flux and cannot be directly compared to each other.

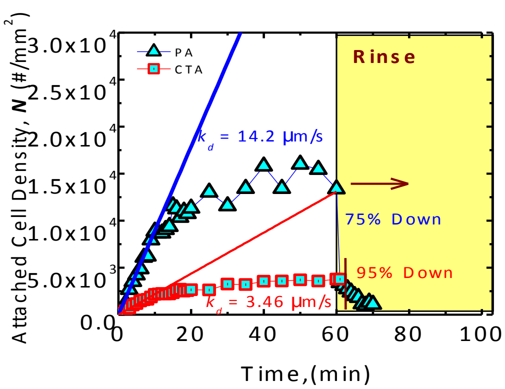


Fig. 1. Comparison between PA and CTA membrane.

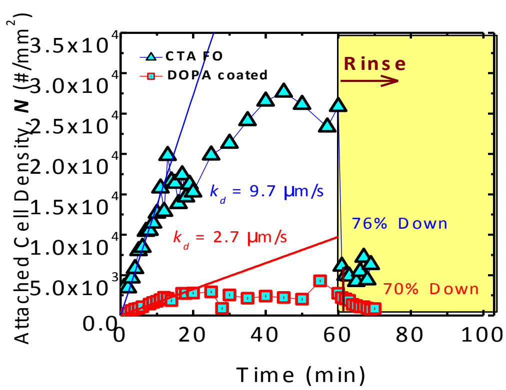


Fig. 2. Dopamine coating effects

(3) Development of a method to directly measure the force interactions between a live bacterium and the membrane surface.

The force measurement experiments are conducted on Digital Instruments (Veeco) Multimode AFM. We are currently working on developing a method to effectively attach a bacteria cell to the AFM probe in order to test the force between the bacteria cell and membrane surface.

Future Work

Based on the results obtained so far, we are planning to perform the following experiments to further understand the biofouling mechanisms: (1) measure the force interactions between a live/dead bacterium and the membrane surface in order to better understand the interaction mechanisms; (2) develop and examine different membrane surface modification strategies and study their effects on bacteria deposition rate; (3) perform long-term biofouling experiments under constant driving force to monitor membrane flux decline caused by biofouling; and (4) characterize biofilm formation in long-term biofouling experiments using microscopic approaches.

NATIONAL WATER RESEARCH INSTITUTE
NWRI Fellowship Program

2011-2012 Progress Report

NWRI-AMTA Fellowship for Membrane Technology

(Fall 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

alberto.tiraferri@yale.edu

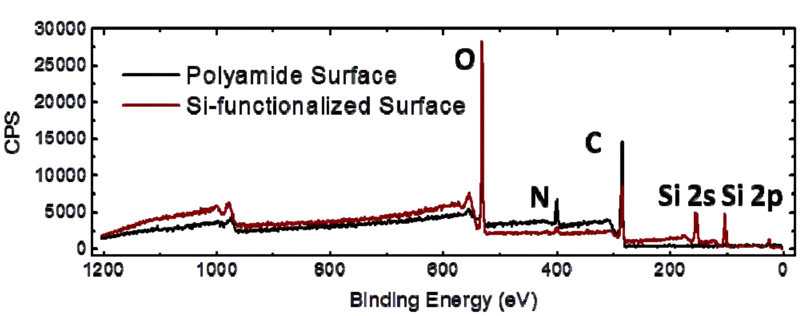
October 1, 2011

In the last progress report, a membrane surface functionalization was reported employing shortened and carboxylated single-walled carbon nanotubes (SWNTs) to create a non-depleting cytotoxic membrane surface, which is expected to delay biofouling during membrane operation. This work was published in *ACS Applied Materials and Interfaces*: Tiraferri, A.; Vecitis, C. and Elimelech, M. "Covalent Binding of Single-Walled Carbon Nanotubes to Polyamide Membrane for Antimicrobial Surface Properties", *ACS Applied Materials and Interfaces*, 3 (8), August 2011, 2869-2877

