Final Report

Department of Water Resources

Project:
Role of Microfiltration (MF) Cake Layer Composition and Stability in Desalination Efficiency

Submitted by:

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Introduction

In recent years, microfiltration (MF) has been shown to be less costly and more effective than conventional lime clarification as a pre-treatment method for reverse osmosis (RO). OCWD plans to utilize an MF/RO process in a 70-mgd advanced water reclamation facility. The feedwater for this large facility is a municipal activated-sludge effluent, which possesses significant nutrient loading, and high biological activity. These factors contribute to rapid biofouling (i.e., cake formation) of the MF membranes with consequent loss of performance. MF fouling is associated with increased hydrodynamic resistance (i.e., flux loss) and necessitates frequent chemical cleaning of the MF membranes, thereby driving up operational costs. Better understanding of MF fouling and dynamics are needed to improve the efficiency of the MF/RO process at OCWD and other agencies. With MF pretreatment becoming the mainstream RO pretreatment technology, it is critical that the MF fouling be effectively managed and controlled.

Background

Microfiltration can be separated into two mechanisms surface and depth filtration. Surface filtration is dependent on particle size. In this mechanism, particles are blocked from passing through the membrane pores. Only particles smaller than the pore size of the membrane pass through to the permeate side. Surface filtration may be conducted under two modes: dead-end or cross-flow filtrations. In dead-end filtration the feed flows perpendicularly toward the membrane surface. The liquid passes through the membrane (permeate) and all particles larger than the pore size are retained at the surface forming a fouling layer (cake). Flux decreases as the cake thickness increases. In the cross-flow filtration process part of the feed water passes through the membrane as permeate and the other portion of the feed water passes tangential along the membrane forming a cross flow. Particles in the feed water deposited at the membrane surface and swept away by the sheer force of the feed as it passes over the membrane surface. Cross-flow filtration may have higher permeate fluxes over longer periods of time compared to dead-end filtration, however, this mode may result in higher energy and operation costs. In depth filtration, particles smaller than the pore size of the membrane move

into the filter matrix and adhere to the collecting surfaces of the filter. In depth filtration particles are not affected by crossflow or surface hydraulic sheer and backwashing by reverse pressure flow can dislodge the fouling material from the membrane surface.

Project Objective

The MF fouling layer is perhaps the most critical factor responsible for overall process efficiency economics. Membrane fouling is characterized as the reduction of permeate flux through the membrane caused by pore blocking, concentration polarization, and cake formation. Therefore, the primary objective of this project was to elucidate the fouling mechanism of MF membranes, including permeability, stabilization and removal of filter cakes.

Project Approach

This project examined the formation, structure, and stability of MF cakes formed on polypropylene membrane material under controlled conditions. The experimental approach was divided into three tasks:

Task 1. Acquire and configure a bench-scale MF apparatus to conduct MF cake investigations, including formation, structural, stability, and dynamics. Experimental MF cakes were formed under controlled laboratory conditions on 0.22-µm polypropylene (PP) MF membrane material.

Task 2. Evaluate the formation, structure and stability of nanoparticulate organic material fouling, which may be the primary contributors in MF fouling and decreased membrane performance, and to screen selected chemicals capable of targeting these foulants (organic solvents such as ethanol, protease and phosphotase) for MF fouling removal or prevention.

Task 3. Test those cleaning agents determined to be effective under laboratory conditions in field trials using a pilot size MF unit operated with secondary treated wastewater (STW) under actual operating conditions.

Task 3 was not completed as proposed in the original test plan for two reasons. 1) The scope of the project was changed to evaluate dissolved organic material (DOM) fouling instead of testing chemical agents to remove microparticualte MF cakes from membrane surfaces, and 2) an MF pilot scale test unit was not available (could not be acquired in time and at a reasonable cost) to be used in this study. However, at the field scale one aspect of the study, exposure of PP membranes in secondary treated wastewater without applied pressure (soaking) was inadvertently tested using a 5 MGD MF plant with the fouling results favorably agreeing with laboratory observations (see below).

Membrane Characterization

Atomic Force Microscopy (AFM)

Membrane structural properties (pore size, pore shape and distribution) of clean and fouled PP membranes were determined by AFM (CP AutoProbe, Park Scientific Instruments, Sunnyvale, CA). AFM provides essential information about the sub-micron surface topography and fundamental material properties of polymer membranes. Such information has been correlated with the performance (flux and solute rejection) and fouling potentials of separation membranes, and therefore is critical in optimizing function and designing novel antifouling surfaces.

Attenuated Total Reflection Fourier Transform Infrared Spectrometry

Absorption in the mid-infrared (IR) region (4000 – 500 cm^{-1}) was employed to acquire spectroscopic 'fingerprints' of clean and fouled polypropylene (PP) membranes used in the study.

Membrane Hydraulic Properties

Membrane material was cut into 55 mm diameter disks and placed in a bench-scale AMICON apparatus. The apparatus was filled with feed solution and sealed. A vacuum of 12 psi was applied, and membrane permeate flux was measured continuously with an electronic balance

connected to a computer through a RS 232 interface equipped with a data acquisition. A new PP membrane disk was used in each experiment. Because PP membrane has a highly hydrophobic surface making it initially impermeable to water, prior to each experiment the disk was wetted by immersion in 100 % ethanol for 15 minutes followed by flushing with 18 megohm-cm water.

MF Cake Formation and Characterization

MF Cake Formation

Prior to cake formation, the membrane permeate flux was measured. Cake was then deposited on the surface of the membrane by filtration of source water (filtered or unfiltered) at a constant transmembrane pressure (12 psi) with feedwater replacement to a volume of 180 mL. Permeate flux was calculated at regular (5 second) intervals.

MF Cake Formation Using Secondary Treated Wastewater

Source water for the study was secondary treated wastewater (from Orange County Sanitation District). MF cake formation began immediately upon introduction of the source water, and the progression of deposition of fouling materials was quantified by monitoring the rate of decrease in hydraulic conductivity (flow/pressure) through the membrane.

MF Cake Formation Using Microparticulate-free Filtered Secondary Treated Wastewater (FSTW)

STW was first filtered through a glass microfiber to remove large solids, then filtered using a hydrophilic, low protein binding, sterile, 0.2 µm polyethersulfone filter designed for microbiological analysis of potable, waste, process and natural waters. Microparticulate (bacterial) removal was confirmed by epifluoresence microscopy using the DNA-specific fluorochrome 4,6-diamidino-2-phenylindole (DAPI).

Active, Inactive and Lysed Bacterial Component Analysis in MF Cake

STW effluent used in the study contained active, inactive and lysed (ruptured) bacterial cell components. It was anticipated that each of these components may give rise to fouling of MF membrane material. Cell components (debris) may include phospholipid fatty acids (PFLAs), proteins and carbohydrates. Analysis for protein and carbohydrate were performed on feedwaters, cakes and permeate.

PROJECT OUTCOMES

Task 1. Acquire and Configure a Bench-scale MF Apparatus to Conduct MF Cake Investigations

Proposed MF Cake Characterization

At the onset of the study, it was presumed that the fouling components of MF cakes would be mostly comprised of bacteria and large particulates (> 0.2µm), and this would be the major contributor to decreased MF performance. Cake structure was proposed to be studied by using mass by weight measurements and cake stability by light scattering (optical density), and by particle sizing using a Coulter Multisizer. In addition, genetic microbial identification, protein assay, carbohydrate assay, epifluorescence microscopy and light microscopy, would be used to study the nature of microbial material accumulating on the membrane surface during cake formation and flux reduction. These techniques were initially employed in study of the MF cake, but through experimentation it was discovered that MF fouling was principally influenced by other factors besides microparticulates.

Task 2: Evaluate MF Cake Fouling by Nanoparticulates and DOM

Flow Dynamics Using STW and FSTW Feedwater

A hypothesis was formed that material smaller than bacteria were primarily responsible for the flux decline observed during MF cake formation on STW. To test the theory, all macroparticulate solids were removed from the feedwater by passage through a 0.2-µm filter. To confirm FSTW was particle free equal volumes of STW and FSTW feedwaters were

filtered onto 25 mm, black 0.2 µm filter membranes, stained with DAPI and examined with fluorescence microscopy to confirm that FSTW was bacteria free. Filtering STW through the 0.2 µm filter did remove bacteria and presumably particles >0.2 µm. The two feedwaters (STW with microparticulates and FSTW without microparticulates) generated similar permeate flux decay curves, suggesting that flux decay kinetics were not principally influenced by the microparticulate fraction of STW. Permeate flux difference between the STW and FSTW curves were attributed to the bacteria and other larger particulates present in STW. This demonstrated that bacterial or particulate fouling (MF cake) is responsible for a far smaller portion of the overall fouling than was previously thought.

Confirmation Particle Free STW

MF Foulant Characterization Using AFM with and without Microparticles

STW and FSTW foulants deposited on PP membranes were also examined with AFM. AFM images showed fouling on both STW and FSTW membranes. The STW fouling appeared to be thick and multi-layered, and composed of bacteria and other particulates. FSTW fouled membranes did not have bacteria or particles but still were fouled with what appeared to be on amorphous material that covered the membrane pores. AFM showed pores of the PP membrane were blocked. The dissolved foulants or nanoparticulates (<0.2 µm) seemed to enter the membrane matrix and block the pores from within, indicating pore clogging is occurring along with pore blocking. The images support the observation that the most significant amount of MF fouling is not due to bacteria and other microparticulates, but to DOM and nanoparticulates.

MF Foulant Characterization – Chemical Analysis

MF Foulant Characterization Using ATR/FTIR

To further characterize MF fouling, ATR/FTIR spectrometry was employed to analyze the fouling layer left behind at the membrane surface by STW and FSTW. Bands designating both protein and carbohydrate fouling were equally represented in both STW and FSTW spectra, providing additional evidence that primary MF fouling may be the result of mostly biological detritus as opposed to bacteria and other particles larger than 0.2 µm.

MF Cake Characterization - Protein and Carbohydrate

To further characterize the OCWD FSTW cake, protein and carbohydrate analysis of the bacterial-free (FSTW) feedwater, STW, FSTW permeate and fouling layer was performed. A significant concentration of carbohydrates (64%) remained following removal of bacteria from STW (5.60 µg/mL) and FSTW 3.60 µ/mL. Dissolved carbohydrates appeared to be strongly deposited on the PP membrane representing approximately 71% of the acellular carbohydrate in the feed.

Phospholipid Fatty Acid Analysis

Cell debris may contain fragments of cell membranes that anneal to form nanoparticlates (liposomes). The material fragments are largely made up of phospholipids. Of the lipids, the phopholipid fatty acids (PFLAS) represent the major component of cell membranes. PFLA, when exposed to hydrophobic membrane surfaces such as PP, may attach and actually intercalate into the membrane matrix. An analysis to determine the presence of PFLA was conducted at various stages of the MF process using the bench top AMICON MF assay.

STW- fouled membrane had a 60% higher concentration of PFLAs than FSTW fouled membrane. STW foulant is comprised of the total PFLAs (microbial plus nanoparticulate). FSTW foulant contains phopholipids that were present in solution (DOM and nanoparticulates), since all microparticualtes (bacteria) were removed by filtration using a 0.2-µm filter. This supports the hypothesis that PLFAs are deposited on the membrane surface during microfiltration and affecting membrane performance

Phospholipid Fouling of PP Membrane

The adherence, movement through the PP membrane matrix and affect on permeate flux of a pure phosphlipid was investigated using phosphatidylethanolamine, dipalmitoyl-sulforhodamine B, (PTEDSB). Using the AMICON unit assay, a PP membrane was exposed to 1.0 µg/mL of PTEDSB and permeate flux loss was measured as a function of time. As soon as PTEDSB was added to the system, permeate flux dropped and continued to drop as

more PTEDSB was drawn to the membrane surface. The PTEDSB could not be washed off with DI water.

MF Cake Stability – Effects of Specific Foulants

Protein Stability at the Membrane Surface

An experiment was performed to test adsorption and removal of a pure protein from the PP membrane surface. PP membrane surface was fouled with 0.01% gelatin protein. Upon protein introduction into the system, permeate flux dropped from 620 GFD to 520 GFD in 5 seconds. Washing the protein-fouled membrane with 5 mg/L Proteinase K reversed the fouling, restoring flux to above 600 GFD.

When proteinase K was used to remove protein from STW and FSTW fouled membranes, the results were not as positive as gelatin alone, indicating other factors are involved in the fouling process besides simply protein deposition.

Phospholipid Stability at the Membrane Surface

Since lipids are capable of contributing to MF fouling, lipase was investigated for its potential effect on flux recovery. PP membranes were fouled with FSTW, and then treated with lipase (100 µg/mL, dissolved in buffer at pH 7.7 for 1 hour). Lipase did not restore flux in fouled membranes; flux remained below 400 GFD. It is unclear why lipase failed to affect MF water flux as lipids are an integral part of the MF fouling; however, it is known that lipases require an oil/water interface for maximum activity and binding of lipids to polypropylene may disrupt this interface. Alternatively, monoglycerides formed by lipase activity may also effectively foul PP membranes, resulting in continued water flux reduction.

A pretreatment experiment with lipase was conducted. PP membrane was pretreated with 100 µg/mL of lipase at pH 7.7 for 1.5 hours. After pretreatment, the membrane was exposed to FSTW using the AMICON unit. A control (no lipase) was exposed to NPM buffer solution for 1.5 hours concurrently. The lipase pretreated membranes started at a lower flux but appeared to have slower drop in performance as compared to the untreated membranes.

