Advanced Thermoplastic Membranes for Water Filtration

Final Report

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Acronyms and Abbreviations

Term	Definition
µm	Micrometer
A	Water Permeability Constant
abs	Absorbance
ANSI	American National Standards Institute
Avg	Average
B	Solute Permeability Constant
BSA	Bovine Serum Albumin
C_f	Feed Concentration
Cl_2	Chlorine
cm	Centimeter
COD	Chemical Oxygen Demand
CONUS	Continental United States
C_p	Permeate Concentration
Ct	Concentration×Time
CTMA	Commercial Technologies for Maintenance Activities
d	Days
DOD	Department of Defense
D_s	Diffusion Coefficient
e	Euler's Constant
EDTA	Ethylenediaminetetraacetic Acid
ft^2	Feet Squared
g	Gram
gal	Gallon
gph	Gallons Per Hour
GVSC	Ground Vehicle Systems Center
GW	Graywater
hrs	Hours
IgA	Type A Immunoglobulin
J_s	Solute Flux
J_w	Water Flux
kDa	Kilodalton
L	Liter
m	Meter
m^2	Square Meter
MF	Microfiltration
mg/L	Milligram Per Liter
mg/L C	Milligram of Carbon Per Liter of Liquid
min	Minutes
mL	Milliliter
MRO	Maintenance Repair and Overhaul
NaOCl	Sodium Hypochlorite
NCMS	National Center for Manufacturing Sciences
NDSU	North Dakota State University
nm	Nanometer
NSF	National Sanitation Foundation
NTU	Nephelometric Turbidity Units

°C	Degree Celsius
ODASD-MR	Office of the Deputy Assistant Secretary of Defense
ORP	Oxidation-Reduction Potential
pH	Power of Hydrogen Ion Concentration
ppm C	Parts of Carbon Per Million Parts of Liquid
psi	Pounds Per Square Inch
R^2	Correlation Coefficient
R&D	Research and Development
RO	Reverse Osmosis
s	Seconds
SEM	Scanning Electron Microscopy
T	Temperature
TDS	Total Dissolved Solids
TOC	Total Organic Carbon
UF	Ultrafiltration
UV_{254}	Ultraviolet Absorbance at 254 Nanometers
ΔP	Change in Pressure
Δx	Membrane Thickness
$\Delta \pi$	Change in Osmotic Pressure

1. Executive Summary

Since only 1% of the world's water is available for human use[1], efforts to increase water availability must include both reuse and generating new potable water sources. This is a problem for both domestic agencies and the Department of Defense (DOD) operating worldwide. The DOD in particular has significant force projection costs, and depot maintenance and operational expenses associated with potable water, making DOD an ideal testbed for developing new water treatment technologies.

One of the largest sources of water reuse is graywater. Being able to reuse graywater can reduce the water burden on municipalities, government facilities, and forward operating bases. Thermoplastic membrane technology has shown the ability to provide superior pre-filtration for reverse osmosis (RO), without the fouling and complexity of other technologies.

The scope of the initiative included research into membrane flux rates, fouling resistance, chemical resistance, reliability, and low-cost maintainability that will lead to improved module design and filter system component development. Work scope also included delivery of prototypes for testing.

Funding was secured through the National Center for Manufacturing Sciences (NCMS) Commercial Technologies for Maintenance Activities (CTMA) Program and the Office of the Deputy Assistant Secretary of Defense, Materiel Readiness (ODASD-MR).

1.1 Results

PPG fabricated three designs of prototype 2540 membrane elements, 108 (C, D, E, and F), 109 (E, F, G, and H), and 111 (B, D, E, and G). NDSU evaluated graywater filtration performance of the prototype filters. Six runs were completed by installing two spiral wound membranes into the North Dakota State University (NDSU) test skid at a time. The procedure detailed in Section 3.3.3 of this report was used, and graywater was pumped through both membranes for 3 days while total organic carbon (TOC), chemical oxygen demand (COD), ultraviolet absorbance at 254 nanometers (UV_{254}), and turbidity were tested to determine their removal. Tables 8, 9, and 10 in Section 3.3.3 summarize the permeate flow declines, removal efficiencies, and coefficient of variations, respectively. Compared to the clean water flow, the graywater reduced permeate flow by 55-80%. The membranes were best at removing turbidity with >85% removal. COD removal varied from 40-55% and UV_{254} removal varied from 45-90%.

For the skid operation, the goal was to maintain a recovery of greater than 80%; however, the recovery provided by membrane 02117 dropped to 50% immediately after the graywater was added, and after the first day, it dropped again to 10-15%. In terms of constituent removal, membrane 02117 removed 30-60% COD and >90% turbidity for the 14 days that it was operational.

For membranes 108C, 108E, 108F, and 108D, the highest permeate flow reductions were observed in Runs #1 and #4 with 75-80% flow reduction. Incidentally, they were the only two runs that had 2-leaved spiral wound membranes installed, the fewest leaf configuration tested. The rest of the membranes were 4-leaved and only saw reductions between 55-70%. There was no discernable difference in flow reduction between the two permeate carrier design variants tested.

[1] http://www.globalchange.umich.edu/globalchange2/current/lectures/freshwater_supply/freshwater.html

For membrane integrity, the soak tests showed minimal weight loss and shrinkage. Advanced methods such as scanning electron microscopy (SEM) would need to be employed to accurately determine the diminishment of membrane integrity. For membrane longevity, the lifespans of control membrane, membranes 1003, 1035B, UF 833-1689, and MF 769-5412 were estimated based on when the membrane became brittle or when the flux decline by 50%. The only cleaning solution that the control membrane failed with was the 0.2% Cl_2 (pH 9) in which it failed after 4.25 days which gave it an estimated lifespan of 3.6 years. Membrane 1003 failed after soaking in 0.2% Cl_2 (pH 9) and 1.5% PPG cleaner (no EDTA, pH 10); the lifespans were estimated to be 6 years with chlorine cleanings and 2.6 years with the PPG cleaner (no EDTA). Membrane 1035B failed after 7 days in the 0.2% Cl_2 (pH 9) cleaning solution which gave it an estimated 6-year lifespan. Membrane UF 833-1689 failed in 3 cleaning solutions (0.2% Cl_2 (pH 7 and 10) and pH 2 buffer solution; at the typical pH of chlorine cleanings (pH 10) these types of cleanings would give the membrane an estimated 1.5 to 2.1-year lifespan. For membrane MF 769-5412, it failed in 0.2% Cl_2 (pH 10) after 8 days, which would give it an estimated lifespan of 6.9 years (Tables A-1 and A-2, Appendix A, for these estimations and their calculations).

1.2 Benefits

U.S. Army, U.S. Marine Corps, and Special Operations all need reliable, easy-to-use and cost effective systems for producing potable water from graywater. This project has accelerated the development of thermoplastic membrane technology for graywater reuse, seawater desalination, and brackish water use.

Thermoplastic membrane technology can provide advantages for graywater reuse due to the ability to modify porosity and incorporate inorganic fillers to deliver high flux rates. This can result in a high percentage influent stream recapture. Thermoplastic membranes also have shown the ability to operate longer without fouling, reducing the cost for replacements to municipalities, maintenance operations and facilities as well as reducing the waste stream. Thermoplastic membranes offer durability and can be cleaned by backwashing to restore flux, thereby providing long lifetimes and reliability in the field.

A laboratory scale cross-flow testing methodology was developed at NDSU to quantify salt water (i.e. marine) bacteria fouling on flat membrane sheets provided by PPG.

Membrane specimens were soaked in cleaning chemicals typically used including NaOCl (bleach), citric acid, enzyme cleaner, and PPG alkaline cleaner (with and without EDTA). The concentrations of these chemicals were higher than normal to accelerate membrane degradation and estimate lifespan of the membranes.

Deionized water and aqueous solutions of bovine serum albumin (BSA), Type A immunoglobulin (IgA), 270 kDa dextran, 500 kDa dextran, and 0.05 and 0.1 µm latex beads (the solutes were based on pore sizes of the membranes) were fed through the flat sheet membrane specimens in a bench-scale plate and frame cross-flow module to determine constants that relate the water flux with pressure differential [Eq. 1] and solute flux with concentration differential [Eq. 2].

Spiral wound membrane prototypes, assembled by PPG, were installed into a membrane skid The skid was operated by NDSU with a graywater recipe (NSF/ANSI 350 – 2012 synthetic bathing and laundry challenge graywater) to evaluate filter performance under fouling conditions.

1.3 Technology Transition

The results of this project were used by PPG to build a membrane-based filtration subsystem consisting of pumps, pre-filter, a control system, and the PPG membrane filter cartridges. The

subsystem was designed for the Army Ground Vehicle Systems Center (GVSC) evaluation of filtration membrane cartridges for both graywater and pre-filtration for desalination. The system was factory tested by PPG using clean water and was shipped to GVSC. PPG documented how to use the subsystem for the target applications, and will train GVSC personnel in system operation at a future date once installed by GVSC.

Based on the results of the 2540 membrane filter performance evaluation conducted by NDSU, PPG scaled up the 4-leaved 2540 design into a corresponding configuration in the larger 4040 membrane element size by doubling the number of leaves for the standard 4040 design configuration. PPG assembled and tested twelve 4040 prototype membrane filter elements (six control and six enhanced design) for integrity and clean water performance. Mean clean water specific flux normalized at 20°C for enhanced design (20-MB-110) 4040 prototype UF membrane filters was 102% higher than control, 9.79 versus 4.85 gal/ft^2/day/psi. These prototype 4040 membrane filters will be evaluated by GVSC for performance with graywater using the PPG delivered skid.

1.4 Recommendations

Integrity/Soak Tests

NaOCl is the only cleaning chemical used in commercial membrane filtration that caused significant damage and life reduction of the membranes. It is recommended that other cleaning chemicals be used for routine and intensive cleanings when possible. When NaOCl must be used for sanitization or cleaning due to foulant requirements, caution should be exercised not to exceed maximum chlorine concentrations recommended by PPG, otherwise unacceptable life reduction of the membranes could result.

Ultrafiltration Skid Operations

Since the spiral wound membranes with 2 leaves had a permeate flow decline by 75% with graywater, more leaves are recommended. However, all the membranes had a recovery less than 50%, which was lower than the project goal of 80% recovery. Further development, focusing on both cartridge design and system design optimization is required to achieve higher recovery rates with this technology.

1.5 Invention Disclosure

Invention Disclosure Report(s):

DD882 Sent to NCMS ☐
No Inventions (Negative Report) ☒

1.6 Project Partners

- U.S. Army Combat Capabilities Development Command (CCDC) Ground Vehicle Systems Center (GVSC)
- PPG Industries, Inc.
- North Dakota State University (NDSU)
- National Center for Manufacturing Sciences (NCMS)

2. Introduction

2.1 Background

For the last decade, water, and specifically water scarcity has been a mega trend. Many futurists, risk planners, and consultants have issued reports and predictions about the impact of the water economy on the United States and the world. For the last three years, this has been a stark reality shown in the drought conditions in California[2]. The 2015 water crisis in Flint, Michigan was a man-made crisis in an area with an overabundance of clean water. Globally, 663 million people in 2015still used unimproved drinking water sources. Inadequate access to safe water and sanitation services, coupled with poor hygiene practices, kills and sickens thousands of children every day, and leads to impoverishment and diminished opportunities for thousands more (UNICEF, 2015). The DOD conducts global disaster relief efforts and providing clean water is a major portion of all such efforts. DOD expeditionary missions must either carry water with them, a huge logistics effort, or use technology to produce it in situ. Even maintenance repair and overhaul (MRO) efforts, both domestic and expeditionary, require large amounts of clean water.

Since only 1% of the world's water is available for human use, efforts to increase water availability must include both reuse and generating new potable water sources. This is a problem for both domestic agencies and the DOD operating worldwide.

Reverse osmosis is effective at cleaning water for potable use; however, the expensive and sensitive reverse osmosis membranes require a pre-filtration process. Fouling of the reverse osmosis membranes and pre-treatment components is a significant cost driver for the approach. Current pre-filtration processes are either maintenance intensive and the filtration cartridges are treated as disposable, single use items or expensive, highly complex, sensitive membrane modules. Industry is developing a thermoplastic membrane technology that has superior pre-filtration for reverse osmosis operations. The new pre-filter membrane resists fouling, is easily back-flushed for longer operation, and is less complex to operate than other reverse osmosis pre-filter technologies. DOD first investigated the technology under a U.S. Army CERL contract (W9132T-09-C-0046) to explore the development of a thermoplastic membrane for water security. Industry continued that work using internal research and development (R&D) funds. For example, PPG developed a variant of this technology to treat water for hydraulic fracturing under a Department of Energy RPSEA project (12123-18).

2.2 Purpose

One of the largest sources of water reuse is graywater. Being able to reuse graywater can reduce the water burden on municipalities, government facilities, and forward operating bases. Graywater reuse can include a spectrum of activities from recirculating showers and washing machines, to creating potable water from these sources.

Thermoplastic membrane technology can provide advantages for graywater reuse due to the ability to modify porosity and incorporate inorganic fillers to deliver high flux rates. This can result in a high percentage influent stream recapture. Thermoplastic membranes also have shown the ability to operate longer without fouling, reducing the cost for replacements to municipalities, maintenance operations and facilities as well as reducing the waste stream. Thermoplastic membranes offer durability and can be cleaned by backwashing to restore flux,

[2] California Water Commission https://cwc.ca.gov/Pages/Home.aspx

thereby providing long lifetimes and reliability in the field.

Another method to provide potable water is to extract it from seawater or brackish water. Municipalities and maintenance facilities have used desalination technology for decades. However, these process are generally very energy intensive. The most successful operations have been co-located with power plants, which is not always practical. Current desalination systems employ cartages to filter the incoming water prior to the reverse osmosis step. These cartridges are relatively inexpensive, and protect the sensitive reverse osmosis membrane. However, they provide a cost and logistics burden for maintenance facilities and municipalities plus disposal contributes to the waste stream. These issues are exacerbated in military forward operating bases. Membrane pre-filtration has shown promise in reducing this burden, but the systems are complex and the backwashing requirements are more onerous than filter cartridge management.[3] As a result, many membrane pre-filtration systems in operation at maintenance facilities have reverted to cartridge operation.

Thermoplastic membrane technology has shown the ability to provide superior pre-filtration for reverse osmosis, without the fouling and complexity of other technologies. These membranes can operate with high concentration solids source streams. Systems with advanced membrane technology overcome the issues found in other pre-filtration systems.

The project objective was to apply thermoplastic membrane filtration technology to graywater reuse and pre-filtration for reverse osmosis seawater desalination systems – to develop module systems that can readily integrate into typical maintenance and operating facility water systems.

2.3 Project Scope

Project scope was divided into the following applications:

- Graywater Membrane Development
- Graywater Fouling Research
- Pre-filtration for Desalination Membrane Development
- Pre-filtration for Desalination Fouling Research
- Filtration Subsystem Development
- Filtration Subsystem Evaluation

[3] http://www.usbr.gov/research/AWT/reportpdfs/Report106.pdf

3. Project Narrative

3.1 Project Approach

The project approach included research into membrane flux rates, fouling resistance, chemical resistance, reliability, and low-cost maintainability that would lead to module design and filter system component development. Work also included delivery of filter prototypes and a skid for testing. Tasks for the project were divided according to application of filtration technology:

Graywater Membrane Development

Task 1.1 – PPG evaluated membrane variations to optimize flux and permeate quality using cross-flow filtration with a graywater feed. Variables to be explored for graywater optimization included material formulations, membrane characteristics, and coating technologies. Particular attention was placed upon emulsified feed streams containing soaps. This task accounted for the findings from Task 2.1 for improving fouling resistance.

Task 1.2 – Lab-scale filter cartridge designs were built to take advantage of the membrane performance. Prototype filters were fabricated and evaluated in lab-scale equipment. The goal was an effective combination of permeate quality, flux, and downstream filtration system performance. Chemical analysis was conducted on the filtration samples before and after testing. The impact of concentrating the feed stream to achieve 80% recovery was assessed.