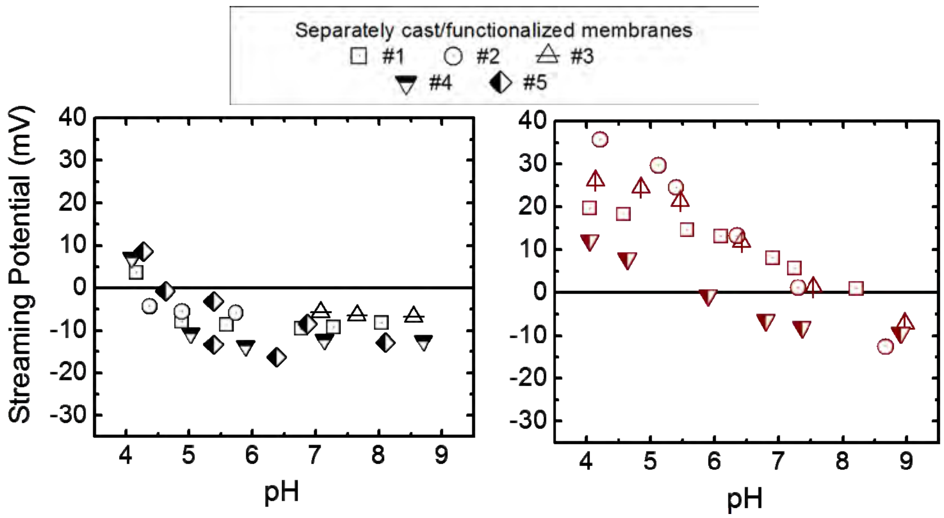
Specific, desired properties are imparted to water purification membranes by irreversibly binding nanoparticles to the membrane surface. Recently, super-hydrophilic silica nanoparticles have been used to render the surface of polyamide TFC membrans super-hydrophilic. The silica nanoparticles were functionalized with N-trimethoxysilylpropyl-N,N,N-trimethylammonium chloride. The positively charge ammonium groups could be exploited to create electrostatic and ionic bonds with the surface carboxylic groups of polyamide. The functionalized silica nanoparticles have a diameter of 18.5±3.5 nm and a zeta potential of +31.5±3.5 mV in deionized water at unadjusted pH of approximately 7.2

TFC membranes designed for osmotically-driven processes, such as forward osmosis (FO) and pressure retarded osmosis (PRO), were fabricated. A polysulfone (PSf) support layer was initially hand-cast starting from a casting solution of 9% PSf in DMF and utilizing DI water to initiate the phase inversion. Subsequently, polyamide was cast on top of the PSf support by interfacial polymerization of MPD and TMC.

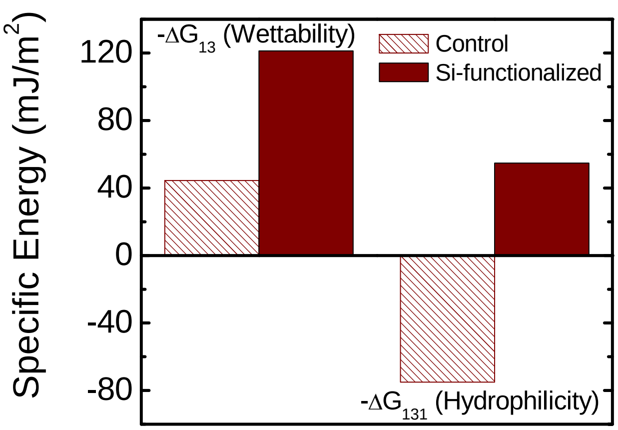
The membrane functionalization protocol was a dip-coating procedure, whereby the polyamide membrane surface was contacted with the nanoparticle suspension overnight at room temperature (23 °C). The presence of silica nanoparticles at the membrane surface was evaluated after functionalization by SEM imaging and XPS. SEM micrographs showed a uniform and multilayer coating of nanoparticles on the polyamide thin film features. XPS confirmed the presence of silica at the surface (Graph on the left). AFM measurements suggested that the presence of nanomaterials does not affect the surface roughness of the polyamide thin film.



The streaming potential of the membrane surface was measured before and after functionalization. We observed a more positively charged surface in the presence of silica nanoaparticles. A more positively charged surface is expected due to the nature of the nanoparticle coating and due to screening of the negatively charged moieties of the membrane by the nanomaterials (Graph below).