Although lipase did not restore flow of the fouled membrane when applied post-fouling, pretreating the membrane surface slowed down the formation of the MF fouling layer.

Membrane Cleaning Using Caustic and Surfactant

Fouled membranes were treated with Memclean C at 40ºC, 250 rpm (magnetic stir rod 2 mm above the membrane surface) for 15 minutes. The cleaning solution was removed and permeate flux was measured using DI water. Flux was restored, but not to the original level seen before the membrane was fouled.

Membrane Cleaning Using Polar Solvents

PFLAs are soluble in polar organic substances such as ethanol and acetone. Ethanol was used as a cleaning agent to restore membrane flux after being fouled with STW and FSTW. Ethanol restored flux for both STW and FSTW-fouled membranes. FSTW-fouled membrane recovered better than STW fouled membrane. Over 80% removal of PLFAs from FSTW fouled membrane was observed (61% of TerBrSats, 73% of Monos, 100% or BrMonos and MiBrSats, and 64% of Nsats phospholipids) using ethanol. This suggests that polar organic molecules or nanoparticles are perhaps responsible for a large part of the observed flux reduction driving microfiltration of secondary treated wastewater. By comparison, ethanol recovered membrane performance to its original permeate flux, and thus may more efficiently have removed foulant material.

Task 3. Fouling of PP MF Membranes Independent of Transmembrane Pressure-Laboratory and Field Experience

DOM fouling occurs rapidly as the feedwater contacts the membrane surface, with no driving pressure required, as opposed to microparticulate cake formation. This was investigated in the laboratory by exposing PP membranes to STW for 24 hours. The membrane was then treated with ethanol and flux was measured. Flux did not recover as seen in previous short-term tests. This result was also observed in the field in the 5 MGD MF plant at OCWD. New PP hollow fiber membranes were immersed in the same STW used in laboratory experiments for seven

days with periodical STW replacement. This resulted in decreased membrane performance and required earlier than planned chemical cleaning-in-place (CIP).

CONCLUSIONS AND RECOMMENDATIONS

- STW and FSTW both demonstrate similar flux decay curves, suggesting bacterial or microparticulate fouling (MF cake) is a far smaller portion of the overall fouling than was previously thought.
- AFM imaging showed FSTW fouled membranes lacking microparticulates, suggesting dissolved foulants (<0.2 µm) enter the membrane matrix and block pores from within, suggesting pore clogging is occurring along with pore blocking.
- Evidence suggests that in addition to surface coverage (reversible fouling), pore blockage and/or pore constriction (potentially irreversible fouling) is occurring during MF filtration using PP membranes.
- MF fouling may be principally influenced by other factors besides cake formation by deposited microparticulates (bacteria).
- Protein and carbohydrate ATR/FTIR bands were equally represented in both STW and FSTW, which provides evidence that primary MF fouling may be the result of mostly biological detritus as opposed to bacteria and particles larger than 0.2 µm.
- Dissolved carbohydrates strongly adhere to the PP membrane surfaces.
- The presence of phospholipids in the feedwater decreases membrane performance. Phospholipids can be removed from the membrane surface by polar organic solvents like ethanol.
- Ethanol works well to remove DOM fouling form PP membrane surfaces, restoring water flux.
- DOM fouling occurs rapidly as the feedwater contacts the membrane surface with no driving pressure required, as opposed to microparticulate cake formation.

Classical models of MF cake fouling suggest the accumulation of particles close to the membrane surface covers membrane pores, resulting in water flux reduction. The implication from this work is that there are actually two mechanisms of MF fouling, the classical MF cake formation, which may result in less reduction of hydraulic conductivity, and deposition of

microbial cell residue (proteins, carbohydrates and phopholipids) and nanoparticulates (e.g. liposomes) which results in the majority of the observed fouling.

Recommendations

The results from this study suggest water agency professionals need to seriously consider this other MF fouling, and revaluate the current cleaning practices so that they specifically target biological detritus. The current cleaning methods may in some ways be increasing the rate of fouling, for example by extraction of the lipids from whole bacteria in the cake that subsequently may be transported and deposited on the MF membrane surface. Therefore, additional research characterizing the DOM and nanoparticulates is needed. Cleaning agents specific for phopholipids, proteins and carbohydrates should be further investigated. In addition, modification of membrane polymers to reduce adsorption of biological detritus is desirable. Implementation of improved methods of foulant removal and improvement of hydraulic conductivity in MF membranes will reduce operating costs and prolong membrane lifetime.

Benefits to California

With MF pretreatment becoming the mainstream RO pretreatment technology, it is critical that the MF fouling be effectively managed and controlled. Understanding the fundamental principles of MF fouling during water reuse leads to more efficient MF operations, increases the reliability of the process and reducing the cost of the product water.

ABSTRACT

In recent years, microfiltration (MF) has been shown to be less costly and more effective than conventional lime clarification as a pre-treatment method for reverse osmosis (RO). Orange County Water District (OCWD) plans to utilize an MF/RO process in a 70-mgd advanced water reclamation facility. The feedwater for this large facility is municipal secondary treated wastewater, which possesses significant nutrient loading, and high biological activity. These factors contribute to rapid biofouling of the MF membranes with consequent loss of performance. MF cake formation is associated with increased hydrodynamic resistance (i.e., flux loss) and necessitates frequent chemical cleaning of the MF membranes, thereby driving up operational costs. Bacteria, nanoparticulates and dissolved organic matter (DOM) are the major components of membrane fouling. The primary objective of this project was to elucidate the fouling mechanism of MF membranes and to suggest mitigation strategies based on this mechanism. Experimental MF cakes were formed under controlled laboratory conditions using a 0.22-μm polypropylene membrane material and secondary treated wastewater. Two mechanisms of MF fouling were observed; the classical MF cake formation by microparticulates and fouling by microbial cell residue (such as DOM proteins, carbohydrates and phopholipids) and nanoparticulates. The cake layer (bacterial large particulate layer) is responsible for a relatively small fraction of the observed loss of hydraulic conductivity, and the cake is easily removed by backwashing (air sparging), which forces the cake off the surface. On the other hand, microbial residues such as (DOM and nanoparticulates with dimensions smaller than 0.2 μm) are responsible for the majority of the observed reduction of hydraulic conductivity and may be more difficult to remove. Adsorbed material may foul MF membranes in the absence of applied transmembrane pressure.

1 INTRODUCTION

In recent years, microfiltration (MF) has been shown to be less costly and more effective than conventional lime clarification as a pre-treatment method for reverse osmosis (RO). Orange County Water District (OCWD) plans to utilize an MF/RO process in a 70-mgd advanced water reclamation facility. The feedwater for this large facility is secondary treated wastewater, which possesses significant nutrient loading, and high biological activity. These factors contribute to rapid biofouling (i.e., cake formation) of the MF membranes, with consequent loss of performance. MF fouling is associated with increased hydrodynamic resistance (i.e., flux loss) and necessitates frequent chemical cleaning of the MF membranes, thereby increasing operational costs. Better understanding of MF fouling and dynamics are needed to improve the efficiency of the MF/RO process at OCWD and other agencies.

2 BACKGROUND

MF is increasingly becoming popular as a pre-treatment process in conventional water and wastewater treatment to meet the increasingly stringent water quality requirements proposed by state and federal regulatory agencies. MF is widely used to remove colloidal particles and microorganisms from drinking water, as well as to treat secondary or tertiary effluent in wastewater treatment (Albert *et.al*, 2002, Wiesner *et.al,* 1996, Zeman *et.al*, 1996, Reith *et.al*, 1998). With MF becoming the mainstream RO pretreatment technology, it is critical that the MF fouling be effectively managed and controlled.

Microfiltration can be separated into two mechanisms: surface filtration and depth filtration (www.engineering.rowan.edu/~toba6555/microfiltration.htm). In surface filtration, particles are blocked from passing through the membrane pores, depending on size. Only particles smaller than the pore size of the membrane pass through to the permeate side. Surface filtration may be conducted in dead-end or cross-flow modes. In dead-end filtration the feed flows perpendicularly toward the membrane surface. The liquid passes through the membrane (permeate) and all particles larger than the pore size are retained at the surface, forming a fouling layer (cake). Flux decreases as the cake thickness increases. In the cross-flow filtration process, part of the feed water passes through the membrane as permeate and the other portion of the feed water passes tangentially along the membrane, forming a cross flow.

Particles in the feed water may deposited at the membrane surface are swept along by the sheer force of the feed as it passes over the membrane surface preventing cake formation. Cross-flow filtration may have higher permeate fluxes over longer periods of time compared to dead-end filtration, however; this mode may result in higher energy and operation costs (Bai *et.al,* 2001).

In depth filtration, particles smaller than the pore size of the membrane move into the filter matrix and adhere to the collecting surfaces of the filter. Particles are not affected by crossflow or surface hydraulic sheer, and backwashing by reverse pressure flow is required to dislodge the fouling material from the membrane surface.

Membrane fouling is characterized by the reduction of permeate flux through the MF membrane matrix as a result of increased flow resistance due to pore blocking, concentration polarization, and cake formation (Bai et.al., 2002 and Wiesner et.al., 1992). Pore blocking may occur in both dead-end and cross-flow filtration modes, but the effect of cake formation and concentration polarization on permeation flux may be reduced in cross-flow filtration (Bai et.al., 2001). The extent of fouling on flux decline depends on membrane pore size, solute loading and distribution, membrane polymer material, source water quality and operating conditions. Fouling causes a rapid reduction in permeate flux; the long term effects of fouling may include irreversible fouling resulting in reduction of membrane performance and reduction of membrane lifetime (Lim et.al., 2003). To reduce operational and maintenance costs, membrane facilities strive to keep membrane fouling to a minimum. Various strategies have been developed to reduce costs and membrane life spans such as the development of new membrane polymers (Wang et.al., 2002, and Brink et.al., 1993), improved module engineering (Bai et.al., 2001, 2002, and Leow et.al, 2001), modification of feed flow pattern, improved backwashing techniques, and incorporation of novel cleaning techniques.

MF fouling may be mitigated by removal of the cake *in situ* with transmembrane pressure pulsing or backwash. Backwashing is an effective way of reducing fouling in membranes, improving the overall filtration rate and extending the cleaning interval (Zhao, Y., 2002 and Sondhi et.al., 2001). Backwashing involves a temporary reverse flow of either the permeate

or air. The permeate or air is flushed through the membrane from the permeate side by applying a pulse of higher pressure on the permeate side or suction on the feed side. The required pressure for backwashing is several times higher that of the transmembrane pressure difference and increases with increasing number of particle layers accumulated on the membrane surface. Backwashing then forces the MF foulant ("cake") from the membrane surface which is then flushed away by the retentate flow. Backwash cycles are set at regular intervals to maintain membrane fouling at a minimum. MF backwashing works well in removing build-up of MF cakes comprised of bacteria and larger particulates on membrane surfaces. By applying reversed pressure they can be dislodged and removed.

Other major contributors to MF fouling are dissolved organic matter (DOM) and nanoparticulates (AWWA Report, Membrane Processes, 1998). DOM is a heterogeneous mixture of chemicals produced by biological activity, and includes aquatic humic substances (humic acids and fulvic acids), proteins, carbohydrates and phospholipids as well as other organic compounds. Secondary treated wastewater contains a variety of DOMs that may contribute to MF fouling. DOM and residues of microbial activities are frequently cited as a major membrane foulant in MF (Makdissy et.al., 2004).

2.1 Project Objective

The MF fouling layer is perhaps the most critical factor responsible for overall process efficiency economics. Membrane fouling is characterized as the reduction of permeate flux through the membrane caused by pore blocking, concentration polarization, and cake formation. Therefore, the primary objective of this project was to elucidate the fouling mechanisms of MF membranes, including permeability, stabilization and removal of filter cakes.

2.2 Report Organization

The report consists of discussion of the project approach followed by discussion of experimental and laboratory test methods and procedures. The project outcomes are discussed

in detail, as are results of experiments performed in the study. The report concludes with results and recommendations for further research.

3 PROJECT APPROACH

This project examined the formation, structure, and stability of MF cakes formed on polypropylene membrane material under controlled conditions. The experimental approach was divided into three tasks:

Task 1. Acquire and configure a bench-scale MF apparatus to conduct MF cake investigations, including formation, structural, stability, and dynamics. Experimental MF cakes were formed under controlled laboratory conditions on 0.22-µm polypropylene (PP) MF membrane material (Osmonics, San Diego, CA). The original test plan proposed to use additional feedwaters donated by other agencies: Metropolitan Water District of Southern California (surface water), University of California, Riverside (agricultural drainage water) and Alameda County Water District (conventionally treated secondary wastewater). However due to time and staffing shortages, only secondary treated wastewater (STW) from OCWD was used in the study.

Task 2. It was initially anticipated during generation of the proposal and test plan that microparticles, (bacteria and large particulates > 0.2µm), forming a "cake" on the membrane surface was the major contributor to MF performance decrease (flux decline). Based on this assumption, the study proposed to elucidate the mechanism of action of monochloramine and chemical cleaning agents on MF cake deposition, permeability, stabilization and removal. However, results from several experiments performed at OCWD and more recent perusal of the available literature (Howe, et.al, 2002, Makdissy, et.al, 2002, and Palacio et.al, 2002) suggested that the major cause of MF fouling was not due to accumulation of particulate MF cakes as proposed, but to accumulation of organic matter such as nanoparticulates (e.g. liposomes) and dissolved organic matter (DOM) including proteins, carbohydrates and polysaccharides present as microbial debris in the feedwater. This view was supported by experiments where all microparticulate solids (> 0.2 µm) were removed by filtration and MF fouling still occurred. These observations resulted in a change of scope for this study (results

presented in subsequent sections of this report). *Task 2* was therefore redefined to: evaluate the formation, structure and stability of nanoparticulate and organic material fouling, which may be the primary contributors in MF fouling and decreased membrane performance, and to screen selected chemicals capable of targeting these foulants (e.g. organic solvents such as ethanol, protease and phosphotase) for MF fouling removal or prevention.