Task 1.3 – Filtration performance of the prototype filters in graywater feed streams was characterized using an independent laboratory for items like bacteria reduction.

Graywater Fouling Research

Task 2.1 – NDSU researched the mechanism of reverse osmosis fouling of standard PPG filtration membrane from graywater. The findings were provided to PPG for PPG Task 1.1. The optimized membrane from PPG was characterized for fouling.

Task 2.2 – NDSU researched filter design characteristics that can reduce pre-filter/reverse osmosis filter fouling. The need to achieve 80% recovery and its impact on pre-filter/reverse osmosis filter fouling was explored.

Pre-filtration for Desalination Membrane Development

Task 3.1 – PPG evaluated membrane variations to optimize flux and permeate quality using cross-flow filtration with a salt-water feed. Variables explored for desalination reverse osmosis pre-filtration optimization included material formulations, membrane characteristics, and coating technologies. Treatments that minimize biofouling were explored. This task accounted for the findings from Task 4.1 for improving fouling resistance.

Task 3.2 – Lab-scale filter cartridge designs were built to take advantage of the membrane performance. Prototype filters were fabricated and evaluated in lab-scale equipment. The goal was an effective combination of permeate quality, flux, and downstream filtration system performance. Chemical analysis was conducted on the filtration samples before and after testing. The focus was to achieve highest operational performance while maintaining low capital and operational cost.

Task 3.3 – Filtration performance of the prototype filters in salt-water feed streams was characterized using an independent laboratory for items like bacteria reduction.

Pre-filtration for Desalination Fouling Research

Task 4.1 – NDSU researched the mechanism of reverse osmosis fouling of standard PPG filtration membrane in desalination. The findings were provided to PPG for PPG Task

3.1. The optimized membrane from PPG was characterized for fouling.

Task 4.2 – NDSU researched filter design characteristics to reduce pre-filter/reverse osmosis filter fouling with salt-water desalination. The focus was biofouling that can occur in sea water feed streams. The ability to mitigate biofouling through membrane treatments was evaluated.

Filtration Subsystem Development

Task 5.1 – The results of Tasks 1-4 were used to build a membrane-based filtration subsystem consisting of pumps and filters, a control system and the filter cartridges. The subsystem was designed to evaluate filtration cartages for both graywater and pre-filtration for desalination. PPG documented how to use the subsystem for both target applications. This included cleaning and component swaps to avoid contamination of the subsystem between the two filtration target applications.

Task 5.2 – PPG factory tested the filtration subsystem to demonstrate performance with clean and test water. When the subsystem passed factory test, it was cleaned and packaged for shipment to GVSC.

Filtration Subsystem Evaluation

Task 6.1 – The membrane-based filtration subsystem was delivered to GVSC for evaluation. PPG will train GVSC to use the system and demonstrate the system performance. PPG will support GVSC during GVSC's evaluation of the membrane-based filtration subsystem.

Task 6.2 – GVSC will document possible system modifications based subsystem operation for possible future funding.

3.2 Soak Tests

Membrane specimens were soaked in cleaning chemicals typically used including NaOCl (bleach), citric acid, enzyme cleaner, and PPG cleaner (with and without EDTA). The concentrations of these chemicals were higher than normal to accelerate membrane degradation (Table A-1, Appendix A).

In practice, routine cleanings (integrity) are typically done by soaking the membranes in a solution of 200 to 3,000 mg/L Cl_2 (NaOCl) for 20 minutes to 10 hours every other day. When NDSU received a commercially-available membrane (control membrane), the degradation of their integrity was determined by cutting 5×10 cm specimens from the bulk roll and soaking three replicates in 250 mL of various concentrations of NaOCl (0, 200, 600, 1,000, 2,000, and 3,000 mg/L Cl_2) for various soak periods (0.33, 3, 5, and 10 hours). The weight loss, shrinkage, leached total organic carbon (TOC), oxidation-reduction potential (ORP), total dissolved solids (TDS), and conductivity were measured to determine loss of integrity. All these soak tests were at room temperature (25°C) and lightly shaken.

To determine the lifespan of the membranes (longevity) 5×10 cm specimens were soaked in high concentrations of cleaning chemicals for 7 days to accelerate failure. For example, the Cl_2 soaks were based on a routine cleaning schedule with 200 mg/L Cl_2 for 60 minutes every other day and an intensive cleaning schedule with 2,000 mg/L Cl_2 for 5 hours every 6 months.

Calculation to determine short-term soaking concentration×time (Ct):

$$\text{Yearly routine Ct} = \frac{365 \text{ days}}{\text{routine soakings every 2 days}} * 1 \text{ hrs routine soak time} * 200 \frac{\text{mg}}{\text{L}} Cl_2$$

$$\text{Yearly routine Ct} = 182.5 \text{ hrs} * 200 \frac{\text{mg}}{\text{L}} Cl_2$$

$$\boldsymbol{Yearly\ routine\ Ct = 36,500 \frac{mg}{L}\ Cl_2 * hrs}$$

$$\text{Yearly intensive Ct} = \frac{365 \text{ days}}{\text{intensive soak every 180 days}} * 5 \text{ hrs intensive soak time} * 2000 \frac{\text{mg}}{\text{L}} Cl_2$$

$$\text{Yearly intensive Ct} = 10.13 \text{ hrs} * 2000 \frac{\text{mg}}{\text{L}} Cl_2$$

$$\boldsymbol{Yearly\ intensive\ Ct = 20,277 \frac{mg}{L} Cl_2 * hrs}$$

$$\boldsymbol{Yearly\ intensive\ Ct + yearly\ routine\ Ct\ = 56,777 \frac{mg}{L} Cl_2 * hrs}$$

4-year lifespan: Ct = 227,108 mg/L Cl_2
6-year lifespan: Ct = 340,662 mg/L Cl_2
10-year lifespan: Ct = 567,770 mg/L Cl_2

To simulate these Ct values in 7 days, the concentrations of 1,500, 2,000, and 3,500 mg/L Cl_2 were used for soakings. Similar calculations were used with different cleaning solutions. The membranes were considered unusable based on specimen brittleness and cracking or flux decline to below 50% original flux.

3.2.1 Integrity Tests (Routine Cleanings)

Based on the integrity tests (soaking control membranes under NaOCl solutions for ≤ 10 hours), the average weight loss was 0.125% while the average shrinkage (reduction in area) was 0.234%. The conductivity and TDS were measured, but since the amount of leached material was small, the conductivity and TDS of the NaOCl made it hard to determine any difference in the soaking solution. Measuring the TOC of the soaking solution made it easier to distinguish leached membrane material from the NaOCl. After the first 20 minutes, the amount of TOC increased to 0.39 ppm C and 1.19 ppm C for concentrations of 2,000 mg/L Cl_2 and 3,000 mg/L Cl_2, respectively (Figure 1). The ORP for all the soaking solutions showed an increase after 20 minutes which remained steady throughout the soakings, indicating a completed reaction between the specimen and the cleaning solution (Figure 2). These tests were not done for the other membranes, since there was very little inference that could be made.

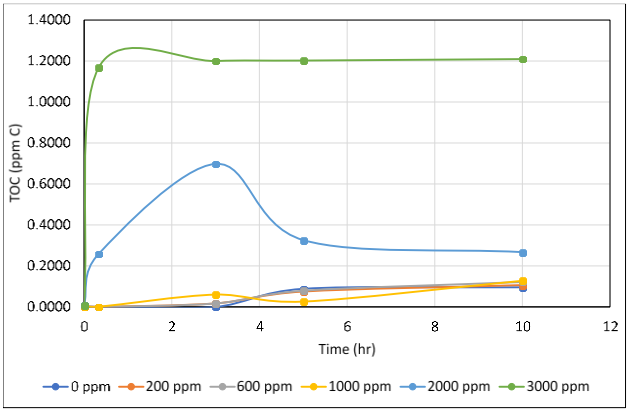

Figure 1. TOC Leached for Short-Term Integrity Soakings Under 0-3,000 ppm NaOCl Solution for Control Membrane

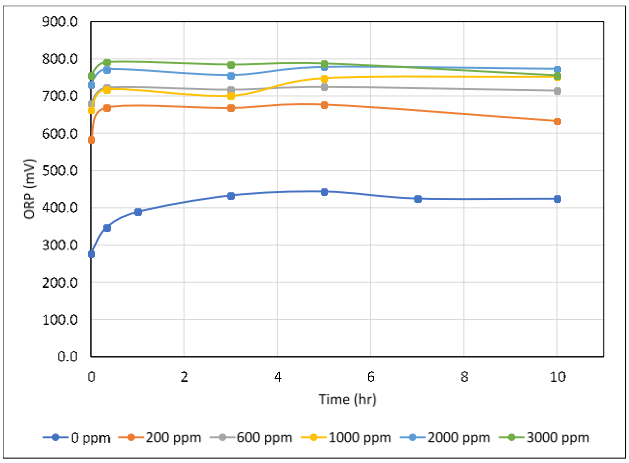

Figure 2. ORP for Short-Term Integrity Soakings Under 0-3,000 ppm NaOCl Solution for Control Membrane

3.2.2 Longevity Tests (Routine and Intensive Cleanings)

Initial Control Membrane Results

After conducting the long-term soakings in 1,500, 2,000, and 3,500 mg/L Cl_2, brittleness and cracking was observed after the 7 days. From these soakings, it was determined that the lifespan was between 4-6 years. To get a more accurate lifespan, the soak tests were redone. Since the 3,500 mg/L Cl_2 caused the membrane to degrade quickly, soakings were redone with the 2,000 mg/L Cl_2 concentration alone. This time membrane was removed periodically and bent to determine its brittleness. After 4.25 days (102 hours), the membrane cracked, and a life-span of around 4 years was concluded with the previously described routine and intensive NaOCl cleanings. Afterwards, SEM images were taken to get a closer look at failure (Figures 3 and 4). Figure 3 shows the 2,000 mg/L Cl_2 concentration causing the microscopic clusters to shrink after the first 20 minutes. Figure 4 shows cavities of membrane degradation after soaking the membrane at the same Cl_2 concentration for 4 days.

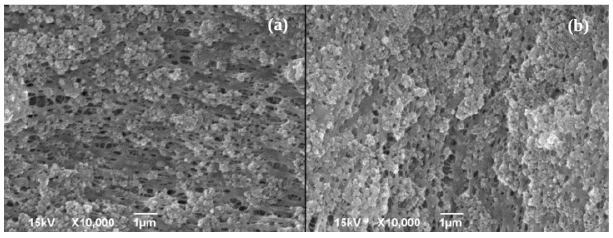

Figure 3. SEM Images of Control Membrane After Soaking for 20 Minutes at pH 9: (a) 0 ppm Cl_2 and (b) 2,000 ppm Cl_2

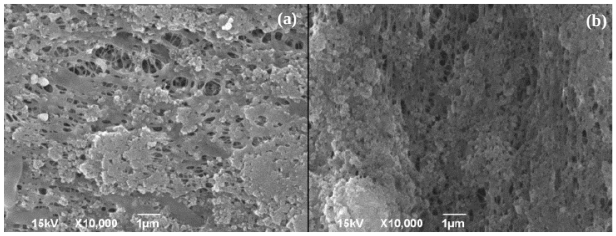

Figure 4. SEM Images of Control Membrane After Soaking for 4 Days at pH 9: (a) 0 ppm Cl_2 and (b) 2,000 ppm Cl_2

Membranes 1003 and 1035B

NDSU received membranes 1003 and 1035B for soak tests to compare to the control. Other cleaning chemicals were also used in the soakings. The membrane specimens soaked in varying pH buffers (2, 7, 9, and 10) along with 2% citric acid, 1.5% enzyme cleaner, 2,000 ppm (0.2%) Cl_2, 1.5% PPG cleaning solution (with EDTA), and 1.5% PPG solution (without EDTA) and a combination of the chemicals at different pH values. Weight loss, shrinkage, and flux decline/increase were used to indicate membrane integrity loss.

Tables 1, 2, and 3 summarize the percent weight loss, shrinkage, and flux decline/increase (negative values indicate flux decline and positive values indicate flux increase) of the control membrane with membranes 1003 and 1035B. Weight loss increased with pH. The highest weight losses for all the membrane specimens were at a pH of 10 with the PPG cleaning solution with EDTA. The same trend was observed for shrinkage. For the flux, the control membrane maintained a steady flux throughout the experiments; membrane 1003 showed significant flux decline for all but the pH 10 buffer; and membrane 1035B showed significant flux decline in the pH 9 and 10 buffers and the PPG cleaning solutions. The control membrane was the only one that could be tested for flux after the 0.2% Cl_2 soak due to 1003 and 1035B being too brittle to install in the cross-flow unit. However, all the membranes exhibited significant brittleness and cracked after 7 days in the 0.2% Cl_2 solution.

Due to the high weight loss with the PPG cleaning solution at pH 10, the membranes were soaked again, but the pH was adjusted to 7. Table 4 shows the results for the weight losses, shrinkage, and flux declines/increases for the control and membrane 1003 (there was no more membrane 1035B available to test). The weight loss and shrinkage were minimal for these soakings. The flux decline was a lot less for the control membrane and slightly lower for

Table 1. Percent Weight Loss of Control Membrane and Membranes 1003 and 1035B After Soaking for 7 Days

	pH 2 buffer	2% Citric Acid (pH 2)	1.5% Enzyme cleaner (pH 7)	pH 9 buffer	0.2% Chlorine (pH 9)	pH 10 buffer	1.5% PPG solution (EDTA) (pH 10)	1.5% PPG solution (no EDTA) (pH 10)
Weight loss control	0.0%	0.6%	1.3%	2.3%	2.8%	7.6%	18.4%	13.2%
Weight loss 1003			11.1%	27.2%	28.4%	42.0%	45.1%	38.7%
Weight loss 1035B	0.3%	0.0%	-2.9%	20.7%	27.2%	22.6%	36.6%	23.9%

Table 2. Percent Weight Shrinkage of Control Membrane and Membranes 1003 and 1035B After Soaking for 7 Days

	pH 2 buffer	2% Citric Acid (pH 2)	1.5% Enzyme cleaner (pH 7)	pH 9 buffer	0.2% Chlorine (pH 9)	pH 10 buffer	1.5% PPG solution (EDTA) (pH 10)	1.5% PPG solution (no EDTA) (pH 10)
Shrinkage control	0.1%	0.0%	0.9%	3.4%	4.9%	1.4%	4.5%	1.2%
Shrinkage 1003			14.5%	17.3%	12.8%	22.0%	29.7%	33.9%
Shrinkage 1035B	0.8%	1.5%	1.9%	26.0%	29.8%	29.3%	43.8%	23.6%

Table 3. Percent Flux Decline/Increase of Control Membrane and Membranes 1003 and 1035B After Soaking for 7 Days

	pH 2 buffer	2% Citric Acid (pH 2)	1.5% Enzyme cleaner (pH 7)	pH 9 buffer	0.2% Chlorine (pH 9)	pH 10 buffer	1.5% PPG solution (EDTA) (pH 10)	1.5% PPG solution (no EDTA) (pH 10)
Flux decline/increase control			11.9%	11.7%	-12.6%	9.6%	15.2%	5.6%
Flux decline/increase 1003			-27.8%	-58.3%	CRACK	-11.6%	-38.8%	-77.9%
Flux decline/increase 1035B	-16.0%	15.0%	3.2%	-59.4%	CRACK	-36.1%	-84.0%	-46.6%

Table 4. Percent Weight Loss, Shrinkage, and Flux Decline/Increase of Control Membrane and Membranes 1003 and 1035B After Soaking for 7 Days

	1.5% PPG solution (no EDTA) (pH 7)
Weight loss control	-1.1%
Weight loss 1003	4.6%
Weight loss 1035B	n/a
Shrinkage control	0.5%
Shrinkage 1003	14.8%
Shrinkage 1035B	n/a
Flux decline/increase control	-5.9%
Flux decline/increase 1003	-28.0%
Flux decline/increase 1035B	n/a

membrane 1003. A higher pH seemed to be a contributing factor for the longevity of these membranes.