The presence of silica nanoparticles effectively rendered the membrane surface more hydrophilic and wettable. The measured contact angle of deionized water decreased to values equal or lower than 10° for the silica-functionalized polyamide. Calculations of the surface wettability and hydrophilicity showed that both parameters increase significantly after the membranes were functionalized with the super-hydrophilic naoparticles (Graph on the right). The irreversibility of the functionalization was assessed by subjecting the functionalized surfaces to chemical and physical stress. Chemical stress consisted of solutions of high salinity (0.6 M NaCl), high pH (pH 12 adjusted with NaOH), and low pH (pH 2 adjusted with HCl). Physical stress was applied by bath sonication. The contact angle of deionized water on the functionalized surface did not change after the membranes were subjected to stress, suggesting that the silica nanoparticles were still present at the surface.



The super-hydrophilic nature of the functionalized membranes is expected to lower the attachment kinetics of bacteria in cross-flow operations, thereby delaying the onset of biofouling. Also, minimized organic fouling is anticipated. Fouling experiments are currently in progress and are carried out using *E. coli* bacteria, alginate, SRNOM, and BSA protein solutions in a cross-flow cell under forward osmosis conditions. The intermolecular forces between foulants and membrane surface and between foulants and fouled membrane surface will be evaluated using AFM. By combining fouling data and AFM intermolecular forces measurements, the fouling mechanism will be elucidated for membranes before and after functionalization with silica nanoparticles. The transport characteristics of the membranes were observed not to be affected by the presence of silica nanoparticles in both FO and PRO experiments.

NATIONAL WATER RESEARCH INSTITUTE
NWRI Fellowship Program

2011-2012 Progress Report

NWRI-Southern California Salinity Coalition Fellowship

(Fall 2010-Present)

Kari Varin
Chemical Engineering Major
University of California, Los Angeles

Graduation Date: June 2013
Advisor: Dr. Yoram Cohen

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

Kari Varin
October 1, 2011
Chemical and Biomolecular Engineering Department
University of California, Los Angeles

Project Overview

Effective use of RO/NF membranes in brackish desalination and water reuse applications requires adequate 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 could act as both 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 is utilized to generate a high surface density of active surface sites on a polyamide membrane for subsequent graft polymerization using suitable water soluble vinyl monomers. Surface structuring via graft polymerization is then employed 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 membrane is 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 the grafted polymeric brush layer is confirmed by Fourier Transform Infrared (FTIR) Spectroscopy. Graft polymerization kinetics will be determined, for a number of different candidate water soluble monomers, with respect to the evolving grafted polymer layer thickness with reaction time and initial monomer concentration. The change in surface energy (a measure of the degree of surface hydrophilicity/hydrophobicity) is quantified via contact angle measurements and surface charge is determined by analysis of streaming potential measurements in a specialized RO cell. Performance evaluation of the SNS-TFC-PA RO/NF membranes will be carried out by examining their mineral salt scaling and biofouling propensities. Membranes effectiveness in retarding organic- and bio-fouling will be assessed via flux decline studies with model proteins and polysaccharides solutions and utilizing secondary treated municipal waste water effluent. Reduction in membrane mineral scaling propensity will be quantified from both flux decline studies (using salt solutions supersaturated with respect to the target mineral salt scalant) and via direct observations of the evolution of mineral scaling on the membrane surface in an optically transparent high pressure RO cell. The goal of the present study is to tailor-synthesize SNS-TFC-PA membranes of high permeability, similar or increased salt rejection, with reduced mineral scaling propensity and increased fouling resistance.

Research Progress

Since the last fellowship progress report in April 2011, I completed my written and oral Prospectus for Research entitled, "Surface Nanostructuring with Hydrophilic Polymers for Fouling Resistant Membranes" in June 2011. This was completed in partial fulfillment of the requirements for the degree of Doctor of Philosophy at UCLA, and advanced my status to PhD candidate.

In July 2011, I attended the International Congress on Membranes and Membrane Processes (ICOM 2011) in Amsterdam, The Netherlands. While at the conference I presented my paper entitled "High performance nano-structured NF/RO membranes – synthesis, surface characterization and performance."

Current work is being conducted on surface analysis on membrane substrates with atomic force microscopy (AFM). 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. Preliminary results show that polymer grafting increase the features observed with AFM analysis. Further studies will compare the surface roughness values to their contact angle measurements.

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. Once the monomers are chosen, membrane compatibility tests as well as grafting experiments will be conducted.