Task 3. Test cleaning agents that are determined to be effective under laboratory conditions in field trials using a pilot size MF unit operated with STW under actual operating conditions. Task 3 was not completed as proposed in the original test plan for two reasons. 1) The scope of the project was changed to evaluate DOM fouling instead of testing chemical agents to remove microparticualte MF cakes from membrane surfaces, and 2) an MF pilot scale test unit was not available (could not be acquired in time and at a reasonable cost) to be used in this study. However, at the field scale one aspect of the study, exposure of PP membranes in secondary treated wastewater without applied pressure (soaking) was inadvertently tested using a 5 MGD MF plant with the fouling results favorably agreeing with laboratory observations.

3.1 Membrane Characterization

3.1.1 Atomic Force Microscopy (AFM)

Membrane structural properties (pore size, pore shape and distribution) of clean and fouled PP membranes were determined by AFM (CP AutoProbe, Park Scientific Instruments, Sunnyvale, CA). AFM provides essential information about the sub-micron surface topography and fundamental material properties of polymer membranes. Such information has been correlated with the performance (flux and solute rejection) and fouling potentials of separation membranes, and therefore is critical in optimizing function and designing novel antifouling surfaces [Knoell, *et.al*, 1999]. The AFM is an excellent tool for examining topography of polymer membrane surfaces in air-dried as well as fully hydrated forms.

The AFM used in this study was equipped with a non-contact/contact head and a 100-µm scanner operated in a constant force mode. Membrane coupons were attached to a circular

stainless-steel sample holder using 12-mm carbon conductive tape (Ted Pella, Inc., Redding, CA). The holder with the attached membrane was mounted on the piezo scanner of the AFM. Images were acquired using silicon Ultralevers (force constant = 0.24 N/m; Park Scientific Instruments, Sunnyvale, CA), which were gold-coated cantilevers with integrated height-aspect ratio silicon nitride conical tips designed for maximum penetration into pores and other surface irregularities frequently encountered on polymer membranes. Tapping mode AFM (similar to non-contact mode AFM) was generally employed to minimize translational forces between the AFM tip and polymer membrane surface. In the taping mode, the AFM cantilever was maintained at some distance from the membrane surface (on the order of 1000 Å) and oscillated at relatively high amplitude at or near its resonant frequency. The vibrating cantilever/tip was then moved closer to the sample surface until it just touched ('tapped') the sample once during each oscillation. AFM images were acquired at a scan rate of 1.0 – 2.0 kHz with a minimum information density of 256 x 256 pixels.

3.1.2 Attenuated Total Reflection Fourier Transform Infrared (ATR/FTIR) Spectrometry

Absorption in the mid-infrared (IR) region (4000 – 500 cm^{-1}) was employed to acquire spectroscopic 'fingerprints' of clean and fouled PP membranes used in the study. Polypropylene has only C-C and C-H functional groups; its FTIR absorption spectrum contains sharp, well-defined absorption bands. Therefore, the polypropylene spectrum is easy to subtract from the composite spectrum, making the spectrum of the foulants easier to interpret (Howe, *et.al,* 2002).

The membranes were cut into small strips (~ 1 x 4 cm) and dried in a glove box purged with compressed air passed through a dryer (Balston, Havenhill, MA). A piece of membrane was pressed against each side of a 45°, 50 x10 x 2 mm zinc selenide internal reflection element (IRE). A torque of 10 oz-in was applied to the bolt of the pressure plates of the attenuated total reflectance accessory (Harrick Scientific, Ossining, NY). Sample spectra consisted of 256 co-added scans collected at 4-cm^{-1} resolution with a Magna 550 FTIR spectrometer (Thermo Nicolet, Madison, WI). The single-beam spectra were (1) ratioed against a bare IRE background spectrum, (2) converted to absorbance, (3) corrected for the wavelength

dependence of internal reflection and (4) baseline-corrected utilizing GRAMS/32 (Version AI 7.01) software (Thermo Galactic, Salem, NH).

3.1.3 Membrane Hydraulic Properties

Membrane material was cut into 55 mm diameter disks. PP membrane has a highly hydrophobic surface (it is initially impermeable to water). Therefore, prior to each experiment, a new PP MF membrane disk was immersed in 100 % ethanol for 15 minutes followed by flushing with 18 megohm-cm water to hydrate the membrane material. The hydrated PP disk was then placed in the bench-scale test apparatus (Amicon unit, Amicon, Napa, CA) shown if Figure 1 (shown to be a representative test system for MF laboratory testing by Leslie, 1993 and Choi et.a., 1999). The apparatus was filled with feed solution and sealed. A vacuum of 12 psi was applied, and membrane permeate flux was gravimetrically measured continuously with an electronic balance (BP 610, Sartorius, Goettingen, Germany) connected to a computer (Dell Inspirion 8200, Round Rock, TX) through an RS 232 interface using data acquisition software (WinWedge v1.2, TALtech, Philadelphia, PA).

3.2 MF Cake Formation and Characterization

3.2.1 MF Cake Formation

Prior to cake formation, the membrane permeate flux was measured using the method described in section 3.1.3. Cake was deposited on the surface of the membrane by filtration of source water at a constant transmembrane pressure (12 psi) with feedwater replacement to a volume of 180 mL. Permeate flux was calculated at regular (5 second) intervals.

3.2.2 MF Cake Formation Using Secondary Treated Wastewater

Source water for the study was STW (from Orange County Sanitation District). MF cake formation began immediately upon introduction of the source water, and the progression of deposition of fouling materials was quantified by monitoring the rate of decrease in hydraulic conductivity (flow/pressure) through the membrane. Initially, MF cakes were comprised of everything present in the feedwater – visible detritus, microparticulates (bacteria), nanoparticulates and dissolved organic and inorganic constituents.

3.2.3 MF Cake Formation Using Microparticulate-free Filtered Secondary Treated Wastewater (FSTW)

STW was first passed through a glass microfiber filter (47 mm, Whatman, Clifton, NJ) to remove large solids, then filtered through a hydrophilic, low protein binding, sterile, 0.2 µm polyethersulfone filter (PALL Corp., Ann Arbor, MI) designed for microbiological analysis of potable, waste, process and natural waters. Microparticulate (bacterial) removal was confirmed by epifluoresence microscopy using the DNA-specific fluorochrome 4,6-diamidino-2-phenylindole (DAPI). DAPI stained membranes were imaged using an Olympus IX-70 microscope equipped with a color camera (Dage DC 330T, Dage MTF, Michigan City, IN). The FSTW MF cake was comprised of only the nanoparticulate and dissolved portion of the source water; the filters removed all solids larger than 0.22 µm. FSTW was passed through the PP membrane using the AMICOM units under 12 psi as previously described.

3.2.4 Active, Inactive and Lysed Bacterial Component Analysis in MF Cake

STW effluent used in the study contained active, inactive and lysed (ruptured) bacterial cell components. It was anticipated that each of these components may give rise to fouling of MF membrane material. Cell components (debris) may include phospholipid fatty acids (PFLAs), proteins and carbohydrates. Analysis for protein (Strickland, *et.al*, 1968) and carbohydrate (Lowry, O.H., *et.al*, 1951) were performed on feedwaters, MF cakes and permeate. PFLAs are major components of cell membranes; these were analyzed by extraction of the total lipid (White, *et.al*. 1979) followed by separation of the polar lipids by column chromatography (Guckert, *et.al*. 1986). The polar lipid fatty acids were derivatized to fatty acid methyl esters, which were quantified using gas chromatography (Ringelberg, et.al., 1994). Fatty acid structures were verified by chromatography/mass spectrometry and equivalent chain length analysis.

4 PROJECT OUTCOMES

4.1 Task 1. Acquire and Configure a Bench-scale MF Apparatus to Conduct MF Cake Investigations

4.1.1 Proposed MF Cake Characterization

At the onset of the study it was presumed that the fouling components of MF cakes, would be mostly comprised of bacteria and large particulates (> 0.2 µm), and this would be the major contributor to decreased MF performance. Cake structure was proposed to be studied by using mass by weight measurements and cake stability by light scattering (optical density), and by particle sizing using a particle analyzer (Coulter Multisizer II, Beckman Coulter, Inc., Miami, FL). In addition, genetic microbial identification, protein assay, carbohydrate assay, epifluorescence microscopy and light microscopy techniques would be used to study the nature of microbial material accumulating on the membrane surface during cake formation and flux reduction. Some of these techniques were initially employed in study of the MF cake as follows:

1) An initial attempt was made to examine the cake structure using a pressurized microscope flow cell that allowed the PP membrane surface to be examined during cake formation using a microscope (Olympus AX-70). This technique allowed successful visualization of the membrane surface, but did not provide flow dynamics associated with fouling. The membrane chamber in this apparatus was too small to generate an MF cake thick enough to use mass by weight measurements, as available balances were not sensitive enough to provide accurate data. Due to difficulties with this technique, it was abandoned.
2) The AMICON unit was used to build MF cakes using OCWD STW. During experiments, it was observed that permeate flux started to decrease within seconds of feedwater introduction into the system (Figure 2). After approximately 400 seconds it was determined that the membrane was sufficiently fouled. The resulting cake was then dispersed using a stir rod suspended 2 mm above the membrane surface and rotated at 250 rpm for 10 minutes to simulate shearing. An aliquot of the bulk feedwater above the membrane (plus dispersed cake) was removed. Optical density (O.D. @ 600 nm) was first used in an attempt to quantify microparticulate removal. The dispersed cake contained visible clumps of particulates, which made O.D. readings difficult and unreliable. In lieu of optical density, a Coulter Multisizer II Analyzer (Beckman Coulter, Miami, FL)

equipped with a 50-µm orfice was employed to quantify the total particles and size distribution of particles removed from the surface into the bulk solution (Figure 3). Particle sizes from disrupted cake material ranged from 3,576.08 μ^3 down to 0.65 μ^3, with the largest grouping between 3 – 7 μ^3 (corresponding with single bacteria). This technique was not sensitive enough to detect particles smaller than 0.43 μ^3 (nanoparticles).

Following cake removal, the membrane was challenged with FSTW (all particulates were removed with a 0.2 µm filter) and permeate flux was measured. It was expected that removal of the cake would result in significant restoration of membrane flux; moreover, it was anticipated that removal of microparticulates from STW would prevent significant membrane fouling and allow FSTW to be used to test membrane water flux. It was observed that removing the large particles (MF cake) from the membrane surface in this fashion did not restore membrane performance (data not shown). In addition, passage of FSTW through the PP membrane resulted in further decline of water flux. It was concluded at this point that cake formation from deposited microparticulates (bacteria) originally presumed to be responsible for MF fouling, was not the principal mechanism of water flux reduction.

4.2 Task 2: Evaluate MF Fouling by Nanoparticulates and DOM

4.2.1 Flow Dynamics Using STW and FSTW Feedwater

A hypothesis was formed that material smaller than bacteria were primarily responsible for the flux decline observed during MF cake formation on STW. To test the theory, all microparticulate solids were removed from the feedwater by passage through a 0.2-µm filter. To confirm the removal of microparticulates, equal volumes of STW and FSTW feedwaters were filtered onto 25 mm, black, 0.2 µm filter membranes (Nucleopore Corp. Pleasanton, CA), stained with DAPI and examined with fluorescence microscopy to confirm FSTW was truly bacteria (and microparticulate) free (Figure 4). The filtrate (FSTW) was then used as feedwater to test its affect on MF permeate flux. STW and FSTW tests were conducted concurrently under identical conditions using the AMICON test unit. The two feedwaters (STW with microparticulates and FSTW without microparticulates) generated similar

permeate flux decay curves (Figure 5), suggesting that flux decay kinetics were not principally influenced by the microparticulate fraction of STW. Permeate flux difference between the STW and FSTW curves were attributed to cake formation by the bacteria and other larger particulates present in STW. This demonstrated bacterial or particulate fouling (MF cake) is a far smaller portion of the overall fouling than was previously thought. The majority of the flux decline observed (during operation) is, therefore, likely due to nanoparticulate and dissolved organic material (DOM) present in the secondary treated wastewater, both of which can cause blocking (Choi, et.al., 2000, Huang, et.al. 1998 and Lim, et.al., 2003) or plugging (Makdissy et.al., 2004) of PP membrane pores.

4.2.2 MF Foulant Characterization Using AFM with and without Microparticles

STW and FSTW foulants deposited on PP membranes were also examined with AFM. At the completion of a fouling experiment using STW and FSTW as feedwaters, excess water was drained and the membrane disks were carefully removed from the AMICON cell. The disks were air dried, cut into sections and mounted onto stainless steel coupons using double-sided carbon tape. AFM topographic images were acquired using NC-AFM (Figure 6). The AFM images show fouling on both STW and FSTW membranes. The STW fouling appears to be thick and multi-layered, and composed of bacteria and other particulates. The FSTW fouled membrane does not have bacteria or microparticles, but still appears to be fouled with amorphous, nodular material that covers the membrane pores. Pores of the PP membrane appear to be blocked, however the dissolved foulants (<0.2 µm) seem to enter the membrane matrix and block the pores from within. The images support the observation that the most significant amount of MF fouling is not due to bacteria and other microparticulates, but to DOM and nanoparticulates which can adhere to the membrane and form aggregates. Although microparticulate material on the outer surface of the membrane can easily be sheered off with backwashing, the nanoparticulates and DOM may be adsorbing to the membrane matrix, making them more difficult to remove.