Membranes UF 833-1689 and MF 769-5412

NDSU received membrane samples UF 833-1689 and MF 769-5412 for soak tests. Similar protocols were used with a few differences. These membranes shrank tremendously after they dried out (Figure 5), so shrinkage was not measured. Since the flux was to be determined in the cross-flow cell during the soakings, the weight loss was measured after the surface water was dried with a paper towel, otherwise the membranes would shrink too much to test for the flux. Failure was determined based on not only brittleness and cracking, but also the time it took to reach 50% the original flux.

Tables 5 and 6 summarize the soak test results for membranes UF 833-1689 and MF 769-5412. The cleaning chemicals that the specimens soaked in were pH 2, 7, and 10 buffer solution; 7% enzyme cleaner at pH 9; 13.5% PPG cleaning solution (no EDTA) at pH 7 and 10; and 0.2% Cl_2 at pH 7 and 10. For the UF specimens, slight weight loss was observed in the pH 7 buffer, the enzyme cleaner, and both PPG cleaning solutions; significant weight loss was observed in the pH 2 and 10 buffers, and both pHs of the Cl_2 solutions. The flux declined to 50% after 4.5, 7, 2.6, and 1.75 days after soaking in the pH 2 buffer, pH 10 buffer, 0.2% Cl_2 at pH 7, and 0.2% Cl_2 at pH 10; respectively. There was no discernible failure in the pH 7 buffer, 7% enzyme, and neither 13.5% PPG solutions after 7+ days (Table 5). For the MF specimens, slight weight loss was observed in the pH 7 buffer, the enzyme cleaner, and the PPG cleaning solution at pH 7; significant weight loss was observed in the pH 2 and 10 buffers, the PPG cleaning solution at pH 10, and both pHs of the Cl_2 solutions. Brittleness, cracking, and significant flux decline was only observed after soaking in the 0.2% Cl_2 at pH 10 after 8 days (Table 6). The estimated lifespans of all the membranes tested based on soak test results are summarized in Table A-2, Appendix A.

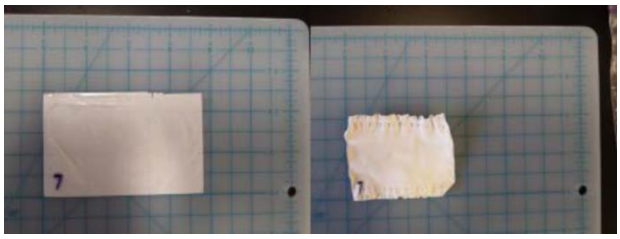

Figure 5. Membrane MF 769-5412 Overly Shrank When Dried Out

Table 5. Summary of Soak Test Results for Membrane UF 833-1689

Membrane UF 833-1689					
Treatment	Time to 50% flux decline (d)	Time to brittleness/cracking (d)	Contact time (d)	Avg pat-dried weight loss	Std dev
pH 7	n/a	n/a	7	0.0%	0.0%
pH 2	4.5	n/a	7	17.1%	0.1%
pH 10	7	n/a	7	14.2%	1.9%
7% enzyme pH 9	n/a	n/a	77	1.7%	1.2%

Table 5. Summary of Soak Test Results for Membrane UF 833-1689 (cont'd)

Membrane UF 833-1689					
Treatment	**Time to 50% flux decline (d)**	**Time to brittleness/cracking (d)**	**Contact time (d)**	**Avg pat-dried weight loss**	**Std dev**
13.5% PPG solution (no EDTA & pH 7)	n/a	n/a	7	-4.9%	3.8%
13.5% PPG solution (no EDTA & pH 10)	n/a	n/a	77	6.2%	6.0%
0.2% Cl_2 (pH 7)	2.6	3-4	4	17.8%	2.5%
0.2% Cl_2 (pH 10)	1.75	2-3	3	15.4%	2.5%

Table 6. Summary of Soak Test Results for Membrane MF 769-5412

Membrane MF 769-5412				
Treatment	**Time to brittleness/cracking (d)**	**Contact time (d)**	**Avg pat-dried weight loss**	**Std dev**
pH 7	n/a	7	0.0%	0.0%
pH 2	n/a	7	14.4%	3.9%
pH 10	n/a	7	17.2%	6.8%
7% enzyme pH 9	n/a	77	0.9%	2.3%
13.5% PPG solution (no EDTA & pH 7)	n/a	7	5.9%	3.4%
13.5% PPG solution (no EDTA & pH 10)	n/a	77	10.3%	1.0%
0.2% Cl_2 (pH 7)	n/a	7	12.6%	4.6%
0.2% Cl_2 (pH 10)	8	8	19.3%	1.0%

3.3 Performance Tests

3.3.1 Water and Solute Permeability Constants

Deionized water and aqueous solutions of bovine serum albumin (BSA), Type A immunoglobulin (IgA), 270 kDa dextran, 500 kDa dextran, and 0.05 and 0.1 µm latex beads (the solutes were based on pore sizes of the membranes) were fed through the flat sheet membrane specimens in a bench-scale plate and frame cross-flow module to determine constants that relate the water flux with pressure differential [Eq. 1] and solute flux with concentration differential [Eq. 2]. Using Equation 1, the constant, A, was determined by measuring the water flux under different transmembrane pressures (5, 10, and 15 psi). The constant, B, was determined by measuring the solute flux with different concentrations of solute in the feed. The water permeability flux and the pressure were held constant at 14.5 mL/min and 5 psi, respectively, as the concentrations of the solute in the feed differed. The concentration differential was determined by measuring the TOC of both sides of the membrane specimen (C_f and C_p). The solute flux was determined based on the permeate flow and solute concentration. Since A and B can vary with temperature, these tests were done at different temperatures by submerging the cross-flow unit in different water bath temperatures; temperature correlation equations were determined with these results.

The water permeability constant relates the pressure and water flux based on the following equation:

$$J_w = A(\Delta P - \Delta \pi) \quad \text{[Eq. 1]}$$

J_w = Water flux, g/(s m^2)
ΔP =Applied pressure differential, psi
$\Delta \pi$ = Osmotic pressure differential, psi
A = g/ (s m^2 psi)

The solute permeability constant relates the solute concentration to the solute flux based on the following equation:

$$J_s = B(C_f - C_p) \quad \text{[Eq. 2]}$$

J_s = Solute flux, g/ (s m^2)
C_f = Feed concentration (g/cm^3)
C_p = Permeate concentration (g/cm^3)
B = $D_s/\Delta X$, m/s
D_s = Diffusion coefficient, m^2/s
ΔX = Membrane thickness, cm

3.3.2 Water/Solute Permeability Constant (A/B) for Control Membrane, Membrane 1003, and Membrane 1035B

After estimating potential lifespans of the membranes, water permeability constants were determined for control membrane, membrane 1003 and membrane 1035B.

Water Permeability Constant (A)

The flux was measured at different transmembrane pressures (5, 10, and 15 psi). An example with membrane 1035B is shown in Figure A-1, Appendix A; the slope of 1.18 g/(s m^2 psi) was determined to be the constant A for 26°C. Because the constant will change based on the temperature, these tests were performed at different temperatures. Correlations between A and water temperature for control membrane and membranes 1003 and 1035B are shown in Equations 3-5, respectively. The experimental results for these correlations are shown in Figures A-2 – A-4, Appendix A.

$\mathbf{A = 1.14e^{0.03T}}$ (control membrane) [Eq. 3]

$\mathbf{A = 0.64e^{0.03T}}$ (membrane 1003) [Eq. 4]

$\mathbf{A = 0.48e^{0.04T}}$ (membrane 1035B) [Eq. 5]

A = Water permeability constant ([g/(s m^2 psi)])
e = Euler constant (2.71828)
T = temperature (°C)

All these equation R^2 correlations were above 0.90.

Solute Permeability Constant (B) Results

BSA as a challenge compound

BSA was used as a challenge compound (solute) to determine the solute permeability constant (B). An example on how B was determined from the experimental data is provided in Figure A-5, Appendix A. B also changes with temperature, so the results are given with the temperature corrections. Correlations between B and water temperature for control membrane and membranes 1003 and 1035B are shown in Equations 6-8, respectively. The experimental results for these correlations are shown in Figures A-6 – A-8, Appendix A.

$\mathbf{B = 3.62e^{0.11T}}$ (control membrane) [Eq. 6]

$\mathbf{B = 0.32e^{0.12T}}$ (membrane 1003) [Eq. 7]

$\mathbf{B = 0.09e^{0.17T}}$ (membrane 1035B) [Eq. 8]

B = Water permeability constant (cm/hr)
e = Euler constant (2.71828)
T = temperature (°C)

270 kDa dextran as a challenge compound

Other solutes were used to determine a cut off molecular weight of solute passages through the membranes (material for membrane 1035B were exhausted at this time). IgA was used, but it was too small to give an accurate value. The next solute used was 270 kDa dextran. Correlations between B and water temperature for control membrane and membrane 1003 are shown in Equations 9-10, respectively. The experimental

results for these correlations are shown in Figures A-9 – A-10, Appendix A.

$\mathbf{B = 14.9e^{0.023T}}$ (control membrane) [Eq. 9]

$\mathbf{B = 4.12e^{0.095T}}$ (membrane 1003) [Eq. 10]

500 kDA dextran as a challenge compound

The final solute used was 500 kDa dextran (material for membrane 1003 were exhausted at this time) and the results are shown in Equation 11 and Figure A-11, Appendix A.

$\mathbf{B = 145.5e^{0.017T}}$ (control membrane) [Eq. 11]

Water Permeability Constants for Membrane UF 833-1689 and MF 769-5412

NDSU received two membrane samples for soak tests (UF 833-1689 and MF 769-5412), and A was determined first in order to see how it might change during the soakings. The results are shown in Equation 12 and Figure A-12, Appendix A for membrane UF 833-1689 and Equation 13 and Figure A-13, Appendix A for membrane MF 769-5412.

$\mathbf{A = 6.92e^{0.026T}}$ (membrane UF 833-1689) [Eq. 12]

$\mathbf{A = 21.84e^{0.028T}}$ (membrane MF 769-5412) [Eq. 13]

NDSU attempted to determine the solute permeability constants for these membranes, but the challenge compounds were either too small or too big, which led to either no change between the feed concentration and the permeate or the compounds blocking the pores of the membrane. The largest challenge compound used was 0.05 µm latex beads for UF 833-1689 and 0.1 µm latex beads for MF 769-5412.

3.3.3 UF Skid Operation

Membrane 02117 was provided by PPG for testing by NDSU in a membrane skid with a bag filter. It was operated with a graywater recipe (NSF/ANSI 350 – 2012 synthetic bathing and laundry challenge graywater) at room temperature while maintaining a TMP of 5 psi for 14 days. The permeate and brine were recycled into the feed tank. New graywater was added every 3-5 days to maintain constituent concentrations. Turbidity and COD were measured once a day.

The spiral wound membranes, provided by PPG and listed below under Step #1, were installed into a membrane skid (Figure 6a). The skid was operated with a graywater recipe (NSF/ANSI 350 – 2012 synthetic bathing and laundry challenge graywater). The details of the operation and tests are as follows.

1. Install 2× 2540 membranes into appropriate housings according to the experimental design for skid operation shown below.

Experimental Design for Graywater Fouling Performance Testing of Prototype 2540 Spiral Wound Membranes

Run	Housing position	Filter Sample #	Batch	# of leaves	Permeate carrier
1	PV-101	19-WKR-108C	A	2	36169
	PV-102	19-WKR-108E	B	2	36169
2	PV-101	19-WKR-109E	A	4	36169
	PV-102	19-WKR-109G	B	4	36169
3	PV-101	19-WKR-111A	A	4	39389
	PV-102	19-WKR-111C	B	4	39389
4	PV-101	19-WKR-108F	B	2	36169
	PV-102	19-WKR-108D	A	2	36169
5	PV-101	19-WKR-109H	B	4	36169
	PV-102	19-WKR-109F	A	4	36169
6	PV-101	19-WKR-111D	B	4	39389
	PV-102	19-WKR-111B	A	4	39389

2. Change bag filter. Use felt filter bag, polypropylene material, 50 microns, (Grainger item #: 4NVF8 or similar).

3. Recirculate deionized water at 30 psi for approximately 30 minutes to rinse off preservative.
    a. Record data points at 30 psi
    b. Record data points at 7 gpm cross-flow (3.5 gpm per cartridge)

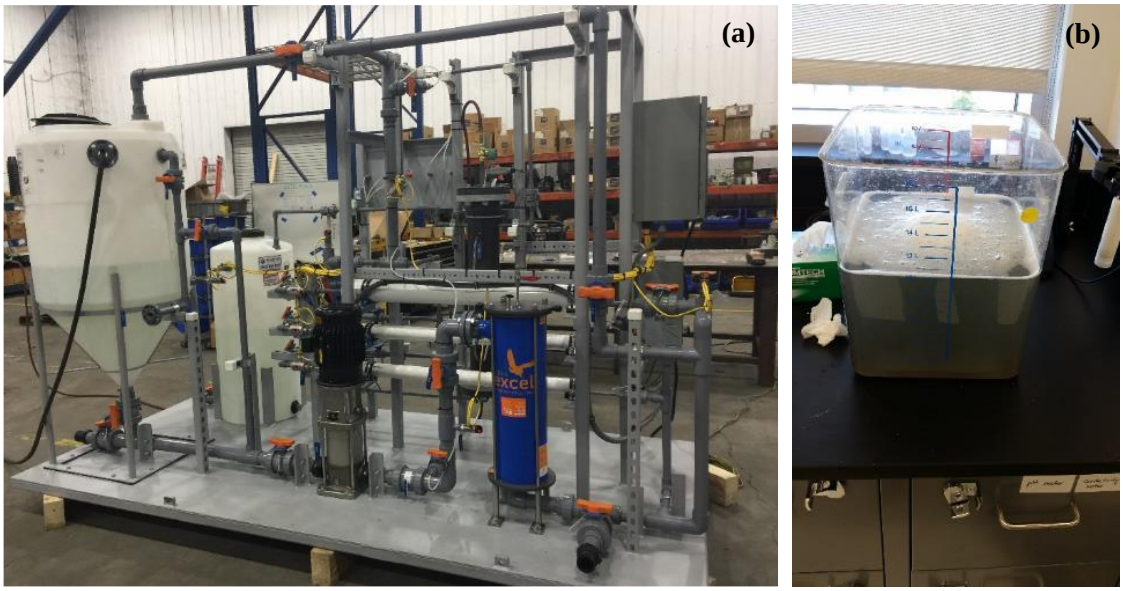

Figure 6. (a) Membrane Test Skid and (b) Synthetic Graywater (NSF 350-12: Bathing and Laundry Mixture)

4. Drain system and tank.
5. Refill tank with 100 gallons of deionized water.
6. Add graywater ingredients (NSF 350-12: bathing and laundry mixture (Figure 1b) (Table A-1, Appendix A).
7. Start run and adjust pump settings to attain 7 gpm.
8. Recirculate concentrate flow, but no permeate flow.
    a. Record data points
    b. Sample water quality samples of feed, concentrate, and permeate.
        i. 0, 6, 12, 24, 26, 48, 60, 72 hours
    c. Analyze water samples.
        i. Turbidity (30 mL)
        ii. COD (2mL)
        iii. TOC (40 mL)
        iv. UV_{254} (2 mL)
    d. Send 80 mL samples of each time point of the feed, concentrate, and permeate to a third-party laboratory to validate results
9. After 75% of the feed tank is emptied, start recirculating permeate flow.
10. After run is complete, drain system and remove membranes and bag filter units.
11. Rinse pipes and cartridges with clean water.

As listed above, the COD, TOC, UV_{254}, and turbidity in the feed, concentrate, and permeate were monitored during the operation to determine their rejections by the membranes. In addition, the TMP and the permeate flows were monitored to determine recovery loss. The goal was to maintain a recovery above 70% and a removal efficiency above 90%, especially for turbidity removal.