4.2.3 MF Foulant Characterization – Chemical Analysis

4.2.3.1 MF Foulant Characterization Using ATR/FTIR

To further characterize MF fouling, ATR/FTIR spectrometry was employed to analyze the fouling layer left behind at the membrane surface by STW and FSTW. ATR/FTIR analyses were performed as described in section 3.1.2. Absorption in the mid-infrared region (4000 – 500 cm^{-1}) was employed to acquire spectroscopic 'fingerprints' of STW and FSTW fouled PP membrane material. Figure 7 shows the FTIR spectrum of components in STW and FSTW water used to foul a polypropylene membrane (the PP membrane spectrum, Figure 8, has been digitally subtracted). The strongest absorption band is observed at 1034 cm^{-1}. Absorption in this region is due to C-O or Si-O bonds, and is commonly associated with alcohols, ethers, polysaccharides, and silicates (Cho et.al., 1998, Howe et.al., 2002 and Thurman, 1985). Carboxylates typically absorb around 1600 and 1400 cm^{-1}, and amides typically absorb around 1650 and 1550 cm^{-1} (Howe et.al., 2002). The presence of absorption in these regions suggests a significant amount of proteinaceous material on the fouled membrane surface. That these bands are equally represented in both STW and FSTW provides additional evidence that primary MF fouling may be the result of mostly biological detritus as opposed to microparticulates (bacteria and particles larger than 0.2 µm).

4.2.3.2 MF Foulant Characterization - Protein and Carbohydrate

MF fouling by relatively clean protein solutions may lead to an order of magnitude reduction of permeate flux (Bowen et.al., 1991, Belfort et.al., 1994, Palacio et.al., 2003, and Ho et.al., 2002). Belfort et.al., 1994 and Ho et.al., 1999 demonstrated that protein fouling is typically caused by the deposition of protein aggregates on the membrane surface. Güell and Davis (Güell et.al., 1996) demonstrated flux decline during microfiltration using bovine serum albumin, which was dominated by pore blockage. To further characterize the OCWD FSTW foulants, protein and carbohydrate analysis of the bacterial-free (FSTW) feedwater, STW, FSTW permeate and fouling layer were performed (Table 1 and Table 2). Protein assays were performed on two different days. The results demonstrate water quality variations can occur; the composition of STW from Orange County Sanitation District can vary with respect to microbial detritus from day to day. Güell and Davis (Güell et.al., 1996) also showed that

different types and size proteins affect MF fouling and flux at different rates. For example they showed that BSA fouling was dominated by pore blockage, while ovalbumin showed a transition between pore blockage and cake filtration.

A significant amount of carbohydrates (64% of the total in STW) remained following removal of bacteria. Dissolved carbohydrates appeared to be strongly deposited on the PP membrane representing approximately 71% of the acellular carbohydrate in the feed (Table 1and Table 2). This finding is in agreement with other studies demonstrating that carbohydrates comprise a large portion of the DOM found on MF membrane surfaces (Makdissy et.al. 2004).

4.2.3.3 Phospholipid Fatty Acid Analysis

Cell debris may contain fragments of cell membranes that anneal to form nanoparticulates (liposomes). The fragments are largely made up of phospholipids. Of the lipids, the phopholipid fatty acids (PFLAS) represent the major component of cell membranes. Phopholipids posses polar heads and nonpolar hydrocarbon tails; they are either amphipathic or polar. These lipids differ in size, shape and charge on their polar head groups. Each type of phospholipid can exist in different chemical species, therefore, differing in their fatty acid constituents. PFLA, when exposed to hydrophobic membrane surfaces such as PP, may attach and actually intercalate into the membrane matrix. An analysis to determine the presence of PFLA was conducted at various stages of the MF process using the bench top AMICON MF assay. PFLA analysis was conducted on PP membranes fouled with STW and FSTW, and on 1 liter of STW (Microbial Insights, Rockford, TN).

STW- fouled membrane had a 60% higher concentration of PFLAs than FSTW fouled membrane (Figure 9). This is not an unexpected result because the STW foulant is comprised of microbial plus nanoparticulate and DOM PFLAs. FSTW foulant contains only phospholipids that were present in solution or as liposomes. This represents a considerable fraction of the PFLAs detected in fouled PP MF membranes (40%). Moreover, these PFLAs are free to associate with the membrane materials, while most of the PFLAs in STW are held up in the intact microorganisms. This supports the hypothesis of PLFAs are being deposited

on the membrane surface during microfiltration, and potentially affecting membrane performance.

4.2.3.4 Phospholipid Fouling of PP Membrane

The adherence, movement through the PP membrane matrix and affect on permeate flux of a pure phosphlipid was investigated using a fluorescently tagged phospholipid, phosphatidylethanolamine, dipalmitoyl-sulforhodamine B, (PTEDSB Sigma, St. Louis, MO). Using the AMICON unit assay, a PP membrane was exposed to 1.0 µg/mL of PTEDSB and permeate flux was measured as a function of time (Figure 10). As soon as PTEDSB was added to the system, permeate flux dropped and continued to drop as more PTEDSB was drawn to the membrane surface. The PTEDSB fouled membrane surface was then challenged with DI water to confirm membrane fouling and to see if the phospholipid could be washed off. The PTEDSB was not washed off with DI water; DI water permeate flux remained at the same (fouled) rate. Adherence of PTEDSB was also visualized using fluorescence microscopy using an Olympus, IX70 epifluorescence microscope at 40 X using a 520 nm excitation and 580 nm emission filter. PTEDSB treated membranes were examined. Feed and product sites of the PP membrane were imaged using a color CCD camera. It appeared that most of the lipid responsible for fouling the membrane was captured by the membrane matrix on the feedwater surface (Figure 11).

4.2.4 MF Foulant Stability – Effects of Specific Foulants

4.2.4.1 Protein Stability at the Membrane Surface

An experiment was performed to test adsorption and removal of a pure protein from the PP membrane surface. PP membrane surface was fouled with 0.01% gelatin protein (Knox, Gelatine, Parsippany, NJ). Upon protein introduction into the system, permeate flux dropped from 620 GFD to 520 GFD in 5 seconds. Washing the protein-fouled membrane with 5 mg/L Proteinase K (Sigma, St. Louis, MO) reversed the fouling, restoring flux to above 600 GFD (Figure 12).

However when the enzyme proteinase K was used to remove protein from STW and FSTW fouled membranes, the results were not as positive as gelatin alone, indicating other foulants were involved in the fouling process besides protein.

4.2.4.2 Phospholipid Stability at the Membrane Surface

Since lipids are capable of contributing to MF fouling, the enzyme lipase was investigated for its potential affect on flux recovery. PP membranes were fouled with FSTW, then treated with lipase (from *Mucor javanicus*, Sigma, St. Louis, MO), 100 µg/mL, dissolved in NPM buffer (see Appendix 1) at pH 7.7 for 1 hour. Lipase did not restore flux in fouled membranes; flux remained below 400 GFD (Figure 13). It is unclear why lipase failed to affect MF water flux, as lipids are an integral part of MF fouling. It is known that lipases are most active at a lipid-water interface (Dodson et.al., 1992). It is possible that the lipid-water interface is disrupted when lipids adsorb to PP rendering lipase ineffective. Further investigation in this area is warranted.

It was thought that pretreatment of PP with lipase might result in lipase binding to the PP membrane. In this state, the enzyme might have been more effective on unbound lipids in the feedwater prior to their binding to the PP MF membrane. PP membrane was pretreated with 100 µg/mL of *Mucor javanicus* lipase at pH 7.7 for 1.5 hours. After pretreatment, the membrane was exposed to FSTW using the AMICON unit. A control (no lipase) was exposed to NPM buffer solution for 1.5 hours concurrently. The lipase-pretreated membranes started at a lower flux but appeared to have slower drop in performance as compared to the untreated membranes (Figure 14). The untreated membrane produced more water over all. Lipase may be fouling the membrane surface and impeding flux. Pretreatment with lipase did not improve water production in this experiment; either the enzyme was ineffective or else the fatty acids released by lipase activity also effectively fouled the PP membrane. Further investigation with pretreatment of MF membranes is necessary to assess the feasibility of membrane pretreatment to improve membrane hydraulic conductivity.

PFLAs are soluble in polar organic substances such as ethanol and acetone (Alexander et.al., 1985). When the PTEDSB fouled membrane was treated with 100% ethanol for 15 minutes

the phospholipid fouling was reversed (Figure 10), membrane flux was restored and maintained when DI water was introduced. The phopholipid removal from the PP membrane by ethanol was confirmed by epiflurescence microcopy (Figure 11C).

4.2.5 Membrane Cleaning Using Caustic and Surfactant

Cleaning-in-place (CIP) procedures at the OCWD 5 MGD MF facility involves use of Memclean C combined with 0.8% sodium hydroxide. This combination of surfactant and caustic saponified lipids and solubilized proteins, which is most probably its principal cleaning mechanism. This cleaning solution combination was tested in the laboratory using the AMICO test unit and FSTW-fouled PP membranes. Fouled membranes were treated with Memclean C at 40ºC, 250 rpm (magnetic stir rod 2 mm above the membrane surface) for 15 minutes. The cleaning solution was removed and permeate flux was measured using DI water. Flux was restored (Figure 15), but not to the original level seen before the membrane was fouled with FSTW, indicating some fouling remains on the membrane surface or in the membrane matrix (also described by Makdissy et.al., 2004).

4.2.6 Membrane Cleaning Using Polar Solvents

Ethanol was used as a cleaning agent to restore membrane flux after being fouled with STW and FSTW. PP membranes were fouled and then exposed to 100% ethanol, for 15 minutes after which flux was measured. Figure 16 shows flux recovery after ethanol treatment for both STW and FSTW-fouled membranes. FSTW membrane recovered to its original water flux level unlike the STW fouled membrane which only recovered partially. STW partial recovery may be the result of microparticulates (bacteria) being present in the feedwater making the fouling layer more complex and therefore requiring additional sheer to completely reverse surface fouling (cake) components. Also, extraction of the lipids from whole bacteria in the cake may have been subsequently transported to the MF membrane surface resulting in increased fouling. It may take additional means of cleaning (e.g. backwashing) to recover the membrane completely. However, by comparison to caustic and surfactant cleaning (Memclean C plus sodium hydroxide), ethanol recovered membrane performance more effectively and thus likely removed more fouling material.

PP MF membrane fouled with FSTW was treated with ethanol, and the ethanol fraction was reversed and analyzed for PFLA content (as described previously). Results of this analysis were compared to the PFLA content present in FSTW. Figure 17 shows the percent removal of PLFAs from FSTW fouled membrane using ethanol. Ethanol removed over 50% of all PFLAs associated with FSTW fouled PP MF membranes (61% of TerBrSats, 73% of Monos, 100% or BrMonos and MiBrSats, and 64% of Nsats phospholids). This suggests that polar organic molecules or nanoparticles are perhaps responsible for a large part of the observed flux reduction of PP MF on secondary treated wastewater.

4.3 Task 3. Fouling of PP MF Membranes Independent of Transmembrane Pressure-Laboratory and Field Experience

DOM fouling may occur rapidly as feedwater foulants diffuse to and contact the membrane surface, with no driving pressure required, as opposed to microparticulate cake formation which requires transmembrane pressure. This was inadvertently evaluated in the laboratory by exposing PP membranes to STW for 24 hours at room temperature without transmembrane pressure applied in the AMICON test unit. After 24 hours, flux was measured using STW as the feedwater. Flux declined immediately upon STW feed (see Figure 18). The test unit was then operated at 12 psi using DI water. The membrane was then treated with 100% ethanol for 1 hour. As seen in Figure 18, treatment with ethanol did not recover membrane performance as seen previously (Figure 16). A similar result was noted in the field in the 5 MGD MF plant at OCWD. New PP hollow fiber membranes were installed, and prior to start up, membranes were immersed in the same STW used in laboratory experiments without application of transmembrane pressure for seven days with periodical STW flushing. This resulted in decreased membrane performance (18 days as opposed to 21 days) and required earlier than planned chemical cleaning (CIP). This 14.3% loss of membrane performance would translate into significant decreased in water production and more frequent CIP cleanings. Loss of water production and more frequent CIP cleanings result in significant increases in operations and maintenance costs. After CIP cleaning, the membranes were soaked in tap water rather than STW; and they operated nominally (21 days) before CIP was required.

5 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

- STW and FSTW both demonstrated similar MF water flux decay curves, suggesting bacterial or particulate fouling (MF cake) formation is responsible for a far smaller portion of the overall fouling than was previously thought.
- AFM imaging showed FSTW-fouled membranes lacked microparticulates (bacteria)This suggests that dissolved foulants (<0.2 µm) may be coating the membrane and/or entering the membrane matrix to block pores from within. Pore clogging (fouling occurs inside the pore reducing water production) may be occurring along with pore blocking (fouling on the membrane surface).
- Evidence suggested that in addition to surface coverage (reversible fouling), pore blockage and/or pore constriction (potentially irreversible fouling) is occurring during MF filtration using PP membranes.
- MF fouling may be principally influenced by other factors besides cake formation by deposited microparticulates (bacteria).
- Protein and carbohydrate ATR/FTIR bands were equally represented in both STW and FSTW, which provides evidence that primary MF fouling may be the result of mostly biological detritus as opposed to whole bacteria and particles larger than 0.2 µm.
- Dissolved carbohydrates strongly adhered to the PP membrane surfaces.
- Carbohydrates remaining in solution after removal of bacteria strongly adhered to the PP membrane surfaces.
- Phospholipid fatty acids (PFLAs) in the feedwater fouled PP MF membranes. Phospholipids were removed from the membrane surface with polar organic solvents like ethanol.
- Ethanol worked well to remove DOM fouling from PP membrane surfaces.

- DOM fouling occured rapidly when the feedwater contacted the membrane surface with no feed pressure applied. In comparison, microparticulate cake formation required a feed pressure to develop fouling in the MF membrane.

Classical models of MF cake fouling have suggested the accumulation of particles close to the membrane surface cover membrane pores, resulting in membrane flux reduction. The implication from this work was that there are two mechanisms of MF fouling: 1) the classical MF cake formation, which may result in minor reduction of hydraulic conductivity, and 2) microbial deposition of cell residue (proteins, carbohydrates and phopholipids) and nanoparticulates (e.g. liposomes) which is responsible for the majority of the observed fouling. The cake layer (bacterial and large particulate layer) is easily removed with regular backwashing (air sparging). Microbial residues such as DOM and nanoparticulates (with dimensions smaller that 0.2 µm) may be more difficult to remove with regular backwashing. The presence of organic materials adsorbed at the membrane surface may have been responsible for a large part of the flux reduction as seen in the difference between the STW and FSTW flux decay curves. This form of fouling occurs simultaneously with "cake" formation but can also occur without transmembrane pressure (through diffusion) which may eventually become irreversible. Makdissy et.al, 2004, indicated that aceteamide, polysaccharides, amino sugars and other cell membrane fragments may be irreversibly bound to membrane surfaces and resist chemical cleaning. AFM, ATR/FTIR and MF fouling experiments (AMICON test unit) suggested that in addition to reversible fouling (MF cake formation), pore blockage and/or pore plugging (potentially irreversible fouling) may be occurring during the filtration of feedwaters containing DOM and nanoparticulates. As indicated by others (Makdissy et.al., 2004, Howe et.al. 2002, Lim et.al, 2003, and Howe et.al, 2002,) fouling properties of a given DOM constituent will depend on the nature and complexity of the organic matrix.

The original test plan proposed to use additional feedwaters donated by other agencies: Metropolitan Water District of Southern California (surface water), University of California, Riverside (agricultural drainage water) and Alameda County Water District (conventionally treated secondary wastewater). However due to time and staffing shortages, only secondary

treated wastewater (STW) from OCWD was used in the study. The budget was adjusted (reduced) to compensate for experiments using OCWD STW only.

5.2 Recommendations

The current MF membrane cleaning practices employed by water agencies concentrate on classical MF cake fouling using backwashing and chemical cleaning agents (like Memclean C) that dislodge bacteria accumulated at the membrane surface. They are not aimed specifically at membrane fouling caused by dissolved organic material (phospholipid fatty acids, proteins and carbohydrates) and nanoparticulates. The presence of DOM adsorbed at the membrane surface may be responsible for a large part of the flux reduction as seen in MF performance. The results from this study suggest water agency professionals need to seriously consider this alternative MF fouling phenomenon and reevaluate the current cleaning practices to specifically target biological detritus. The current cleaning methods may in some ways be increasing the rate of fouling by extraction of the lipids from whole bacteria in the cake that subsequently may be transported and deposited on the MF membrane surface. Therefore, additional research characterizing the DOM and nanoparticulates is needed. Testing other feedwater sources, as proposed in the original proposal, will also help in further understanding the fouling phenomenon. The chemical make up of the feedwater influences the type and extent of fouling occurring at the membrane surface. Cleaning agents specific for phospholipids, proteins and carbohydrates should be further investigated. In addition, modification of membrane polymers to reduce adsorption of biological detritus is desirable. Implementation of improved methods of foulant removal and improvement of hydraulic conductivity in MF membranes will reduce operating costs and prolong membrane lifetime.

5.3 Benefits to California

It is increasingly more difficult to ensure reliable and adequate water supplies due to environmental constraints and rapid population growth. Southern California being a semi-arid region is prone to prolonged droughts and must increase its conservation through water recycling, eliminating groundwater contamination, researching new technologies, and developing alternative water sources.

California relies on many means to enhance the operations and cost effectiveness of water reuse. Using membrane processes such as microfiltration and reverse osmosis greatly benefits Southern California. Membrane processes offer advantages over conventional treatment processes in that they reduce the number of unit processes in the treatment system for clarification and disinfections and increase the potential for process automation and plant compactness. With MF pretreatment becoming the mainstream RO pretreatment technology, it is critical that the MF fouling be effectively managed and controlled. Understanding the fundamental principles of MF fouling during water reuse leads to more efficient MF operations, increases the reliability of the process and reducing the cost of the product water.

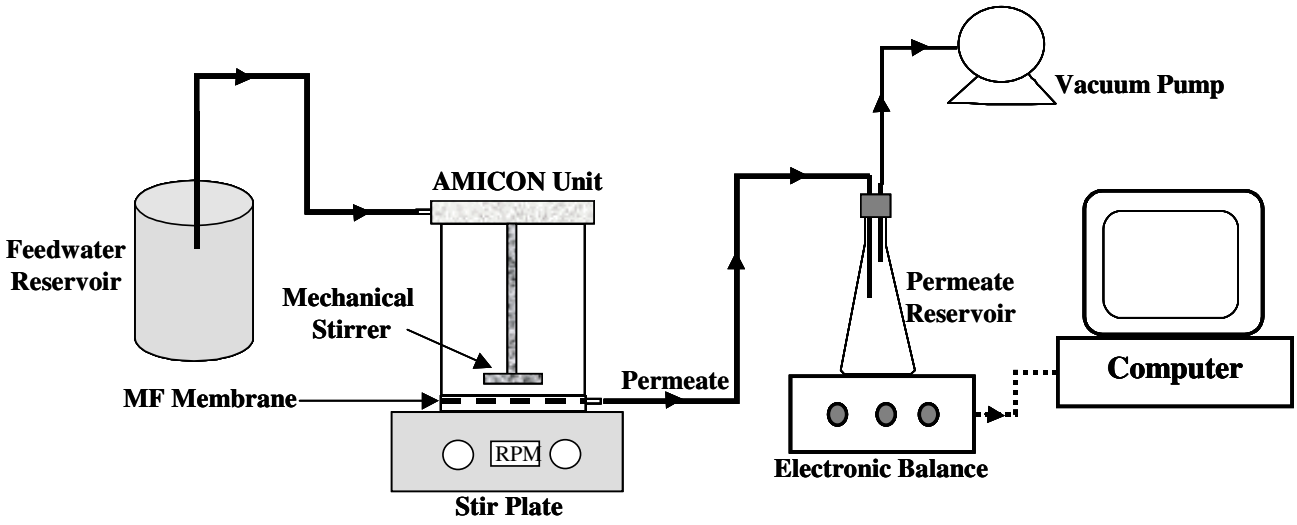


Figure 1. Schematic Diagram of Experimental Microfiltration System (AMICON Unit).

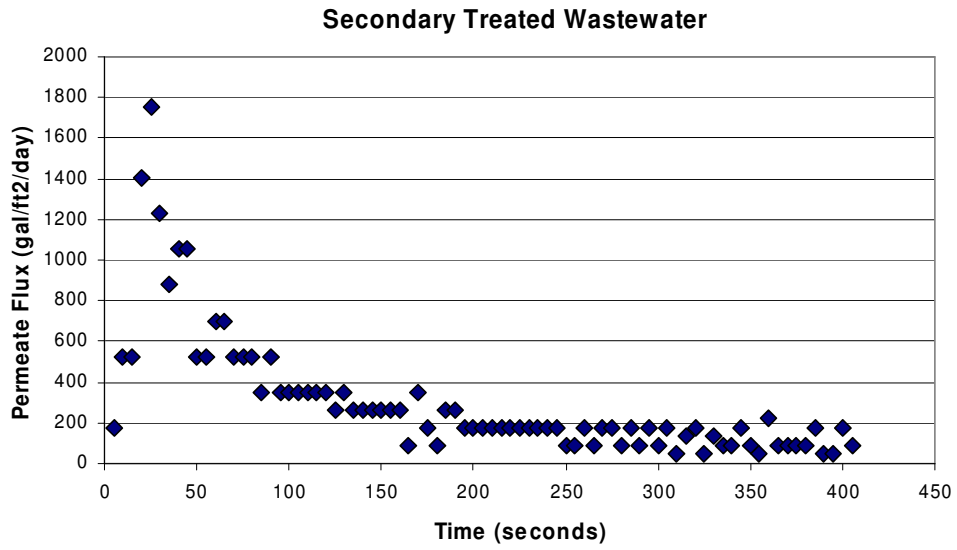


Figure 2: PP Membrane Permeate Flux Using Secondary Treated Wastewater. Flux decreased within seconds of STW introduction to the system.

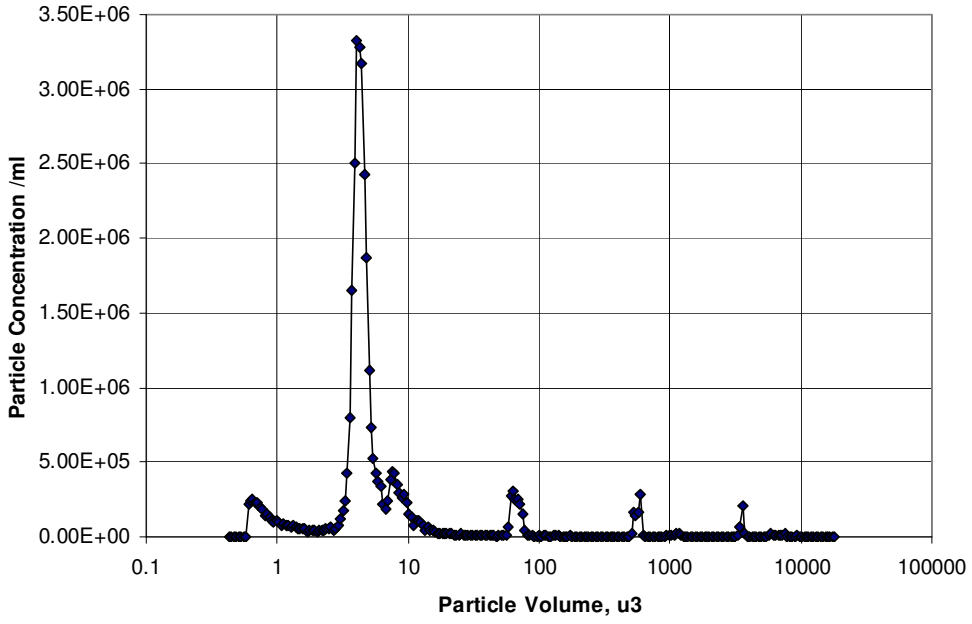
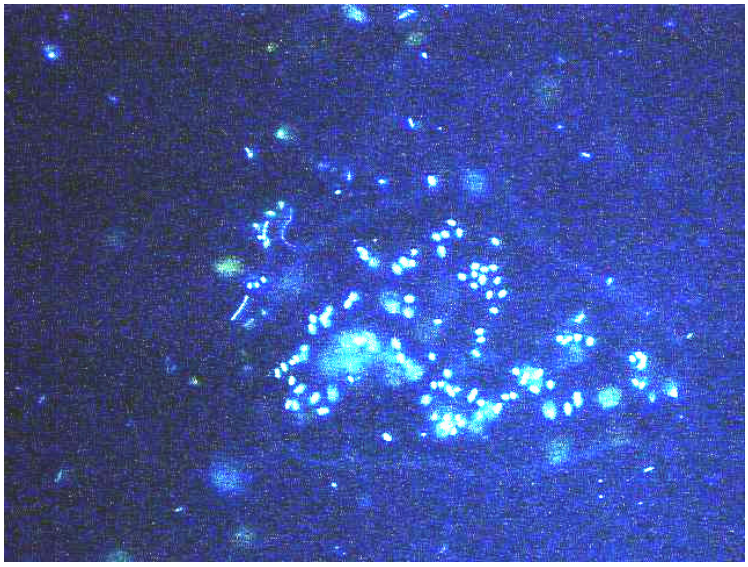
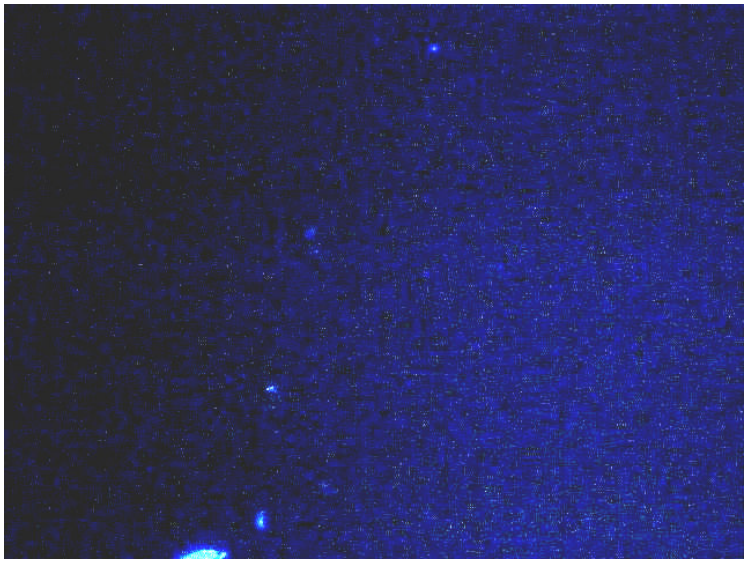


Figure 3: Particle Analysis of Material Disloged from MF Cake Formed by Microfiltration of Secondary Treated Wastewater. Total particle concentration = 3.51 x 10^7 μ^3/mL, total particle volume = 3.20 x 10^9 μ^3/mL. Peaks between 0.5 and 10 μ^3 represent microparticulates (bacteria).