Spiral Wound Membrane 02117

Membrane 02117 was installed into the skid to test its ability to remove constituents such as COD and turbidity. The procedure to run the skid is detailed in Section 3.3.3 with the NSF/ANSI graywater. The graywater was pumped through the membrane for 16 days (Figure 7). Within the first day, the permeate flow dropped from 13.5 to 3 gph. Since the permeate flow steadily increased after the first day, fresh graywater was added on Days 5, 8,

and 12; the permeate flow dropped slightly every time it was added (Figure 7). The recovery was 50% immediate after the graywater was added and after the first day dropped to 10-15% (Figure 8). In terms of COD and turbidity removal, membrane 02117 removed 30-60% COD and >90% turbidity (Table 7).

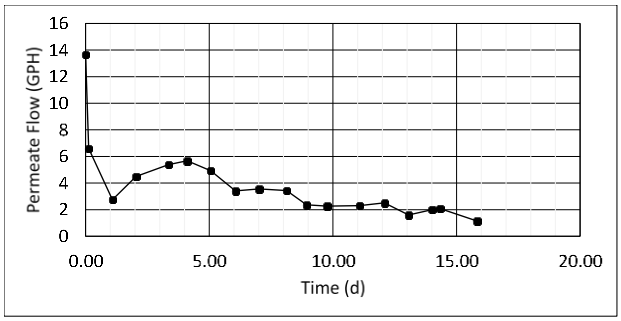

Figure 7. Permeate Flow for Spiral Wound Membrane 02117 with Skid Operation Time

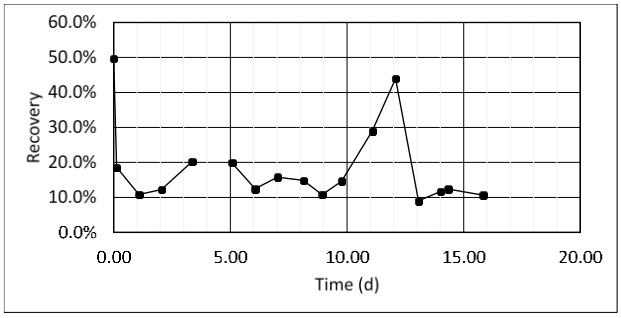

Figure 8. Recovery for Spiral Wound Membrane 02117 with Skid Operation Time

Spiral Wound Membranes 108 (C, D, E, and F), 109 (E, F, G, and H) and 111 (B, D, E, and G)

After membranes 108 (C, D, E, and F), 109 (E, F, G, and H), and 111 (B, D, E, and G) by PPG were fabricated with permeate carriers 36169 and 39839, 6 runs were completed by installing 2 spiral wound membranes into the skid at a time. The procedure detailed in Section 3.3.3 was used, and graywater was pumped through both membranes for 3 days while TOC, COD, UV_{254}, and turbidity were tested to determine their removal. Tables 8, 9, and 10 summarize the permeate flow declines, removal efficiencies, and coefficient of variations, respectively. Compared to the clean water flow, the graywater reduced permeate flow by 55-80% (Table 8). The membranes were best at removing turbidity with >85% removal. COD removal varied from 40-55% and UV_{254} removal varied from 45-90% (Table 9).

Verification of NDSU results were meant to be done by a third-party for all the runs, but it took too long to find a suitable third-party that tested UV_{254}. Instead, third-party verification was done for Run #1 and #3 by Pace Analytical. The results of the comparisons can be found in Tables 11-15. There were slight discrepancies between their results for the turbidity and TOC of Run #1, but otherwise the results were within an acceptable range of each other.

Table 7. Removal of COD and Turbidity in Synthetic Graywater (GW) by Membrane 02117

		COD (mg/L)				Turbidity (NTU)			
	Time (days)	Feed	Permeate	Brine	% Removal	Feed	Permeate	Brine	% Removal
New GW	0	147	71	148	51.7%	7.07	0.658	6.47	90.7%
	0.13	143	71	131	50.3%	7.23	0.338	5.46	95.3%
	1.08	93	64	92	31.2%	4.96	0.408	5.09	91.8%
	2.04	69	39	55	43.5&	2.23	0.196	2.11	91.2%
	3.35	-	-	-		0.829	0.237	0.722	71.4%
	4.1	44	28	44	36.4%	0.777	0.452	0.664	41.8%
New GW	5.06	135	53	119	60.7%	5.61	0.721	4.26	87.1%
	6.06	58	44	56	24.1%	2.46	0.194	1.89	92.1%
	7.02	63	47	63	25.4%	1.05	0.135	1.06	87.1%
New GW	8.13	156	66	133	57.7%	6.96	0.165	4.05	97.6%
	8.94	107	70	101	34.6%	7.83	0.097	4.81	98.8%
	9.77	73	57	63	21.9%	2.58	0.087	2.08	96.6%
	11.08	62	61	58	1.6%	1.8	0.107	1.41	94.1%
New GW	12.08	136	55	84	59.6%	4.01	0.128	3.1	96.8%
	1306	121	95	125	21.5%	7.92	0.107	3.92	98.6%
	14	109	76	105	30.3%	4.28	0.095	3.4	97.8%
	14.33	106	75	94	29.2%	8.84	0.094	3.45	98.9%
	15.83	85	63	70	25.9%	2.73	0.098	2.46	96.4%

Table 8. Permeate Flow After 24 Hours for Membranes 108 (C, D, E, and F), 109 (E, R, F, and H), and 111 (B, D, E, and G)

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
Run	Unit	Housing position	Empty Housing Perm. Flow (GPH)	Clean Water Perm. Flow (GPH)	(4) – (5) (GPH)	$\frac{(4)-(5)}{(5)} * 100\%$	Graywater Perm. Flow (GPH)	(5) – (8) (GPH)	$\frac{(5)-(8)}{(5)} * 100\%$
1	108C	PV-101	104.87	55.19	96.08	63.5%	11.72	43.47	78.8%
	108E	PV-102	90.1	51.32	79.62	52.6%	12.38	38.94	75.9%
2	109E	PV-101	104.87	23.14	128.13	84.7%	10	13.14	56.8%
	109G	PV-102	90.1	20.6	110.34	72.9%	7.76	12.84	62.3%
3	111E	PV-101	104.87	64.97	86.3	57.1%	22.25	42.72	65.8%
	111G	PV-102	90.1	56.18	74.76	49.4%	20.63	35.55	63.3%
4	108F	PV-101	104.87	49.58	101.69	67.2%	8.7	40.88	82.5%
	108D	PV-102	90.1	37.24	93.7	61.9%	7.55	29.69	79.7%
5	109H	PV-101	104.87	64.4	86.87	57.4%	20.8	43.6	67.7%
	109F	PV-102	90.1	54.97	75.97	50.2%	20.66	34.31	62.4%
6	111D	PV-101	104.87	73.4	77.87	51.5%	21.5	51.9	70.7%
	111B	PV-102	90.1	60.29	70.65	46.7%	20.9	39.39	65.3%

Table 9. Average Turbidity, COD, UV_{254}, and TOC Removal for Membranes 108 (C, D, E, and F), 109 (E, F, G, and H), and 111 (B, D, E, and G)

		24 h Average						24 h Standard Deviation			
Run	Unit	Turbidity (NTU)	COD (mg/L)	UV254 (abs)	TOC (mg/L C)	Run	Unit	Turbidity (NTU)	COD (mg/L)	UV254 (abs)	TOC (mg/L C)
1	108C	93.3%	67.8%	111.7%	32.8%	1	108C	2%	2%	7%	50%
	108E	89.0%	46.1%	92.8%	52.7%		108E	2%	37%	17%	24%
2	109E	88.9%	54.9%	60.5%	51.6%	2	109E	10.0%	14.2%	37.9%	20.6%
	109G	81.9%	52.3%	47.8%	43.8%		109G	3.2%	9.8%	7.7%	16.7%
3	111E	90.3%	41.3%	74.2%	N/A	3	111E	4.0%	15.2%	8.9%	N/A
	111G	88.8%	39.5%	49.2%	N/A		111G	9.6%	14.5%	32.6%	N/A
4	108F	94.3%	38.0%	64.0%	N/A	4	108F	4.3%	29.8%	24.2%	N/A
	108D	88.8%	39.5%	49.2%	N/A		108D	3.3%	0.6%	33.7%	N/A
5	109H	90.5%	39.9%	89.1%	N/A	5	109H	7.6%	4.4%	10.8%	N/A
	109F	92.9%	46.7%	70.6%	N/A		109F	5.1%	1.1%	22.2%	N/A
6	111D	87.4%	39.1%	47.2%	N/A	6	111D	6.4%	8.2%	31.1%	N/A
	111B	86.6%	27.6%	32.0%	N/A		111B	6.5%	8.3%	17.2%	N/A

Table 10. Coefficient of Variation of Turbidity, COD, UV_{254}, and TOC Removal Efficiencies for Membranes 108 (C, D, E, and F), 109 (E, F, G, and H), and 111 (B, D, E, and G)

		24 h Coefficient of Variation			
Run	Unit	Turbidity (NTU)	COD (mg/L)	UV254 (abs)	TOC (mg/L C)
1	108C	0.02	0.03	0.07	1.53
	108E	0.02	0.80	0.19	0.46
2	109E	0.11	0.26	0.63	0.40
	109G	0.04	0.19	0.16	0.38
3	111E	0.04	0.37	0.12	N/A
	111G	0.11	0.37	0.66	N/A
4	108F	0.05	0.79	0.38	N/A
	108D	0.04	0.02	0.69	N/A
5	109H	0.08	0.11	0.12	N/A
	109F	0.05	0.02	0.31	N/A
6	111D	0.07	0.21	0.66	N/A
	111B	0.08	0.30	0.54	N/A

Table 11. Comparison of NDSU Water Quality Results (top) to PACE Analytical Results (third-party verification) for a Rerun of Run #1

Time (hour)	Feed				Brine				Permeate 111E				Permeate 111G			
	Turbidity (NTU)	COD (mg/L)	UV254 (abs)	TOC (mg/L C)	Turbidity (NTU)	COD (mg/L)	UV254 (abs)	TOC (mg/L C)	Turbidity (NTU)	COD (mg/L)	UV254 (abs)	TOC (mg/L C)	Turbidity (NTU)	COD (mg/L)	UV254 (abs)	TOC (mg/L C)
0	70.1	755	0.810	166.6	64.3	816	0.570	185.5	8.02	222	0.139	47.43	4.66	237	0.194	53.96
4	61.3	700	0.544	155.3	51.5	691	0.486	150.7	12.2	286	0.359	61.95	12.5	262	0.201	48.79
Average	65.7	727.5	1.5	161	57.9	753.5	1.5	168.1	10.1	254	0.2	54.7	8.6	249.5	0.2	51.4
Std. Dev.	6.2	38.9	1.3	8.0	9.1	88.4	1.4	24.6	3.0	45.3	0.2	10.3	5.5	17.7	0.0	3.7

Table 11. Comparison of NDSU Water Quality Results (top) to PACE Analytical Results (third-party verification) for a Rerun of Run #1 (cont'd)

PACE (3rd Party Verification)																
Time (hour)	Feed				Brine				111E				111G			
	Turbidity (NTU)	COD (mg/L)	UV254 (cm-1)	TOC (mg/L C)	Turbidity (NTU)	COD (mg/L)	UV254 (cm-1)	TOC (mg/L C)	Turbidity (NTU)	COD (mg/L)	UV254 (cm-1)	TOC (mg/L C)	Turbidity (NTU)	COD (mg/L)	UV254 (cm-1)	TOC (mg/L C)
0	56.1	741	0.27	176	37.8	743	-	187	0.65	260	-	85	0.36	275	-	80
4	45.7	728	0.28	184	32.8	760	-	91.8	10.9	307	-	85.7	11.8	363	-	181
Average	50.9	734.5	0.3	180	35.3	751.5	-	139.4	5.8	283.5	-	85.4	6.1	319	-	130.5
Std. Dev.	7.4	9.2	0.0	5.7	3.5	12.0	-	67.3	7.2	33.2	-	0.5	8.1	62.2	-	71.4

Table 12. Comparison of NDSU Water Quality Results (top) to PACE Analytical Results (third-party verification) for a Rerun of Run #3

Time (hour)	Feed				Brine				Permeate 108C				Permeate 108E			
	Turbidity (NTU)	COD (mg/L)	UV254 (abs)	TOC (mg/L C)	Turbidity (NTU)	COD (mg/L)	UV254 (abs)	TOC (mg/L C)	Turbidity (NTU)	COD (mg/L)	UV254 (abs)	TOC (mg/L C)	Turbidity (NTU)	COD (mg/L)	UV254 (abs)	TOC (mg/L C)
0	95.7	658	0.667	135.7	123	684	0.842	148.9	13.9	211	0.319	59.6	16.8	231	0.163	60.15
4	65.7	547	0.77	125.5	84.2	590	1.627	129.5	12.7	291	0.418	61.69	15.4	255	0.654	50.46
Average	80.7	602.5	0.7	130.6	103.6	637	1.2	139.2	13.3	251	0.4	60.6	16.1	243	1.4	55.3
Std. Dev.	21.2	78.5	0.1	7.2	27.4	66.5	0.6	13.7	0.8	56.6	0.1	1.5	1.0	17.0	1.7	6.9

PACE (3rd Party Verification)																
Time (hour)	Feed				Brine				111E				111G			
	Turbidity (NTU)	COD (mg/L)	UV254 (cm-1)	TOC (mg/L C)	Turbidity (NTU)	COD (mg/L)	UV254 (cm-1)	TOC (mg/L C)	Turbidity (NTU)	COD (mg/L)	UV254 (cm-1)	TOC (mg/L C)	Turbidity (NTU)	COD (mg/L)	UV254 (cm-1)	TOC (mg/L C)
0	102	693	0.3	164	50.9	719	-	169	14.8	314	-	86.7	11.7	308	-	91.8
4	70.8	620	0.31	154	10.9	646	-	155	11.7	258	-	89.2	11.2	356	-	88.7
Average	86.4	656.5	0.3	159	40.9	682.5	-	162	13.3	286	-	88	11.5	332	-	90.3
Std. Dev.	22.1	51.6	0	7.1	14.1	51.6	-	9.9	2.2	39.6	-	1.8	0.4	33.9	-	2.2

Table 13. Comparison of Turbidity, COD, UV_{254}, and TOC Removal Efficiencies Based on NDSU Water Quality Results (top) and PACE Analytical Results (third-party verification) for a Rerun of Run #1

Time (hour)	Feed-Permeate 108C reduction				Feed-Permeate 108E reduction			
	Turbidity (NTU)	COD (mg/L)	UV254 (abs)	TOC (mg/L C)	Turbidity (NTU)	COD (mg/L)	UV254 (abs)	TOC (mg/L C)
0	89%	71%	94%	72%	93%	69%	92%	68%
4	80%	59%	34%	60%	80%	63%	63%	69%
Average	84%	65%	64%	66%	86%	66%	78%	68%
Std. Dev.	6%	8%	43%	8%	10%	4%	21%	1%

PACE (3rd Party Verification)								
Time (hour)	Feed-Permeate 108C reduction				Feed-Permeate 108E reduction			
	Turbidity (NTU)	COD (mg/L)	UV254 (abs)	TOC (mg/L C)	Turbidity (NTU)	COD (mg/L)	UV254 (abs)	TOC (mg/L C)
0	98%	65%	-	52%	99%	63%	-	55%
4	67%	60%	-	53%	74%	52%	-	2%
			-				-	
Average	83%	62%	-	53%	87%	58%	-	28%
Std. Dev.	22%	4%	-	1%	18%	8%	-	37%

Table 14. Comparison of Turbidity, COD, UV_{254}, and TOC Removal Efficiencies Based on NDSU Water Quality Results (top) and PACE Analytical Results (third-party verification) for a Rerun of Run #3

Time (hour)	Feed-Permeate 108C reduction				Feed-Permeate 108E reduction			
	Turbidity (NTU)	COD (mg/L)	UV254 (abs)	TOC (mg/L C)	Turbidity (NTU)	COD (mg/L)	UV254 (abs)	TOC (mg/L C)
0	85%	68%	52%	56%	82%	65%	76%	56%
4	81%	47%	46%	51%	77%	53%	-230%	60%
Average	83%	57%	49%	53%	80%	59%	-77%	58%
Std. Dev.	3%	15%	5%	4%	4%	8%	216%	3%