A) STW



B) Filtered STW through 0.2 µm = FSTW

Figure 4. DAPI Stained STW and FSTW Feedwaters Nucleopore Black Membrane. A) STW feedwater contains bacteria and particles, B) FSTW – (bacteria and microparticulates >0.2 µm) were removed during the filtration process.

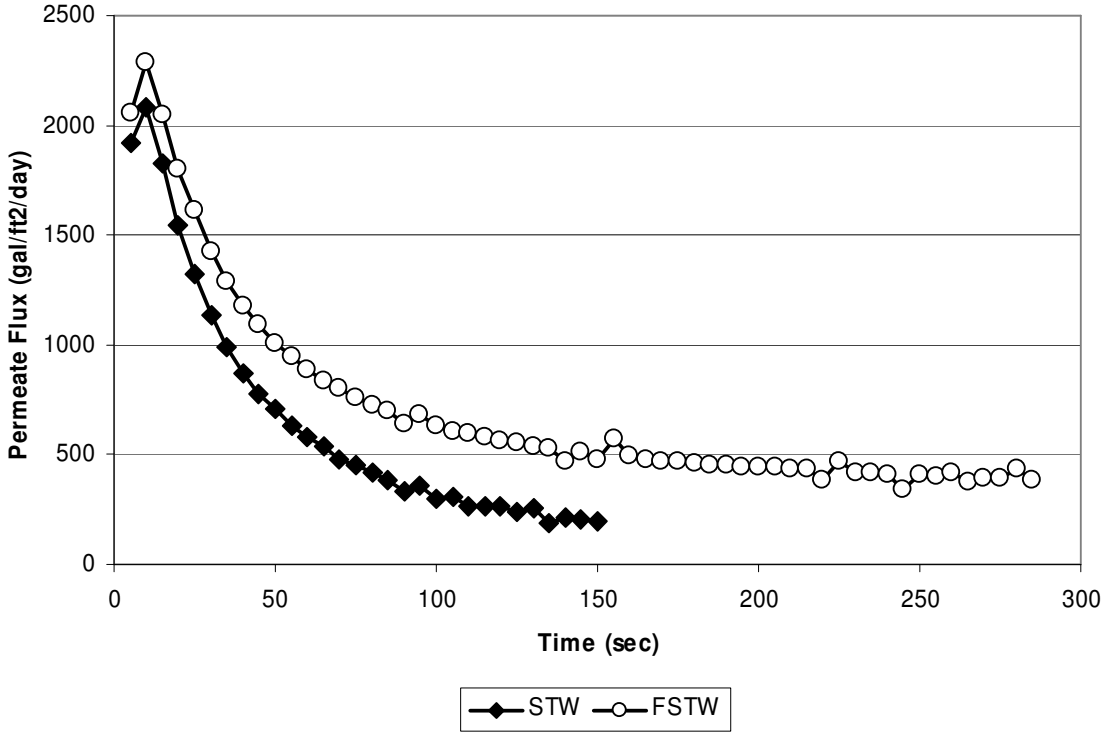


Figure 5. PP Membrane Fouling Using STW and FSTW. Both source waters fouled the membrane; the difference between the curves is presumed to be due to bacterial (microparticulate cake formation) that occurs with STW and not with FSTW.

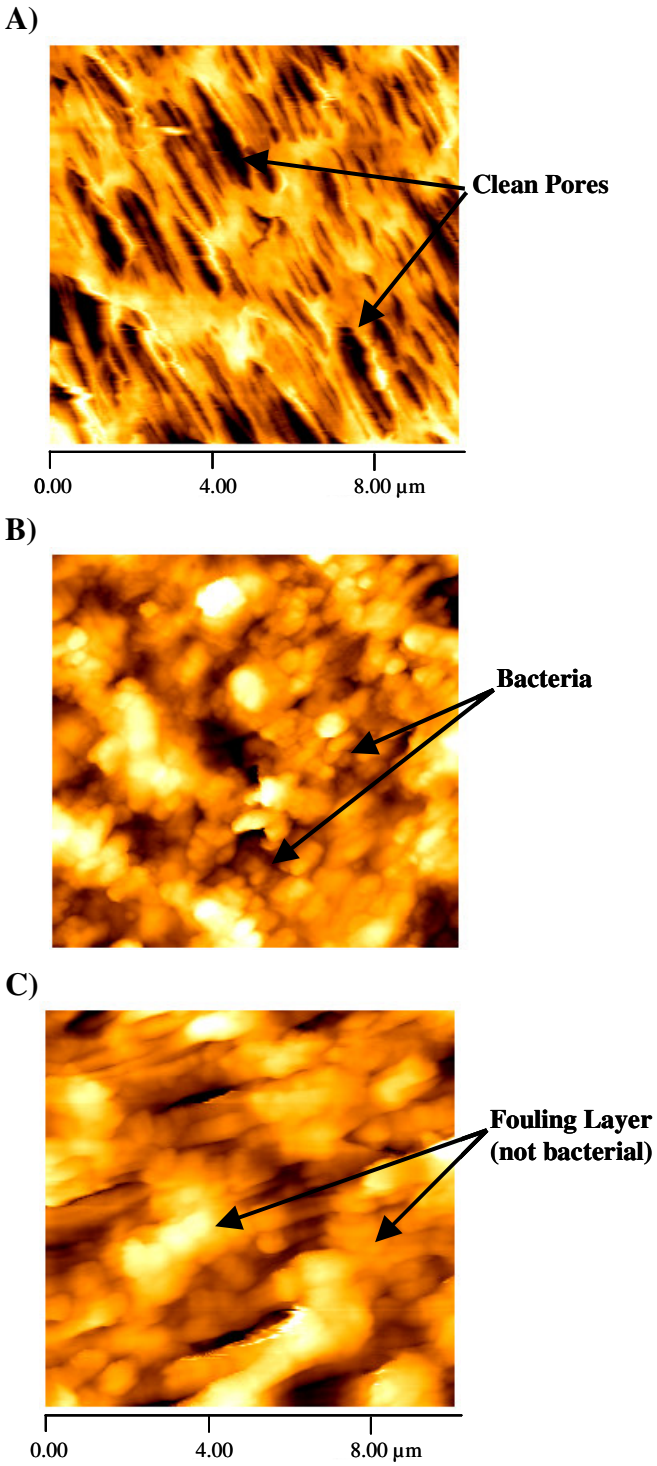


Figure 6. Non-contact AFM, Topographic Images of PP Membrane. A) Clean PP membrane – pores are clean and open, B) STW fouled PP membrane – pores are covered by a fouling layer consisting of bacteria, microparticulates, nanoparticulates and DOM, C) FSTW fouled PP membrane – pores are covered with fouling layer fromed from only nanoparticulates and DOM, which can be seen inside as well outside the pores.

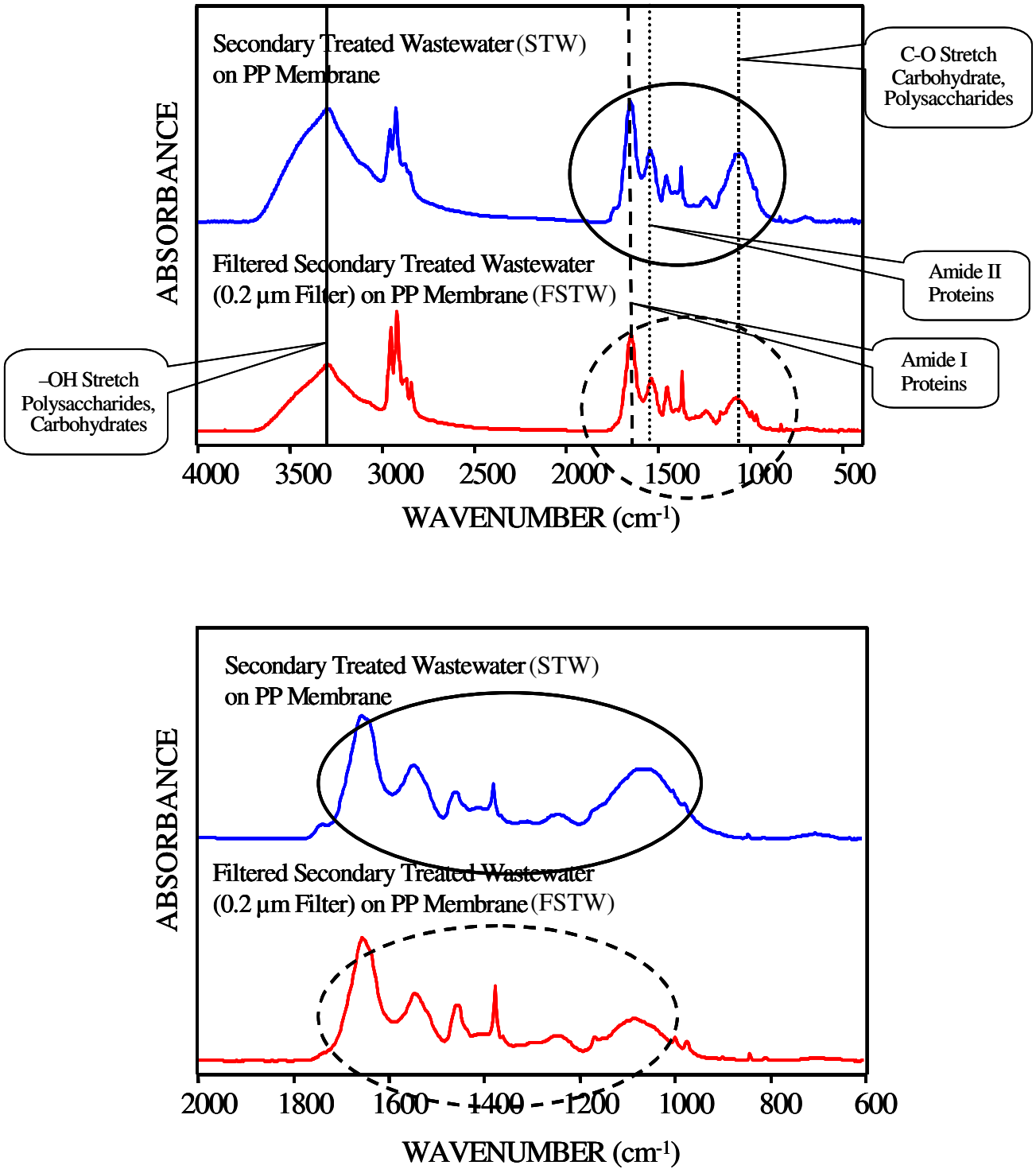


Figure 7. ATR/FTIR Spectra of STW and FSTW fouled PP membranes. Profiles for each water type are similar, each contain carbohydrate and protein bands. Both STW and FSTW waters cause MF fouling.

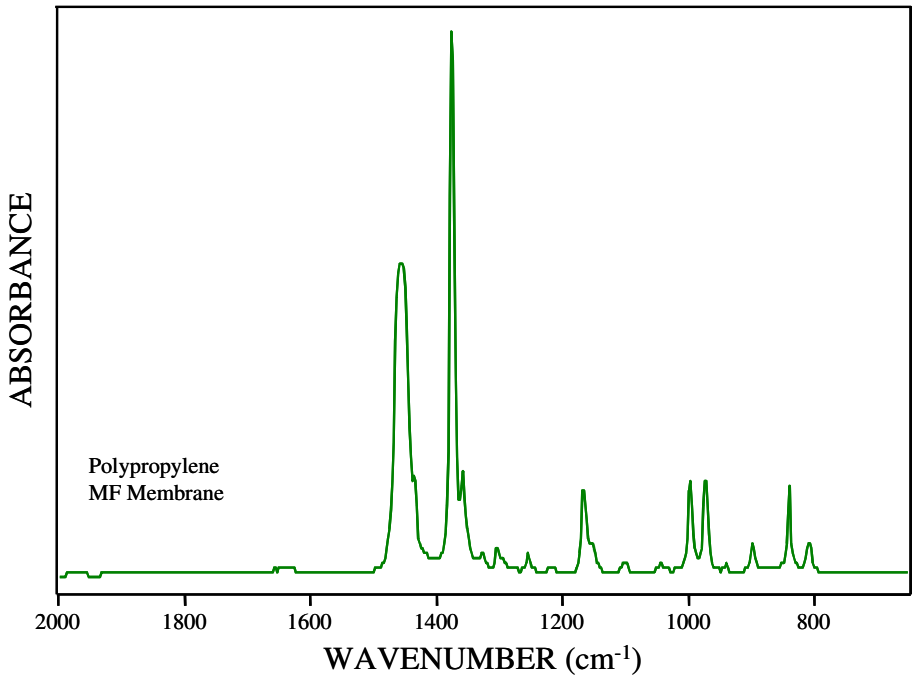


Figure 8. ATR/FTIR Spectra of Clean PP Membrane.