PACE (3rd Party Verification)								
Time (hour)	Feed-Permeate 108C reduction				Feed-Permeate 108E reduction			
	Turbidity (NTU)	COD (mg/L)	UV254 (abs)	TOC (mg/L C)	Turbidity (NTU)	COD (mg/L)	UV254 (abs)	TOC (mg/L C)
0	85%	55%	-	47%	89%	56%	-	44%
4	83%	58%	-	42%	84%	43%	-	42%
			-				-	
Average	84%	57%	-	45%	86%	49%	-	43%
Std. Dev.	1%	3%	-	4%	3%	9%	-	1%

Table 15. Coefficient of Variation of Turbidity, COD, UV_{254}, and TOC Removal Efficiencies Based on Combined NDSU and PACE Analytical Water Quality Results (third-party verification) for Reruns of Run #1 (top) and Run #3 (bottom)

	Feed				Brine				108C				108E			
	Turbidity (NTU)	COD (mg/L)	UV254 (cm^{-1})	TOC (mg/L C)	Turbidity (NTU)	COD (mg/L)	UV254 (cm^{-1})	TOC (mg/L C)	Turbidity (NTU)	COD (mg/L)	UV254 (cm^{-1})	TOC (mg/L C)	Turbidity (NTU)	COD (mg/L)	UV254 (cm^{-1})	TOC (mg/L C)
CV	0.13	0.00	1.27	0.06	0.05	0.02	-	0.22	0.41	0.10	-	0.11	0.91	0.06	-	0.02

	Feed				Brine				111E				111G			
	Turbidity (NTU)	COD (mg/L)	UV254 (cm^{-1})	TOC (mg/L C)	Turbidity (NTU)	COD (mg/L)	UV254 (cm^{-1})	TOC (mg/L C)	Turbidity (NTU)	COD (mg/L)	UV254 (cm^{-1})	TOC (mg/L C)	Turbidity (NTU)	COD (mg/L)	UV254 (cm^{-1})	TOC (mg/L C)
CV	0.33	0.05	0.12	0.05	0.01	0.07	-	0.05	0.21	0.04	-	0.02	0.02	0.06	-	0.03

3.4 Biofouling Test

A laboratory scale cross-flow testing methodology was developed at NDSU to quantify salt water (i.e. marine) bacteria fouling on flat membrane sheets provided by PPG and was adapted from a report by Katebian et al.[4] An illustration of the testing setup is provided in Figure 9, which consisted of four cross-flow cells (CF042, Sterlitech) connected in parallel to a four-channel peristaltic pump to continuously deliver, in recirculating mode without permeation, bacterial feed culture (38.5 g/L Sigma sea salts, 0.5 g/L peptone, 0.1 g/L yeast extract, 10^8 cells/mL) at a rate of 10 mL/min per channel. A hotplate stirrer was utilized to maintain a constant temperature of 28°C ± 1°C and mixing rate of 150 rpm within the glass feed culture vessel. After reaching the desired duration of feed culture exposure (24 hours), the flow was terminated and each cross-flow cell was detached from the peristaltic pump and reconnected to a pressurized tank of artificial sea water (ASW; 38.5 g/L Sigma sea salts) to measure permeate flux under 5 psi of supply pressure for 1 minute (Figure 10).

Subsequent to collecting post-run flux measurements, the membranes were removed from their respective cross-flow cell housing, deposited in plastic containers, and precisely sectioned/partitioned using a utility knife for cell viability (i.e. ATP bioluminescence) and fluorescence imaging of cell/biofilm surface coverage (Wheat Germ Agglutinin (WGA) fluorescent dye conjugate) as delineated in Figure 11.

[4] Katebian, L., Gomez, E., Skillman, L., Dan L., Ho G., Jiang S.C., "Inhibiting Quorum Sensing Pathways to Mitigate Seawater Desalination RO Membrane Biofouling," *Desalination*, 2016, 393, 135-143.

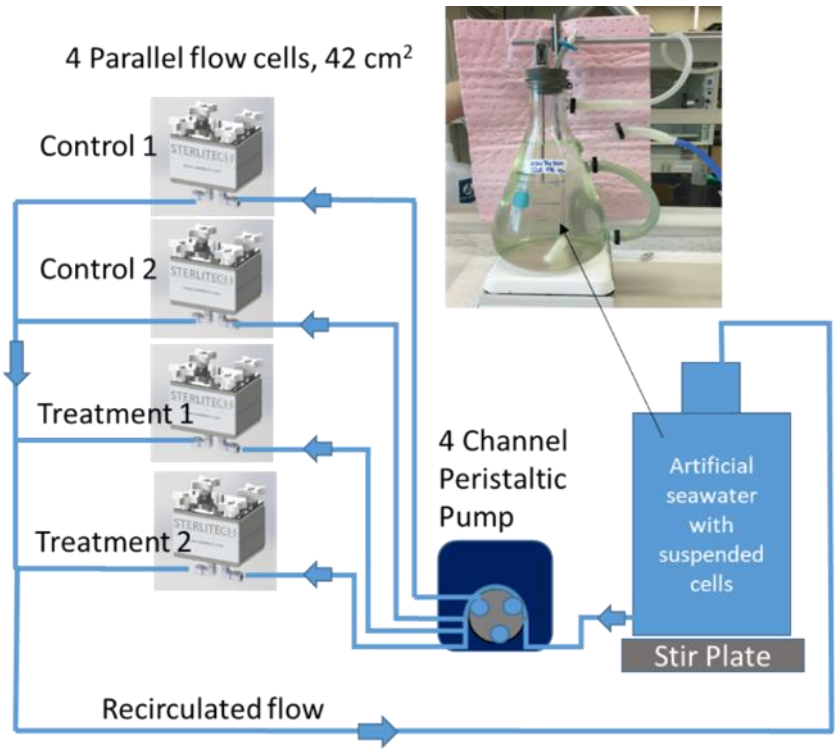

Figure 9. Illustration of Laboratory Scale Cross-Flow Testing Setup at NDSU to Characterize Bacterial Biofouling on Flat Membrane Sheets

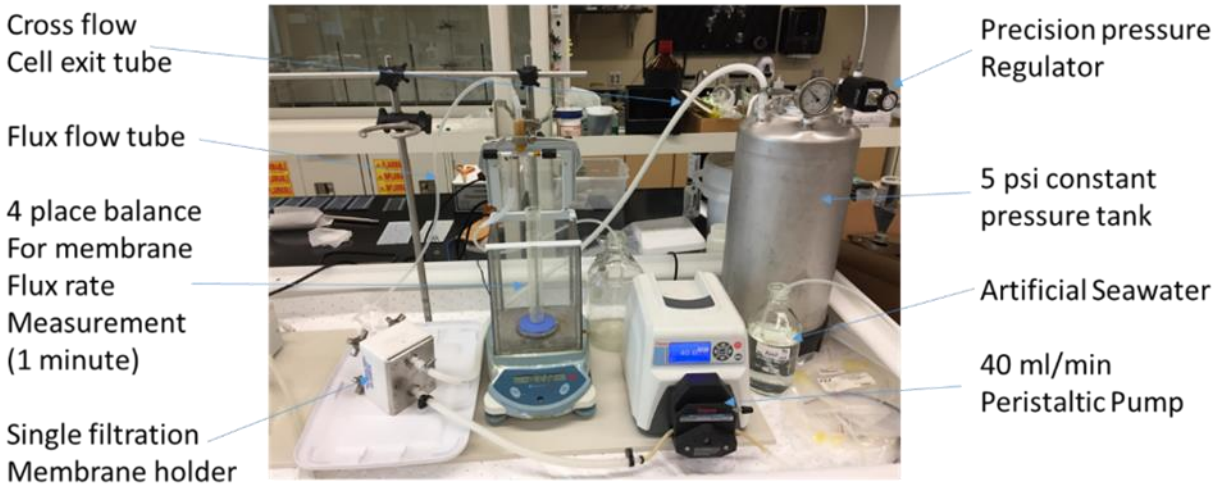

Figure 10. Laboratory Setup for Measurement of Permeate Flux at 5 psi of Supply Pressure for 1 Minute
Flux measurements were collected both pre- and post-exposure to bacteria feed culture

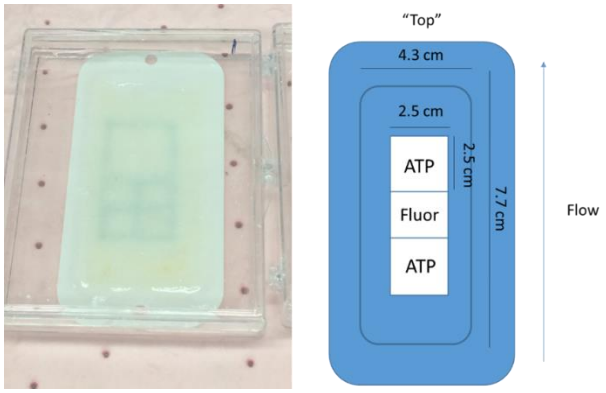

Figure 11. Image of Flat Membrane Sheet Placed in a Plastic Container (left) After Removal From Cross-Flow Cell Post-Bacterial Biofouling Challenge
Illustration of membraned sections excised for ATP bioluminescence assessments (:ATP"; 2 replicates/ membrane) and fluorescence imaging ("Fluor"; 1 replicate/membrane)

The cross-flow cell testing method was initially developed in conjunction with the marine bacterium *Cellulophaga lytica* as the model fouling microorganism for salt water environments. However, due to inconsistent biofouling behavior (i.e. 37-55% intra-experiment and 52-71% inter-experiment variation) as a result of enhanced cell flocculation fostered by the large batch culturing method required for this testing methodology, *C. lytica* was replaced with the marine fouling bacterium *Halomonas marina.* A consistently narrower range of both intra- and inter-experiment variance of 7-35% and 25-46%, respectively, was established for *H. marina* on a UF commercial membrane (769-6259) provided by PPG (Figure 12) and this bacterial strain was henceforth used to assess membrane biofouling for the duration of the project.

Additionally, flux measurements, pre- and post-exposure to bacterial feed culture, were collected for the second and third *H. marina* biofouling experiments of the 769-6259 UF commercial membrane to determine the intra- and inter-experiment variance in flux reductions. In this regard, intra-experiment variance of flux reduction ranged from 26-32% while the inter-experiment variance was 25-58% (Figure 13). The mean flux reduction was 31% ± 5% among the 4 flow cross-flow cells for Experiment 2 and 17% ± 3% for Experiment 3, which established the threshold range in terms of comparative performance assessments among PPG membrane technologies.

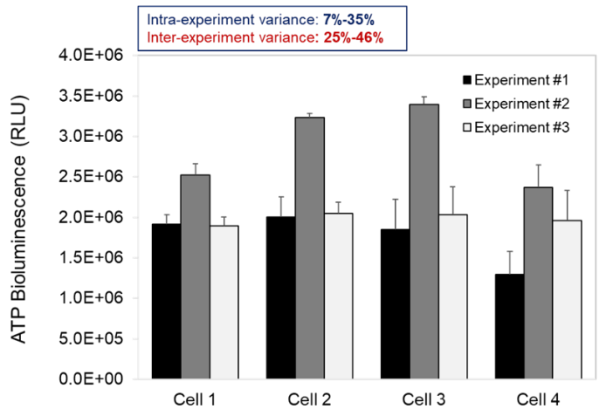

Figure 12. Intra- and Inter-Experiment Cross-Flow Cell Variance of Halomonas marina Biofouling on 769-6259 UF Commercial Membrane
Each data point is the mean relative luminescence units (RLU) value of 8 replicate measurements. Error bars represent one standard deviation of the mean

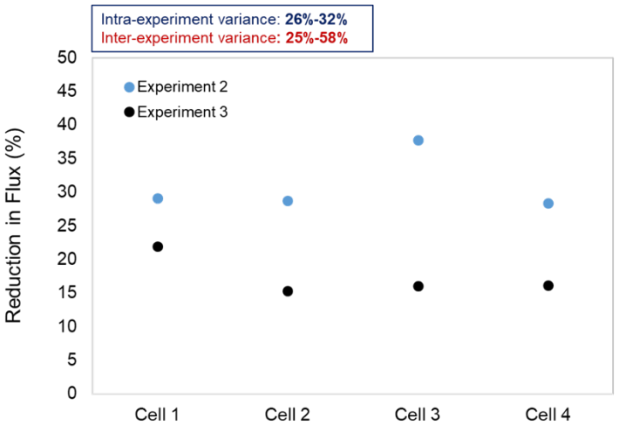

Figure 13. *Intra- and Inter-Experiment Cross-Flow Cell Variance of Flux Reduction After Halomonas marina Biofouling on 769-6259 UF Commercial Membrane (5 psi Pressure for 1 Minute)*

Figure 14 and Figure 15 summarize the results of the first cross-flow cell experiment executed for this project to characterize bacteria biofouling on two water filtration membranes produced by PPG; 833-1035 B (oxidized wax) and 833-1034 B (control). Three independent, replicated experiments were conducted using the marine bacterium *Halomonas marina* by employing 2 cross-flow cells for each membrane per experiment. An increase in bacterial fouling on the 1035 B oxidized wax membrane was observed relative to 1034 B control membrane for Experiment 1 (+ 36%) and Experiment 3 (+ 64%), while bacterial fouling was equivalent for Experiment 2 (Figure 14, left). When examining the three experiments in combination, reported as the pooled average of the three replicated experiments (i.e. 6 cross-flow cells per membrane), the 1035 B oxidized wax membrane accumulated 59% more *H. marina* fouling than the 1034 B control membrane (Figure 14, right). The pre-culture (i.e. 1 hour soak in 60:40 IPA:H_20 and 24 hours equilibration in sterile feed culture medium) and post-culture (i.e. 24 hour exposure to bacterial feed culture) flux measurements are shown in Figure 15, which showed a two-fold higher initial flux for the 1035 B oxidized wax membrane (3.64 g/min) as compared to the 1034 B control membrane (1.81 g/min). The post-flux was essentially unchanged for the 1034 B control membrane (1.76 g/min) and was reduced by 18% for its 1035 B oxidized wax counterpart (3.0 g/min). Fluorescence microscopy revealed a uniform distribution of *H. marina* biofilm across the surface of both membranes, distinguished by a qualitative inspection/comparison of the assay control (i.e. "No bacteria") and sample (i.e. "Bacteria") micrographs provided in Figure 15. In this regard, the biofilm appears as a light-green haze that obscures visualization of the membrane surface topography, characterized by dark "pits" and contours, which seemed to have a more pronounced effect in terms of flux reduction for the 1035B oxidized wax membrane.

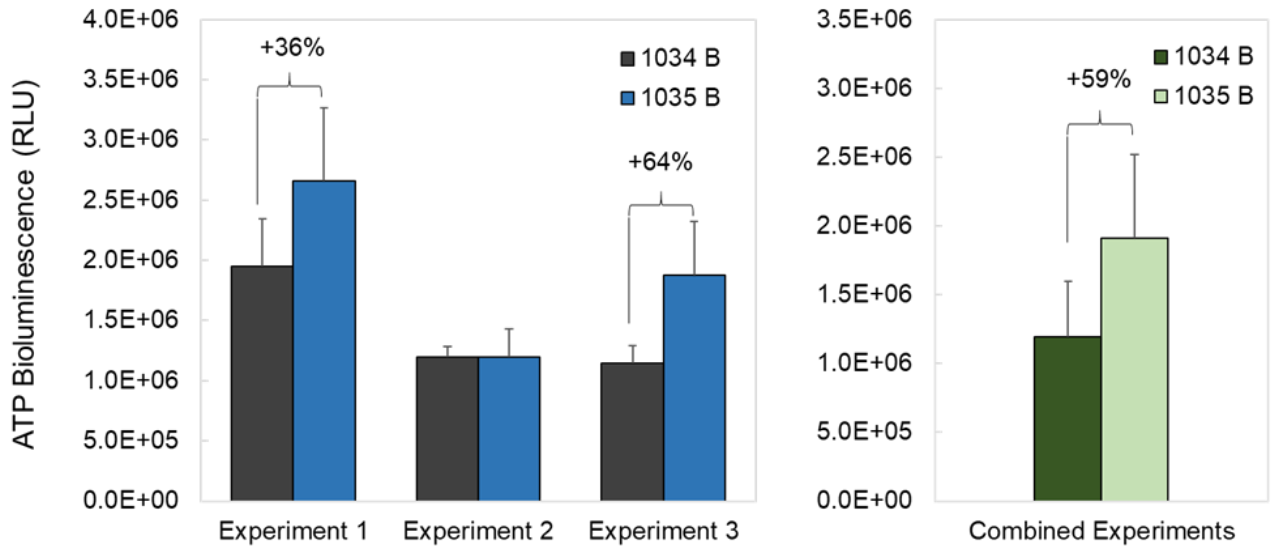

Figure 14. Halomonas marina Biofouling Accumulation (24 hours) on 833-1034 B Control and 833-1035 B Oxidized Wax Membranes as Determined by ATP Bioluminescence (RLU; relative luminescence units)

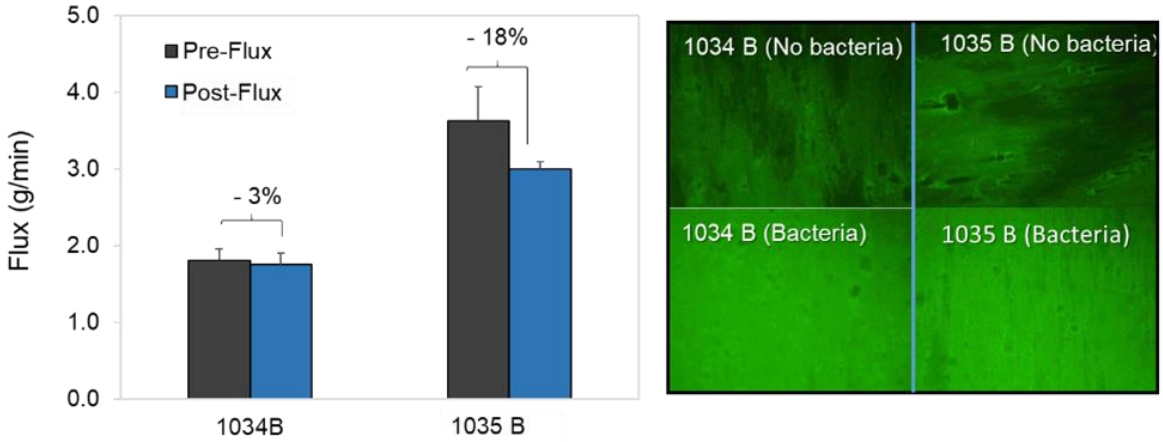

Figure 15. Pre-Culture Exposure and Post-Culture Exposure Flux Measurements for 833-1034 B Control and 833-1035 B Oxidized Wax Membranes (left). Fluorescence Micrographs of Membrane Surfaces (200x magnification) Both Exposed (bottom; "Bacteria") and Unexposed (top; "No bacteria") to H. marina Feed Culture Using WGA-Fluorescent Dye Conjugate (right)

The next set of PPG flat sheet membranes to undergo bacterial biofouling characterization were the 833-1114 B pilot control and 1115 A high surface area silica variants. A 32% reduction in *H. marina* fouling was observed for 1115 A high surface area silica membrane relative to the 1114 B pilot control for the first experiment, but resulted in a 4% and 25% increase for replicated Experiments 2 and 3, respectively (Figure 16, left). This variation between the replicated experiments (57%) was outside the range of inter-experiment variation reported for the developmental/repeatability experiments (25-46%; Figure 16, left), albeit marginally so. In terms of the pooled averages for the combined experimental data, a negligible 4% decrease in *H. marina* fouling was observed for the 1115 A high surface area silica membrane (Figure 16, right). The flux measurements for the two membranes are provided in Figure 17, which indicated that the 1115 A high surface area silica variant restricted pre-culture exposure permeate flow by a factor of 3 as compared to the 1114 B pilot control; 5.13 g/min vs. 1.78 g/min. This relative ratio of flux was preserved after 24 hours of bacterial feed culture exposure, with the membranes exhibiting a 12-15% reduction in permeate.

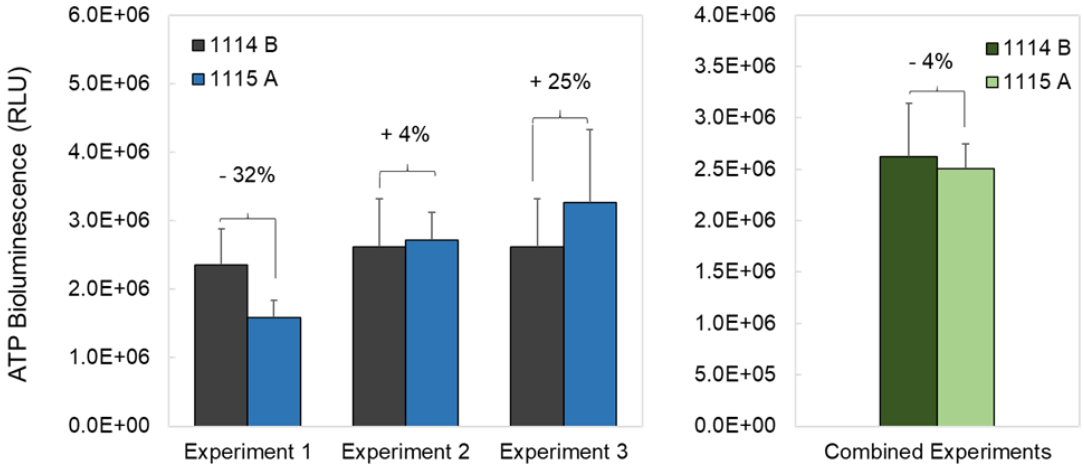

Figure 16. Halomonas marina Biofouling Accumulation (24 hours) on 833-1114 B Pilot Control and 833-1115 A High Surface Area Silica Membranes as Determined by ATP Bioluminescence (RLU; relative luminescence units)

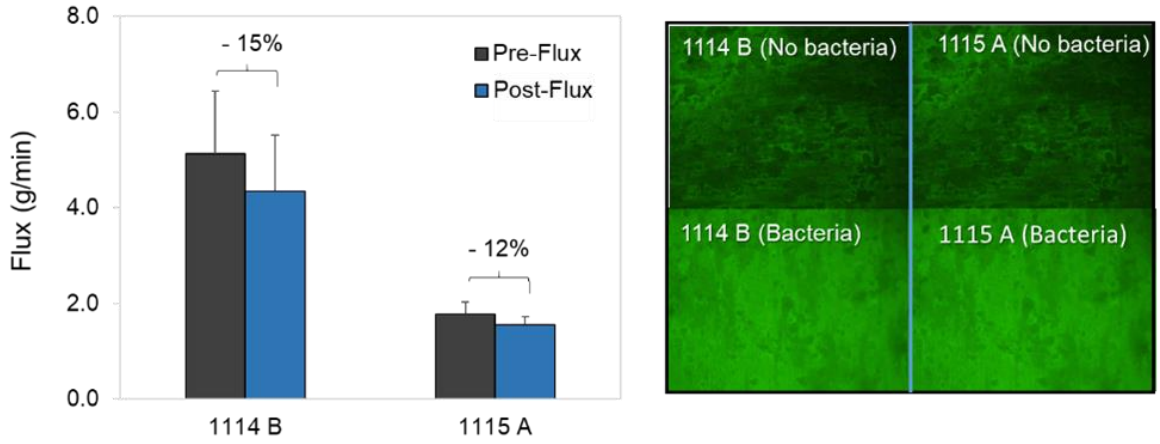

Figure 17. Pre-Culture Exposure and Post-Culture Exposure Flux Measurements for 833-1114 B Pilot Control and 833-1115 A High Surface Area Silica Membranes (left). Fluorescence Micrographs of Membrane Surfaces (200x magnification) Both Exposed (bottom; "Bacteria") and Unexposed (top; "No bacteria") to H. marina Feed Culture Using WGA-Fluorescent Dye Conjugate (right)

flow. As observed for the qualitative fluorescent microscopy characterization of 833-1034 B and 833-1035 B membranes, *H. marina* biofilm appeared to be uniformly distributed across the surface of the 1114 B and 1115 A variants, with no visually discernable differences (Figure 17, right).

Following the biofouling assessments of the 833-1114 B pilot control and 833-1115 A high surface area silica membranes, variants 1068 B pilot control and 1071 C high oil absorption silica were subjected to *H. marina* fouling studies. A similar range of inter-experiment variation was observed here (61%), the 1071 C high oil absorption silica membrane having accumulated 23% more bacterial fouling than the 1068 B pilot control, whereas replicated Experiments 2 and 3 showed an inverse behavior; a 38% and 3% reduction of *H. marina* fouling, respectively (Figure 18, left). In terms of the pooled averages, the 1071 C high oil absorption silica showed a 17% decrease in accumulated bacteria fouling relative to the 1068 B pilot control (Figure 18, right). With respect to permeate flux, only the pre-culture exposure was collected for this set of membranes, which revealed a 5-fold increase in feed culture medium flow for the 1071 C high oil absorption silica membrane (9.74 g/min) relative to the 1068 B pilot control (1.98 g/min) (Figure 19, left). Consonant with the first two sets of membranes evaluated, *H. marina* biofilm appeared to be uniformly distributed across the surface of the 1068 B and 1071 C variants, with no visually discernable differences based on a qualitative inspection of the fluorescence micrographs (Figure 19, right).

In an effort to expand the capacity and enhance the throughput of biofouling characterization, the testing protocol was modified for the remainder of the project to conduct a single experiment for each membrane variant (i.e. 4 total cross-flow cells simultaneously) rather than executing three discrete experiments (i.e. 2 cross-flow cells per experiment; 6 total). The data previously collected for 1114 B pilot control was used as a means to gauge relative biofouling mitigation properties of the PPG 1330 and 1400 series membrane variants (1330 A, 1331 A, 1339 A, 1427 B, 1429 B and 1430 B) in which the pooled average RLU is denoted as a solid green line in Figure 20; the zone of light green shading indicating one standard deviation of the mean RLU value. Membrane 1331 A, 1339 A and 1427 B exhibited a >35% reduction compared to 1114 B pilot control, with variant 1427 B accumulating approximately 2-fold less *H. marina* biofilm. In contrast, membranes 1330 A, 1429 B and 1430 B were shown to be much less effective,

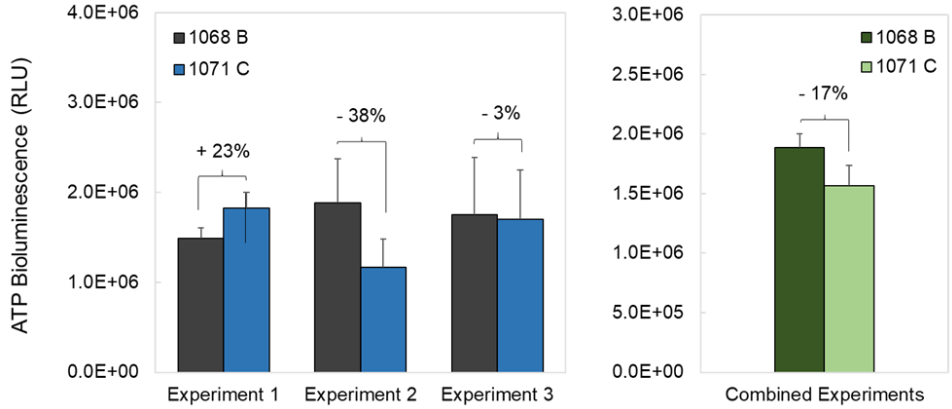

Figure 18. Halomonas marina Biofouling Accumulation (24 hours) on 833-1068 B Pilot Control and 833-1071 C High Oil Absorption Silica Membranes as Determined by ATP Bioluminescence (RLU; relative luminescence units)

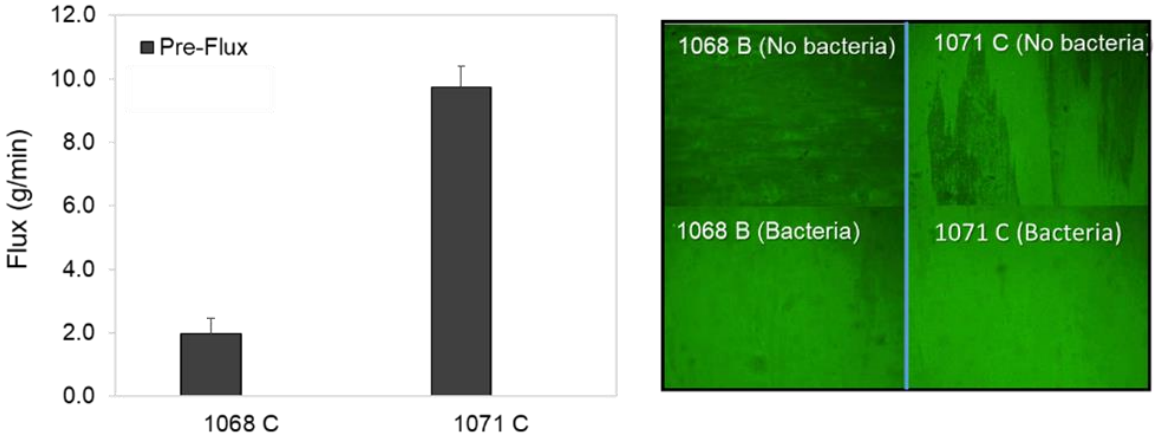

Figure 19. Pre-Culture Exposure Flux Measurements for 833-1068 B Pilot Control and 833-1071 C High Oil Absorption Silica Membranes (left). Fluorescence Micrographs of Membrane Surfaces (200x magnification) Both Exposed (bottom; "Bacteria") and Unexposed (top; "No bacteria") to H. marina Feed Culture Using WGA-Fluorescent Dye Conjugate (right)

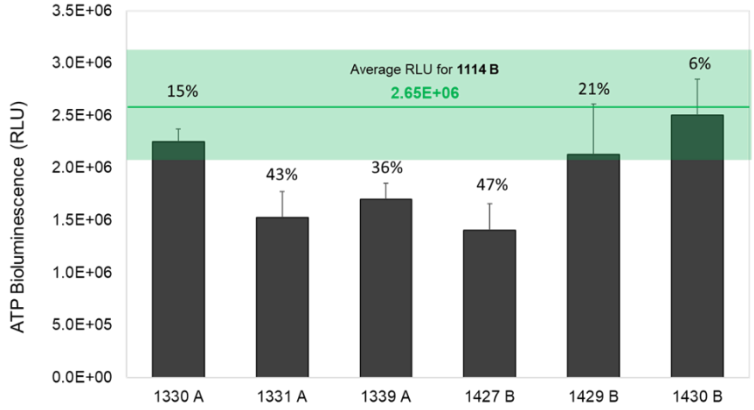

Figure 20. Halomonas marina Biofouling Accumulation (24 hours) on 1330 A, 1331 A, 1339 A, 1427 B, 1429 B and 1430 B Membranes as Determined by ATP Bioluminescence (RLU; relative luminescence units)
Solid green line denotes the pooled mean RLU value for the 1114 B pilot control and light green shading indicates one standard deviation of the mean

achieving reductions of 6-21% and that resided within one standard deviation of the mean bacterial fouling that accumulated on the 1114 B pilot control. With respect to permeate flux, *H. marina* accumulation had no appreciable influence on post-culture exposure flux decline among the six membrane variants (9-19% reduction) (Figure 21). Interestingly, pre-culture exposure flux was markedly reduced (2-fold) for membrane 1427 B (2.28 g/min) and 1430 B (1.12 g/min) relative to the other four membranes (3.48 to 3.91 g/min). Consistent with the previous fluorescence microscopy assessments, all six membranes exhibited uniform *H. marina* biofilm coverage distributed across their respective surfaces but had no discernable or differential impact on flux decline as a function of membrane variant (Figure 22).