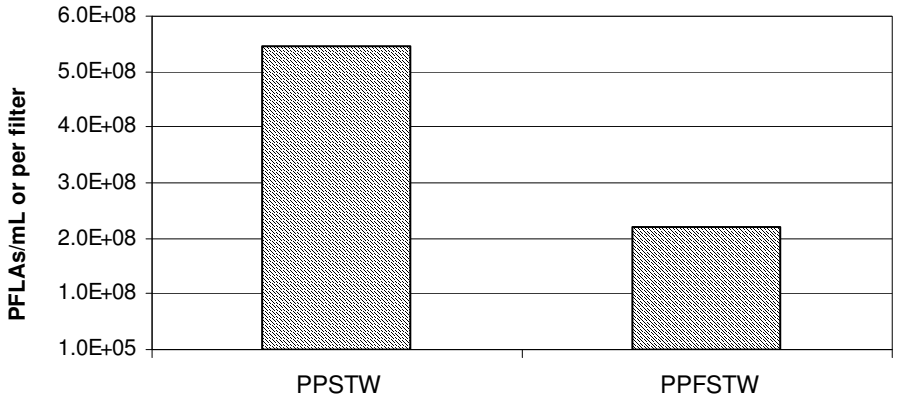


Figure 9. Total Phospholipids Present in STW and FSTW Fouled Membranes. PPSTW bar represents the total PFLAs (microbial plus nanoparticulate DOM) deposited on the membrane surface. PPFSTW bar represents only the deposition phopholipids present in liposomes or as DOM, since all microparticulates (bacteria) were removed by filtration through 0.2 µm filter.

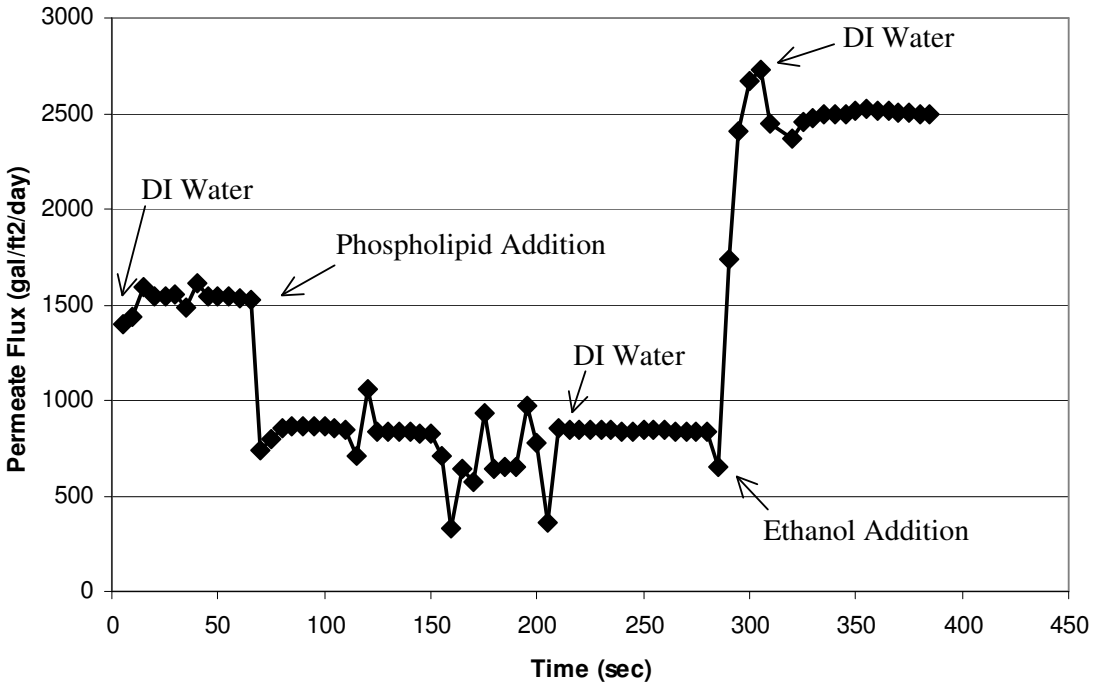
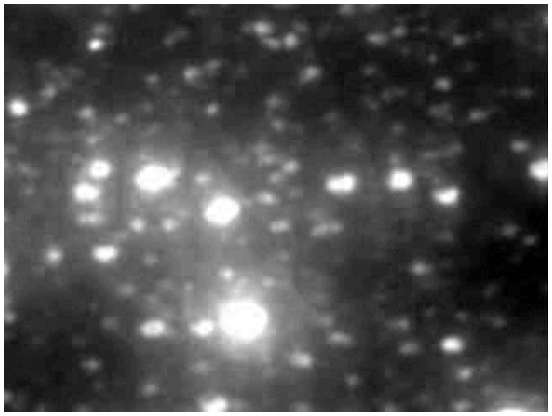


Figure 10. Phospholipid on PP Membrane.

Phospholipid addition causes decrease in permeate flux. Ethanol can reverse phospholipid fouling.



A)

B)

C)

Figure 11. PP Membrane Exposed to PTEDSB. A) PP membrane feedwater surface fouled with 1.0 µg/mL PTEDSB, B) product side of PP membrane exposed to PTEDSB, C) PTEDSB treated PP membrane feedwater surface after ethanol wash**.**

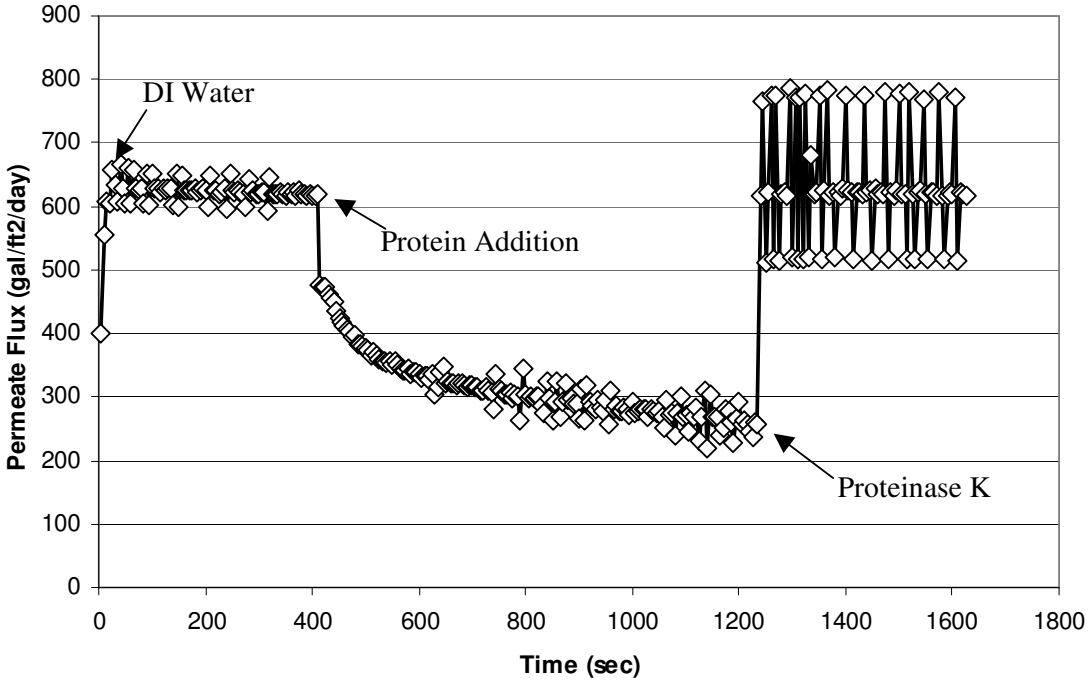


Figure 12. Effect of Protein on PP Membrane Permeate Flux. Soon as gelatin protein was introduced to the system membrane flux started to decline. Enzymatic digestion of protein using Proteinase K returned the membrane to it original flux.

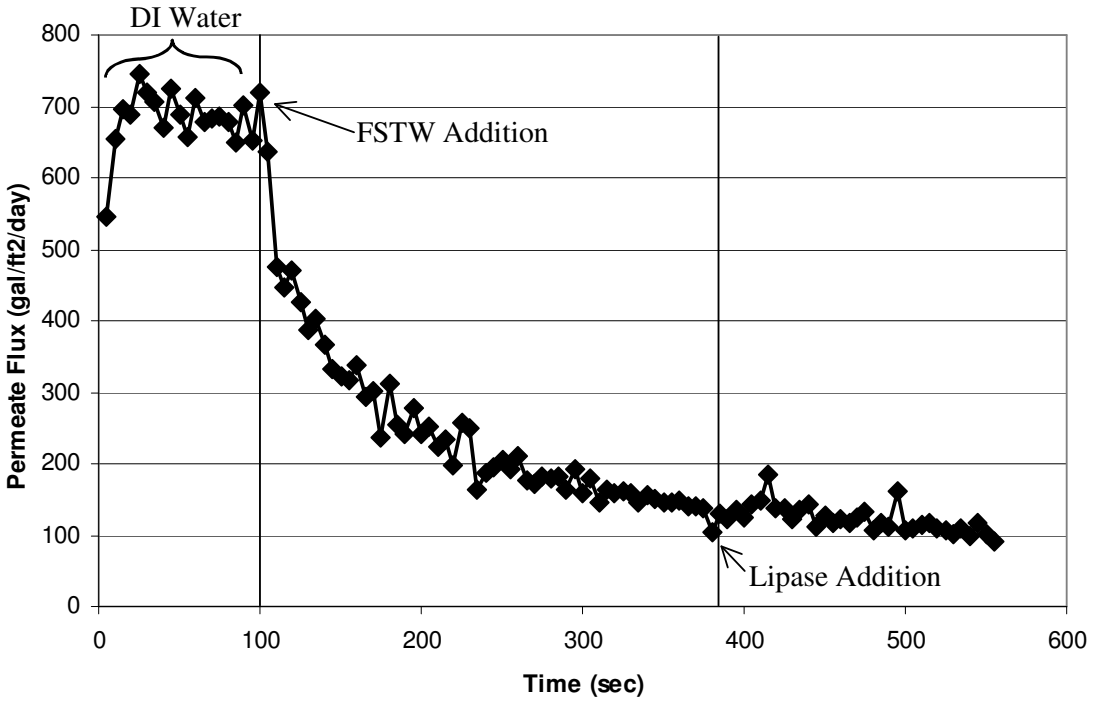


Figure 13. Effect of Lipase on FSTW Fouling on PP Membrane. PP membrane was fouled with FSTW feedwater. Lipids being a major component of the feedwater it was anticipated that lipase could restore membrane flux. Lipase alone did not restore membrane flux of FSTW fouled membrane.

A)

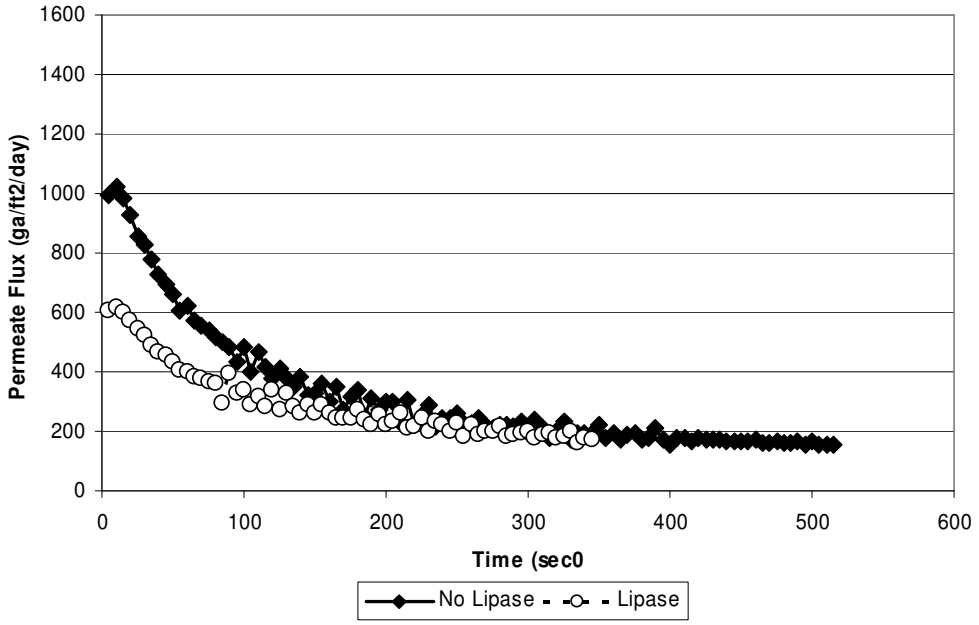


Figure 14. Effect of Lipase Pretreatment on FSTW Fouling. In this experiment, the lipase treated membrane started out at a lower flux but the fouling rate was slower for the lipase pretreated membrane, indicating that lipase may be fouling the membrane surface.