Figure 23 and Figure 24 summarize the results of the cross-flow cell biofouling studies carried out for the final group (i.e. PPG 1500 series) of flat membrane sheets evaluated for this project. All four membrane variants characterized, 1589 B, 1591 B, 1593 B and 1595 B, accumulated a similar degree of *H. marina* biofilm which ranged from a 16% decrease relative to the UF-1689 benchmark/control for 1593 B to a 3% increase for 1595 B (Figure 23). In addition to the 1500 series membranes, a MF-6412 membrane was also characterized which accumulated 32% more fouling than the UF-1689 control, but also resided within one standard deviation of the pooled mean RLU value. Reductions in flux, post-bacterial feed culture exposure, revealed a narrow range of variance (6%) among the four 1500 series membranes, with 1589 B, 1593 B and 1595 B all restricting sterile feed culture medium/permeate by 16% (Figure 24). In terms of initial pre-culture exposure flux, 1593 B (5.53 g/min) was less restrictive to permeate flow than the other three membranes (3.06 to 4.06). However, pre-culture exposure flux through the MF-6412 control/reference (44 g/min) was revealed to be a magnitude of order higher than the 1500 series membranes (3.06 to 5.53 g/min), but decreased precipitously (74%) post-culture exposure (11.43 g/min), suggesting a rather profound and detrimental impact of *H. marina* biofilm accumulation on the water filtration properties of this membrane.

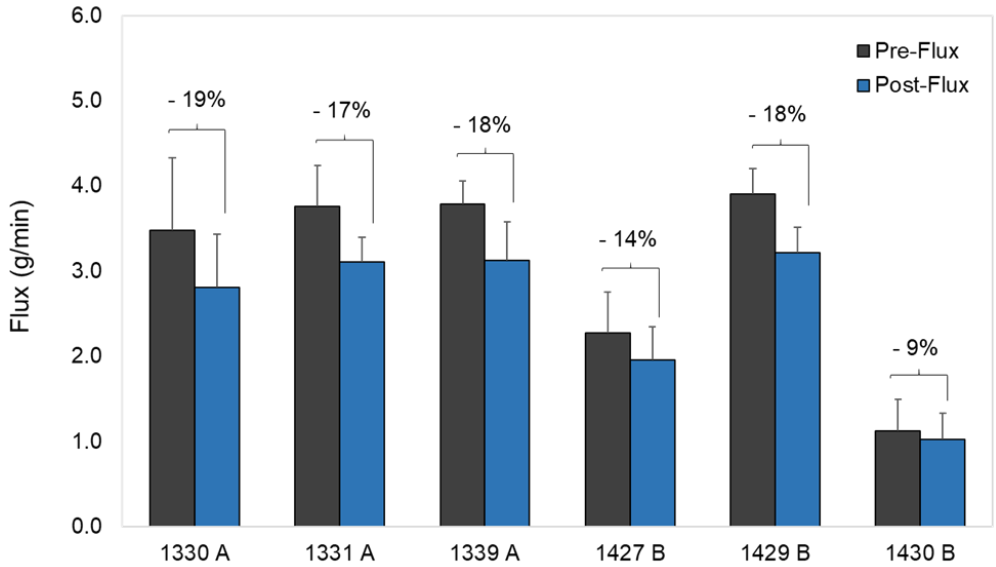

Figure 21. Pre-Culture Exposure and Post-Culture Exposure Flux Measurements for 1330 A, 1331 A, 1339 A, 1427 B, 1429 B and 1430 B Membranes

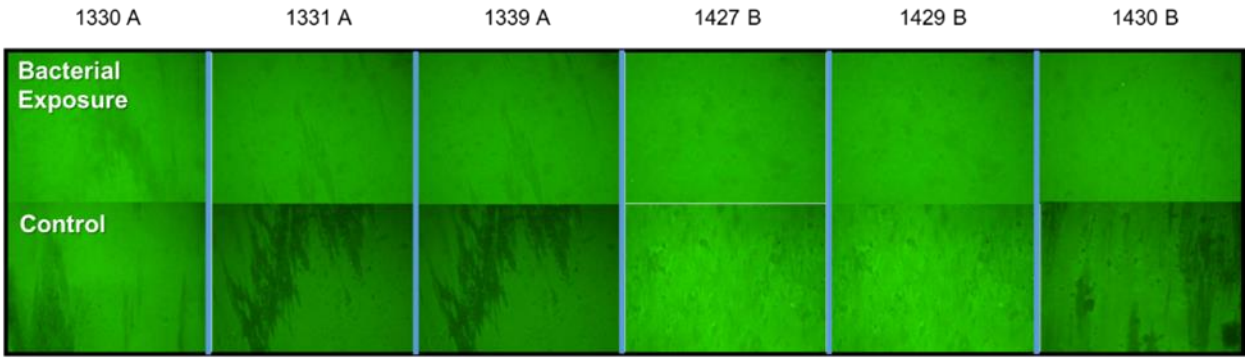

Figure 22. Fluorescence Micrographs of 1330 A, 1331 A, 1339 A, 1427 B, 1429 B and 1430 B Membrane Surfaces (200x magnification) Both Exposed (top; "Bacterial Exposure") and Unexposed (bottom; "Control") to H. marina Feed Culture Using WGA-Fluorescent Dye Conjugate

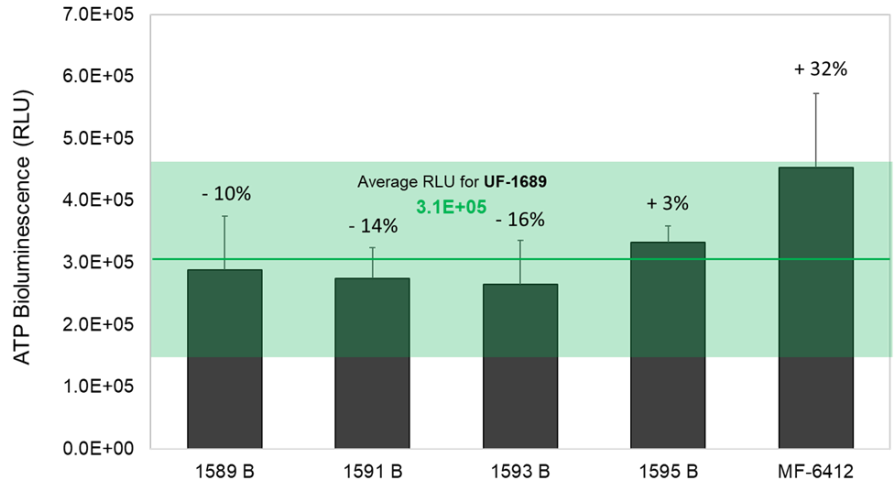

Figure 23. Halomonas marina Biofouling Accumulation (24 hours) on 1589 B, 1591 B, 1593 B, 1595 B and MF-6412 Membranes as Determined by ATP Bioluminescence (RLU; relative luminescence units)
Solid green line denotes the pooled mean RLU value for the UF-1689 membrane and light green shading indicates one standard deviation of the mean

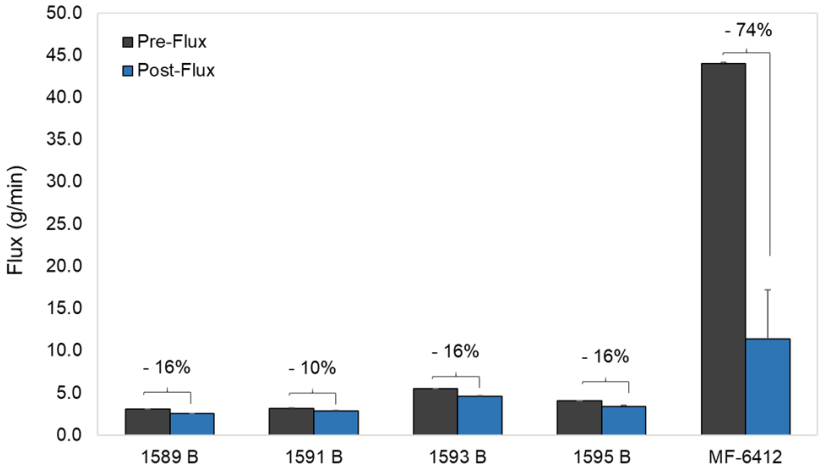

Figure 24. Pre-Culture Exposure and Post-Culture Exposure Flux Measurements for 1589 B, 1591 B, 1593 B, 1595 B and MF-6412 Membranes

4. Conclusions

4.1 Soak Tests

For membrane integrity, the soak tests showed minimal weight loss and shrinkage. Advanced methods such as SEM would need to be employed to accurately determine the diminishment of membrane integrity. For membrane longevity, the lifespans of control membrane, membranes 1003, 1035B, UF 833-1689, and MF 769-5412 were estimated based on when the membrane became brittle or when the flux decline by 50%. The only cleaning solution that the control membrane failed with was the 0.2% Cl_2 (pH 9) in which it failed after 4.25 days which gave it an estimated lifespan of 3.6 years. Membrane 1003 failed after soaking in 0.2% Cl_2 (pH 9) and 1.5% PPG cleaner (no EDTA, pH 10); the lifespans were estimated to be 6 years with chlorine cleanings and 2.6 years with the PPG cleaner (no EDTA). Membrane 1035B failed after 7 days in the 0.2% Cl_2 (pH 9) cleaning solution which gave it an estimated 6-year lifespan. Membrane UF 833-1689 failed in 3 cleaning solutions (0.2% Cl_2 (pH 7 and 10) and pH 2 buffer solution; at the typical pH of chlorine cleanings (pH 10) these types of cleanings would give the membrane an estimated 1.5 to 2.1-year lifespan. For membrane MF 769-5412, it failed in 0.2% Cl_2 (pH 10) after 8 days, which would give it an estimated lifespan of 6.9 years (Tables A-1 and A-2, Appendix A).

4.2 Performance Tests

Membrane 1003 and 1035B had water permeability values close to the control membrane (1.3-2.4 g/(s m^2 psi) at RT). Membrane UF 833-1689 had a much higher water permeability constant, which suggests that it would have a higher recovery. The constant for membrane MF 769-5412 was much higher than the rest, which is expected due to its large pore size.

For the control membrane, the highest solute permeability constant was observed with the largest challenge compound (500 kDa dextran) used (222.6 cm/hr). This was not expected and it may be due to the aggregation properties of BSA (smaller challenge compound) giving it a larger hydration sphere. Nevertheless, with the BSA challenge compound, the control membrane has a significantly higher solute permeability constant than membranes 1003 and 1035B (which is similar at 6.3-6.4 cm/hr).

For the skid operation, the goal was to maintain a recovery of greater than 80%; however, the recovery provided by membrane 02117 dropped to 50% immediately after the graywater was added, and after the first day, it dropped again to 10-15%. In terms of constituent removal, membrane 02117 removed 30-60% COD and >90% turbidity for the 14 days that it was operational.

For membranes 108C, 108E, 108F, and 108D, the highest permeate flow reductions were observed in Runs #1 and #4 with 75-80% flow reduction. Incidentally, they were the only two runs that had 2-leaved spiral wound membranes installed. The rest of the membranes were 4-leaved and only saw reductions between 55-70%. There was no discernable difference in flow reduction between the two permeate carriers (# 36169 and 39389) used.

All membranes with permeate carriers # 36169 and 39389 removed >85% turbidity; the COD removal varied from 40-55% and UV_{254} removal varied from 45-90%. With the pore size of these membranes being on the higher end, it is expected that turbidity would be the main constituent removed; however, since the other constituents are normally dissolved in the graywater (too small for the membrane to reject) they were most likely removed by other means, such as adsorption on the bag filter, membranes, and surfaces of skid materials.

5. Benefit Impacts

Many U.S. municipalities are under drought conditions.[5] This project has accelerated the development of thermoplastic membrane technology for both graywater reuse, seawater desalination and brackish water use. The technology is applicable to defense, domestic, and global applications. Using these filtration systems for municipal, maintenance, and industrial applications will enable more cost effective water development and conservation worldwide. Reduced fouling and energy will reduce the operating and maintenance costs for these facilities.

As water demand increases and water sources become scarcer these membranes will be an important tool in expanding the potential water sources by allowing the use of lower quality water sources and providing improved treatment technology for water reuse. New products that are delivered more quickly at reduced costs benefits everyone, including the U.S. water treatment industry that employ workers and technicians that produce and use those products.

DOD is a huge user of potable water from continental U.S. (CONUS) to Base Camps and Forward Operating Bases around the world. The need for drinking water is obvious, but water is also used extensively for sanitation and in MRO operations. DOD has programs in place to reduce its use of clean water through both conservation and reuse. This technology, if successful, will enable development of reverse osmosis systems in several sizes for use in all its many roles.

Water treatment has been a research area for the TARDEC Force Projection Technology Area for over 15 years. TARDEC Industry Days meetings in 2014 and 2015 highlighted the development of a man-portable water filtration system. GVSC has a test stand used to integrate new filtration technology. Over the years, many new technologies have been integrated into this system. Most have proven more costly to operate than existing water treatment technology. This project will allow new technology to be developed in “ready to integrate” components for GVSC system evaluation.

Army, Marines, and Special Operations all need reliable, easy-to-use and cost effective systems for producing potable water from graywater. The Marines in particular, because of its expeditionary nature, conducts frequent relief efforts in the wake of natural disasters. In addition, although not part of DOD, FEMA is a federal agency that provides domestic natural disaster relief and could also make good use of improved filtration technology.

[5] http://droughtmonitor.unl.edu/

Appendix A – Supporting Information

Soak Test

Table A-1. Calculations for Determining Cleaning Solution Concentrations for a 7-Day Soaking

	Routine cleaning frequency	Intensive cleaning frequency	Routine soak time (min)	Intensive soak time (min)	Routine concentration (mg/L)	Intense concentration (mg/L)	conc*time (mg/l*hr)	Lifespan (yr)	7 day conc (mg/L)
NaOCl	2	180	60	300	200	2,000	56,778	6	0.20%
Citric Acid	0	180	0	300	200	20,0000	2,027,778	6	7.24%
PPG cleaner	7	0	60	0	150,000	0	7,821,429	3	13.97%

Table A-2. Summary of Estimated Lifespans Based on Soak Test Results for the Control Membrane (769-6259), Membrane 1003, 1035B, UF 833-1689, and MF 769-5412

Specimen	Cleaning solution	Time to failure (d)	Estimated Lifespan (yr)
Control	0.2% Cl_2 (pH 9)	4.25	3.6
1003	0.2% Cl_2 (pH 9)	7	6.0
1003	1.5% PPG cleaner no EDTA*	6	2.6
1035	0.2% Cl_2 (pH 9)	7	6.0
UF	0.2% Cl_2 (pH 10)	2.5	2.1
	0.2% Cl_2 (pH 7)	3.5	3.0
	pH 2*	4.5	3.9
	0.2% Cl_2 (pH 10)*	1.75	1.5
	0.2% Cl_2 (pH 7)*	2.6	2.2
MF	0.2% Cl_2 (pH 10)	8	6.9

* Failure determined base 50% flux decline

Water/Solute Permeability Constants

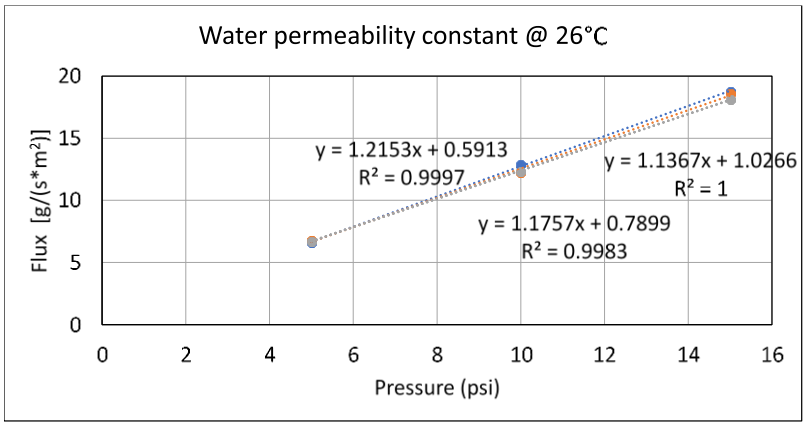

Figure A-1. Example of Membrane 1035B Water Permeability Constant Determination (based on slope of the relationship)

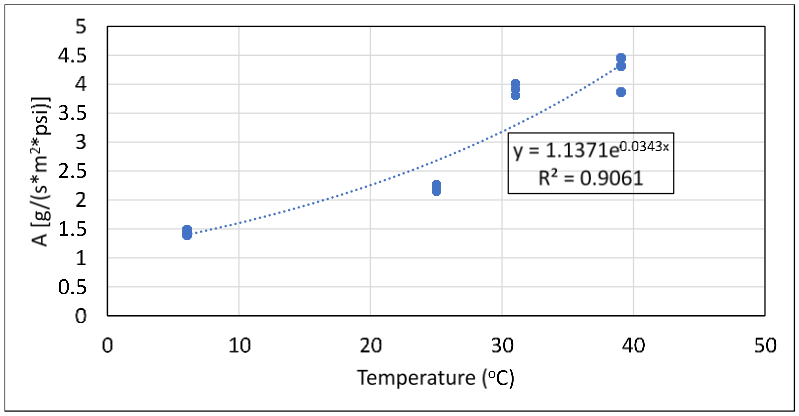

Figure A-2. Correlation Between Water Permeability Constant (A) and Temperature for Control Membrane (769-6259)

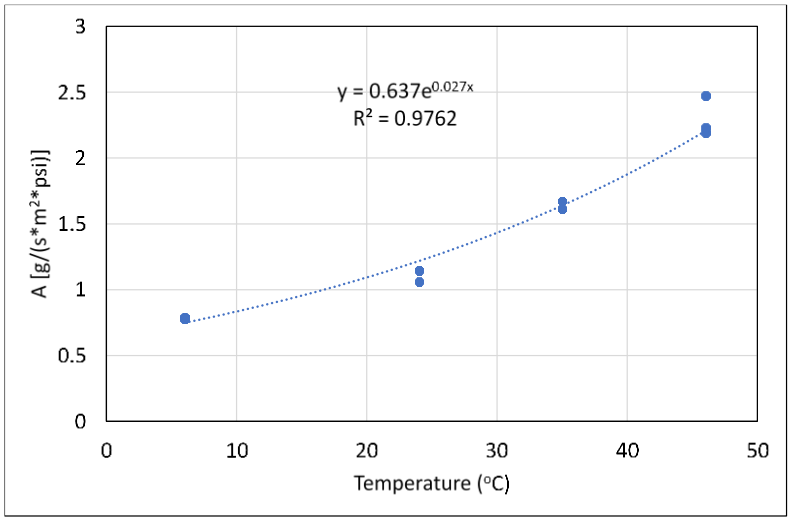

Figure A-3. Correlation Between Water Permeability Constant (A) and Temperature for Membrane 1003

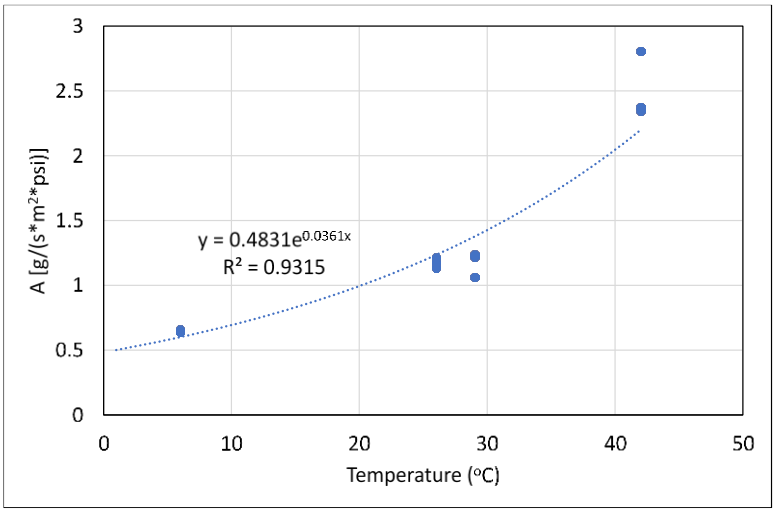

Figure A-4. Correlation Between Water Permeability Constant (A) and Temperature for Membrane 1035B

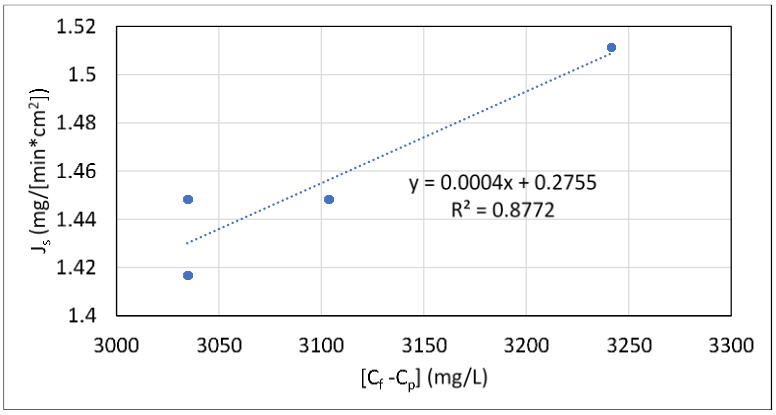

Figure A-5. Membrane UF 833-1689 Solute Permeability Constant Determination (based on the slope of the relationship) Example

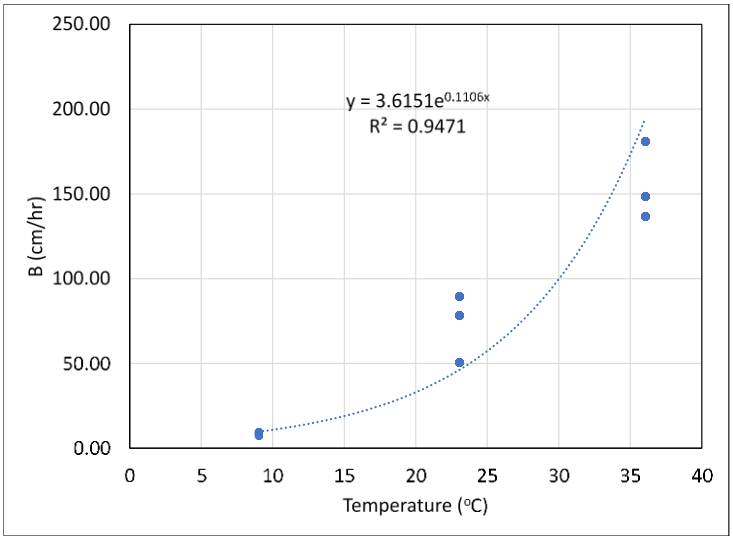

Figure A-6. Correlation Between Solute Permeability Constant (B) and Temperature for Control Membrane with BSA as a Challenge Compound

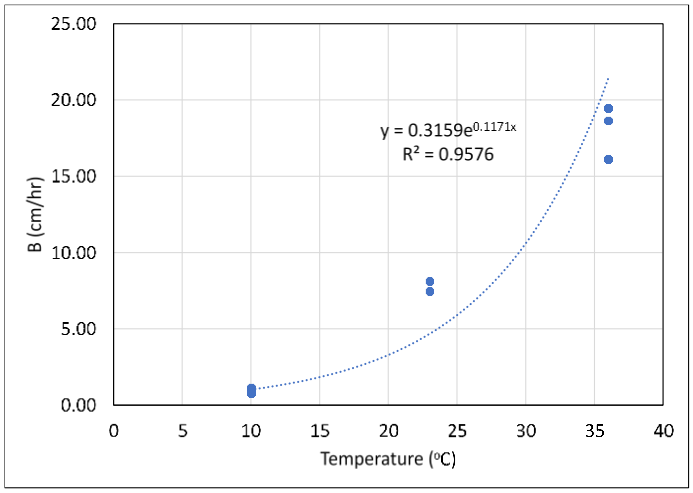

Figure A-7. Correlation Between Solute Permeability Constant (B) and Temperature for Membrane 1003 with BSA as a Challenge Compound

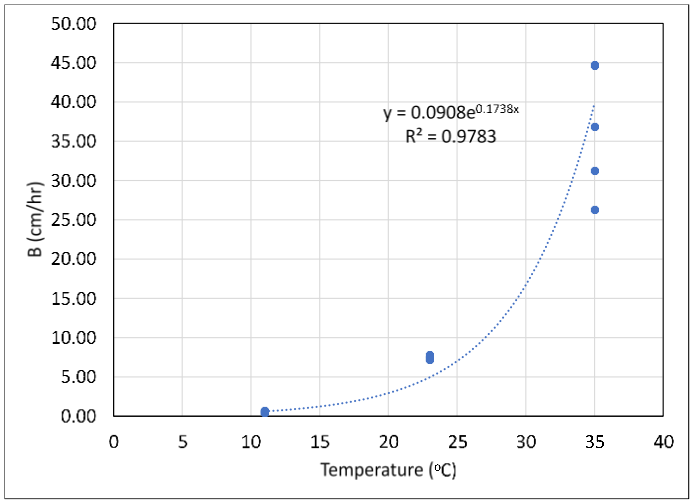

Figure A-8. Correlation Between Solute Permeability Constant (B) and Temperature for Membrane 1035B with BSA as a Challenge Compound

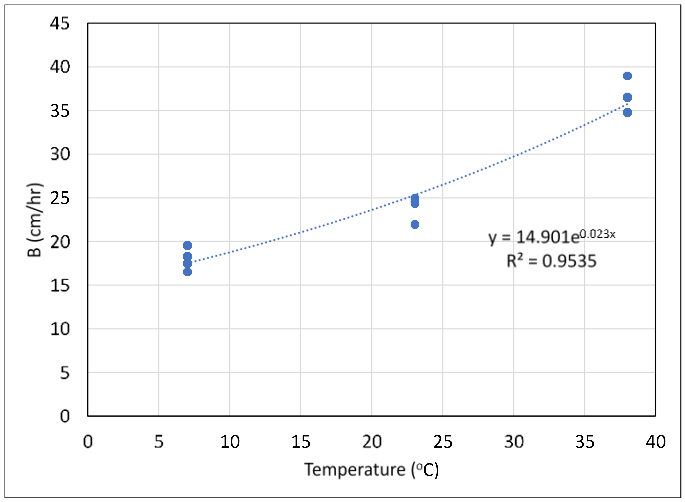

Figure A-9. Correlation Between Solute Permeability Constant (B) and Temperature for Control Membrane with 270 kDa Dextran as a Challenge Compound

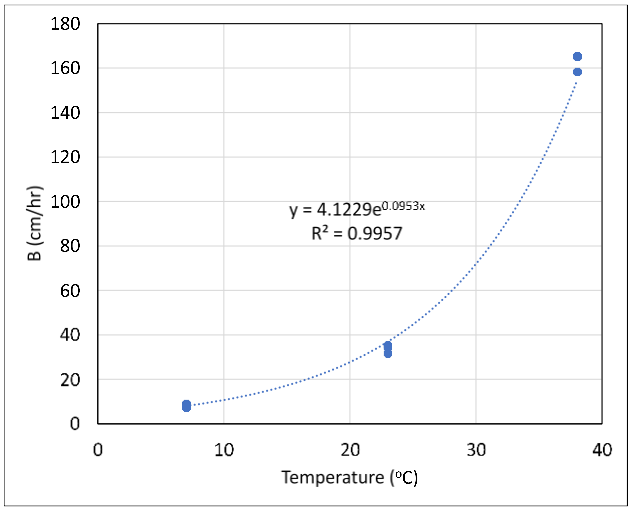

Figure A-10. Correlation Between Solute Permeability Constant (B) and Temperature for Membrane 1003 with 270 kDa Dextran as a Challenge Compound

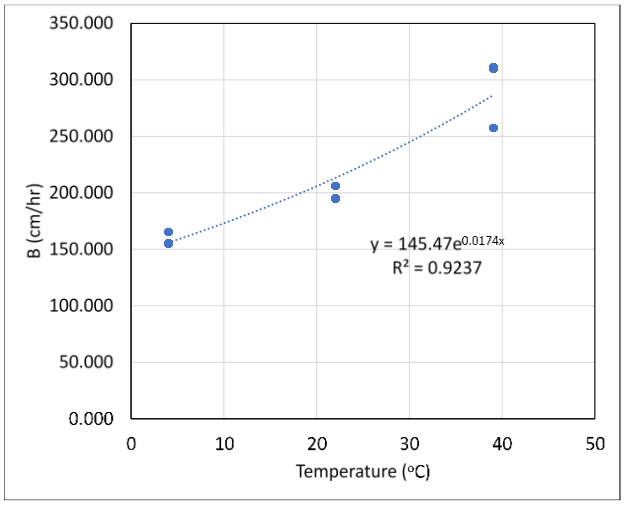

Figure A-11. Correlation Between Solute Permeability Constant (B) and Temperature for Control Membrane with 500 kDa Dextran as a Challenge Compound

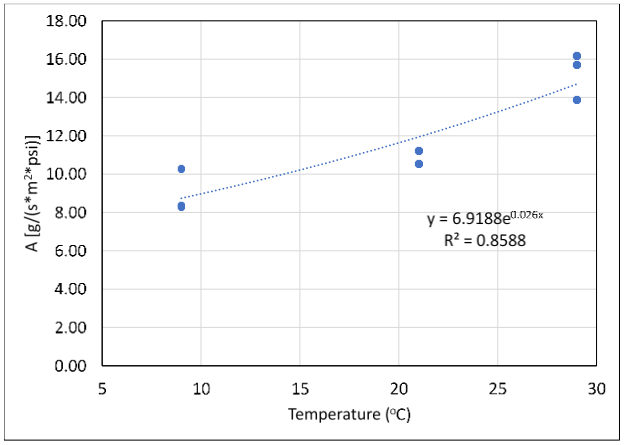

Figure A-12. Correlation Between Water Permeability Constant (A) and Temperature for Membrane UF 833-1689

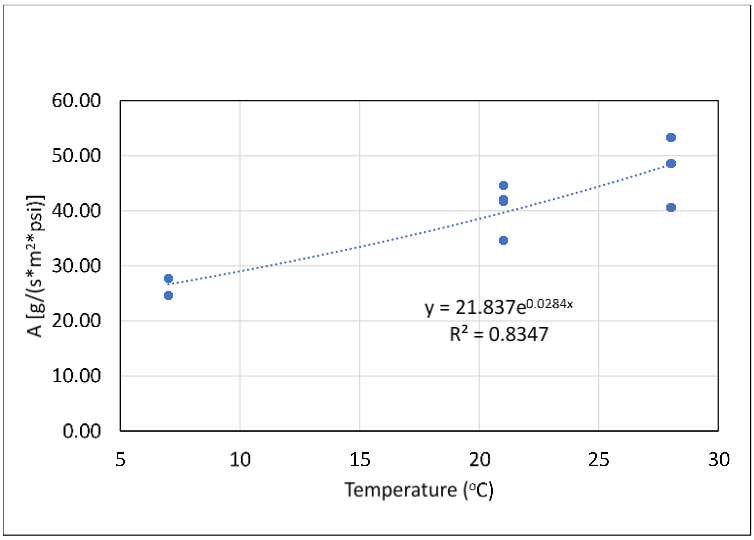

Figure A-13. Correlation Between Water Permeability Constant (A) and Temperature for Membrane MF 769-5412

UF Skid Operations

Table A-3. NSF/ANSI 350-2012 Graywater Recipe (bathing + laundry)

Ingredients	Amount/100L
Body Wash	10 g
Toothpaste	3 g
Deodorant	2 g
Shampoo	19 g
Conditioner	21 g
Lactic Acid	3 g
Secondary Effluent	2 L
Bath Cleaner	10 g
Liquid Hand Soap	23 g
Test Dust	10 g
Liquid Laundry Detergent (2X)	40 mL
Liquid Laundry Fabric Softener	21 mL
Sodium Sulfate	4 g
Sodium Bicarbonate	2 g
Sodium Phosphate	4 g