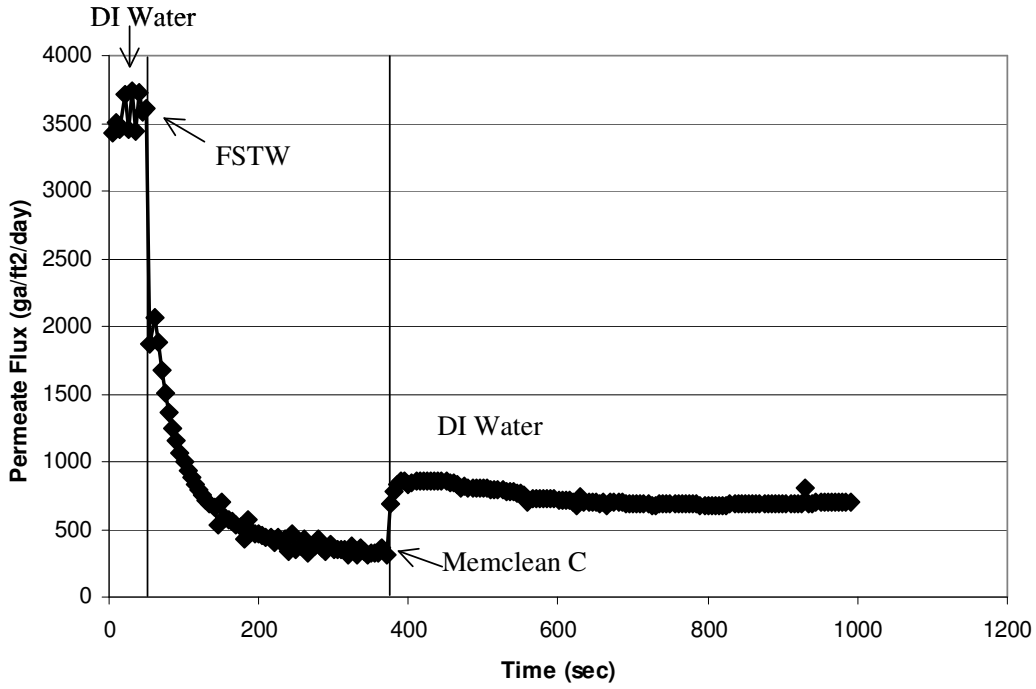
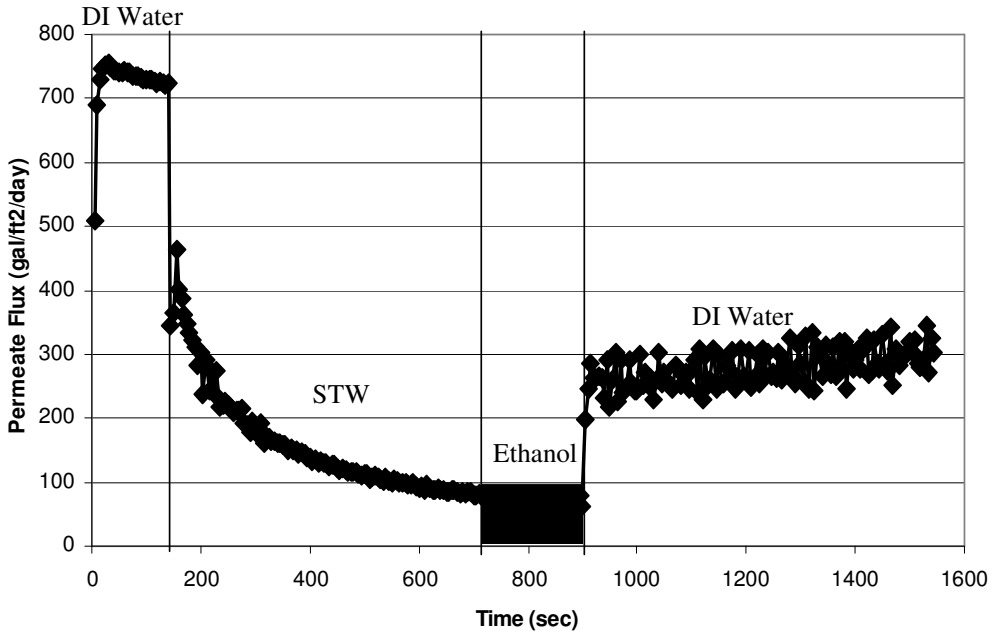


Figure 15. FSTW Fouled PP Membrane Cleaned with Memclean C. Membrane flux was partially restored but not to its original state.

STW Fouled Membrane



FSTW FOULED MEMBRANE

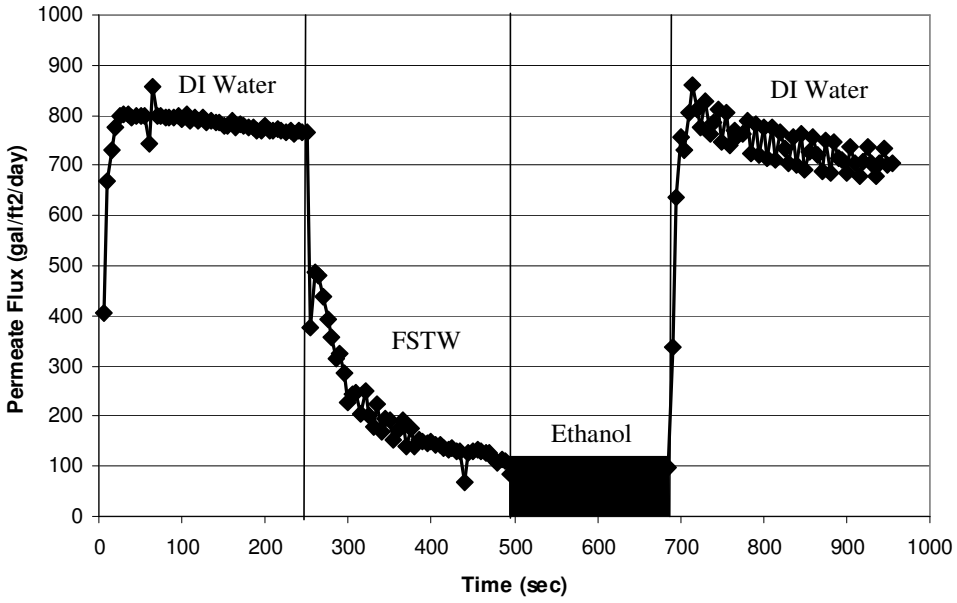


Figure 16. PP Membrane Fouling Reversed with 100 % Ethanol. Ethanol treatment recovered both STW and FSTW fouled membranes; FSTW recovered to original level, but STW did not.

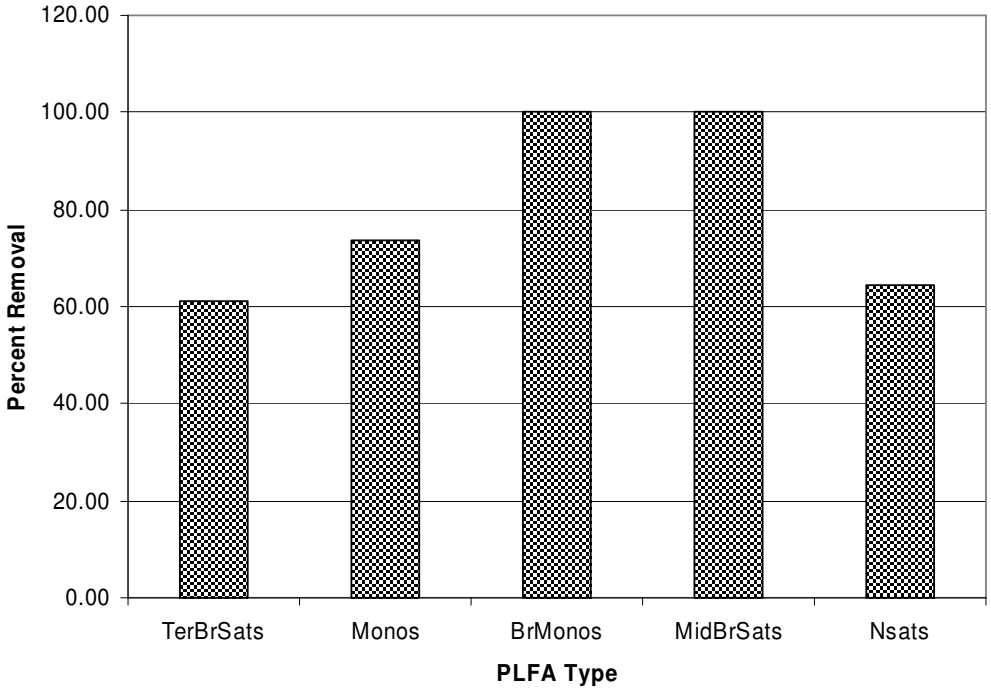


Figure 17. Percent Removal of PFLAs from a FSTW Fouled Membrane Using 100% Ethanol. 61% of TerBrSats, 73% of Monos, 100% or BrMonos and MiBrSats, and 64% of Nsats phospholids were removed from the fouled FSTW membrane using ethanol. Ethanol removed over 50% of all phospholipids identified to be present on FSTW fouled MF membrane.

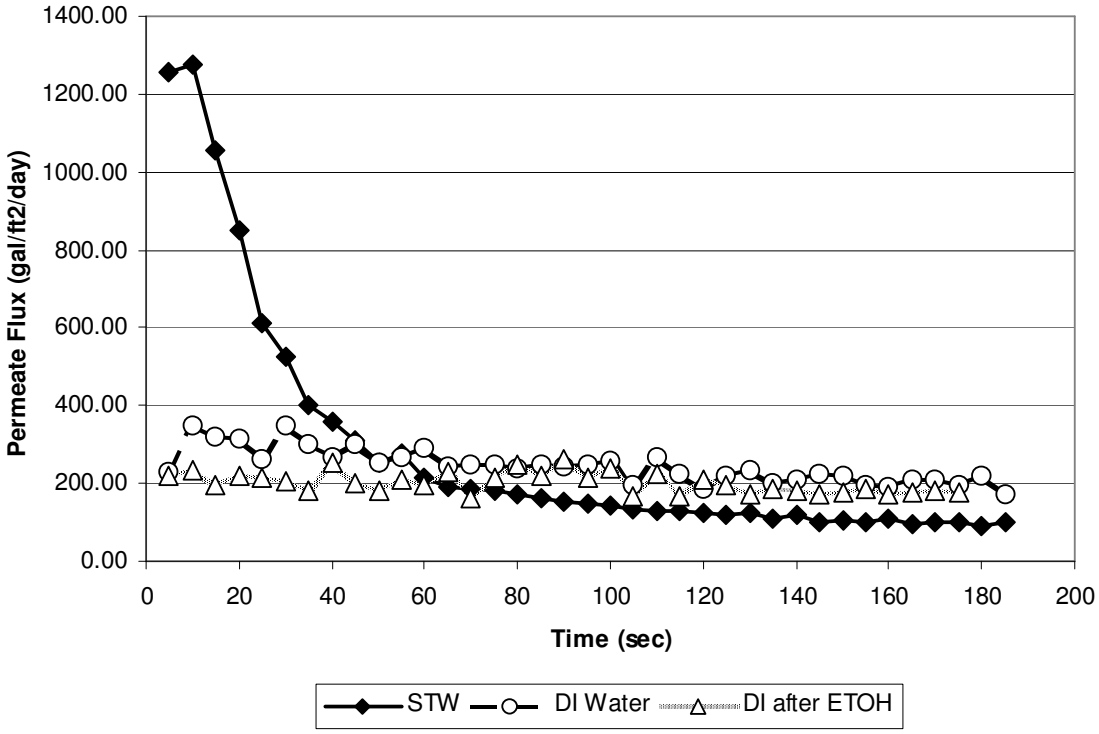


Figure 18. PP Membrane Performance After 24 hrours of Soaking in STW. Flux did not recover as seen in previous tests. Membrane fouling became irreversible even with ethanol.

Table 1. Total Proteins and Carbohydrates. Protein assay was performed two times on different days. Fluctuations in microparticulates, DOM and nanoparticulates in STW occured from day to day.

Sample	µg Protein/mL (Test 1, 081904)	µg Protein/mL (Test 2, 011905)	µg Carbohydrate/mL
STW	19.41	40.00	5.60
FSTW	22.55	34.34	3.60
FSTW Permeate	12.35	36.52	1.04

Table 2. Total Proteins and Carbohydrates Deposited on PP Membrane in AMICON Unit Assay During MF of FSTW.

	µg Protein/cm^2	µg Carbohydrate/cm^2
FSTW Fouled Membrane	8.08 $^{+}$/- 2.12	26.61 $^{+}$/- 2.35

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Glossary

µm	Micron
AFM	Atomic Force Microscopy
ATR/FTIR	Attenuated Total Reflection Fourier Transform Infrared Spectrometry
BrMonos	Branched monenoics
C	Celsius
CIP	Clean-in-place
cm^2	Centimeter squared
DAPI	4,6-diamino-2-phenylindole
DNA	Deoxyribonucleic acid
DOM	Dissolved Organic Matter
FSTW	Filtered secondary treated wastewater
IF	Infrared
IRE	Internal reflection element
MF	Microfiltration
MGD	Million gallons per day
MiBrStats	Mid chain branched saturates
mL	Milliliter
Mm	Millimeter
Monos	Monenoics
MWD	Metropolitan Water District of Southern California
NC-AFM	Non-contact atomic force microscopy
Nm	nanometer
NOM	Nanoparticulate organic material
NPM	Sodium phosphate magnesium buffer
Nsats	Normal saturates
O.D.	Optical density
OCWD	Orange County Water District
oz-in	Ounce per inch
PFLA	Phospholipid fatty acid
pH	
PP	Polypropylene
psi	Pounds per square inch
PTEDSB	Phosphatidylethanolamine, dipalmitoyl-sulforhordamine B
RO	Reverse Osmosis
rpm	Revolutions per minute
sRNA	
STW	Secondary treated wastewater
TerBrSats	Terminally branched saturates

Appendix 1. Sodium Phosphate Magnesium Buffer.

NPM Buffer

1 mM NaH_2PO_4
10 mM $MgCl_2$

pH 7.0