



Arsenic Water Technology Partnership

A Novel Hybrid Forward Osmosis Process for Drinking Water Augmentation using Impaired Water and Saline Water Sources



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A Novel Hybrid Forward Osmosis Process for Drinking Water Augmentation using Impaired Water and Saline Water Sources

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CONTENTS

TABLES	vii
FIGURES	ix
FOREWORD	xiii
ACKNOWLEDGMENTS	xv
EXECUTIVE SUMMARY	xvii
CHAPTER 1 INTRODUCTION AND THEORY	1
Introduction.....	1
Water Reuse	1
Desalination	1
The FO/RO Hybrid Process	2
Theory	3
Energy Demand in Water Treatment Processes.....	3
Osmotically Driven Membrane Processes	4
Flux-Pressure Curves	7
Membranes for Forward Osmosis.....	8
Concentration Polarization.....	8
Water Quality.....	10
Membrane Fouling.....	11
Project Objectives	12
CHAPTER 2 MATERIALS AND METHODS	13
Bench-Scale Experiments	13
Forward Osmosis Experiments with Impaired Water Feed.....	19
Pilot Scale Experiments	19
Sampling	22
Analytical Methods	23
CHAPTER 3 RESULTS AND DISCUSSION.....	27
Water Flux	27
Pure Water Permeability	27
Effect of Feed Water Quality on Water Flux.....	29
Forward Osmosis Membrane Fouling	30
Effect of Feed Water Quality on Membrane Fouling	33
Solute Transport in Forward Osmosis and the Combined FO/RO Process	36
Inorganic Solute Transport in the FO/RO System.....	36
Organic Solute Transport in the FO/RO System	40
Economic Feasibility	44

CHAPTER 4 CONCLUSIONS AND RECOMMENDATIONS	49
Conclusions.....	49
Recommendations.....	50
APPENDIX A WATER FLUX AT VARIOUS DRAW SOLUTION CONCENTRATIONS AND SEVERAL FEED SOLUTIONS	51
APPENDIX B MICROPOLLUTANT CONCENTRATION IN FEED, DRAW SOLUTION, AND PERMEATE STREAMS	55
REFERENCES	59
ABBREVIATIONS	63

TABLES

Table 2.1 Summary of experiments conducted showing combinations of draw solution concentrations and feed water types tested on bench and pilot scales	13
Table 2.2 Instant Ocean synthetic sea salt composition at 35 g/L concentration	15
Table 2.3 Forward and reverse osmosis membrane properties.....	16
Table 2.4 Pilot-scale RO sub-system operating parameters	21
Table 2.5 Summary of average properties of impaired water streams used as feed solutions in pilot scale experiments at DWRP	21
Table 2.6 Properties of micropollutants studied (Kimura et al. 2003, Drewes, Bellona et al. 2005a).....	24
Table 3.1 Results from bench-scale experiments using DI water as a feed solution and increasing concentrations of sea salt draw solution. Feed and draw solution flow rates were 1.4 L/min.....	28
Table 3.2 Reverse ion diffusion for bench-scale experiment with 35 g/L sea salt draw solution and deionized water feed solution. Experiment was conducted at $19\pm0.1^{\circ}\text{C}$ and 1.4 L/min feed and draw solution flow rates (Note that mass values are for the entire 12 L feed solution loop).....	38
Table 3.3 Ammonia and nitrate rejection by the forward osmosis and RO membranes and combined system rejection for the pilot-scale FO/RO experiment with 35 g/L draw solution concentration and secondary effluent feed solution. The temperature of the feed and draw solutions were $22\pm0.5^{\circ}\text{C}$ and feed and draw solution flow rates were 2.4 L/min.....	40
Table 3.4 Rejection of UV absorbing compounds during pilot-scale forward osmosis experiment with 35 g/L draw solution concentration and secondary effluent feed by forward osmosis membrane, RO membrane, and total system. The temperature of the feed and draw solutions was $22\pm0.5^{\circ}\text{C}$ and the feed and draw solution flow rates were 2.4 L/min.....	41
Table 3.5 Concentration of organic solutes after eight days of operation for pilot-scale forward osmosis experiment with 35 g/L draw solution concentration and secondary effluent feed. The temperature of the feed and draw solutions was $22\pm0.5^{\circ}\text{C}$ and the feed and draw solution flow rates were 2.4 L/min (n.d. – not detected)	42

Table 3.6 Rejection of organic solutes during; bench-scale 35 g/L draw solution with deionized water feed by forward osmosis membrane, and pilot-scale forward osmosis experiment with 35 g/L draw solution concentration and secondary effluent feed by forward osmosis membrane, RO membrane, and total system. The temperature of the feed and draw solutions was 22 ± 0.5 °C and the feed and draw solution flow rates were 2.4 L/min.	42
Table 3.7 Operational characteristics for modeling of FO/RO hybrid membrane system for reduction of energy demand during desalination.....	45

FIGURES

Figure 1.1 A schematic drawing of the novel hybrid FO/RO process for water augmentation.....	3
Figure 1.2 Osmotically-driven membrane processes. Feed solution on the left has lower osmotic pressure and the brine solution on the right is a hypertonic solution having high osmotic pressure.....	5
Figure 1.3 Changes in the water flux/pressure curves for feed solution dilution and/or increased membrane permeability. (a) osmotic process regions; FO, PRO, and RO, (b) effect of dilution of brine stream on flux curve, (c) effect of increased membrane permeability on flux curve, and (d) combined effects of diluted brine stream and increased membrane permeability.....	7
Figure 1.4 Areas of concentration polarization during forward osmosis.....	9
Figure 2.1 Schematic drawing of the closed-loop bench-scale forward osmosis experimental setup with the draw solution loop in orange, and the feed solution loop in blue.....	14
Figure 2.2 Feed and draw solution spacers in the bench-scale forward osmosis membrane cell (with membrane installed).....	16
Figure 2.3 Environmental scanning electron microscope (ESEM) micrograph of the HTI CTA forward osmosis membrane with the dense, non-porous, side up	17
Figure 2.4 Control panel of the SCADA system used to maintain draw solution concentration and temperature, and record experimental data	18
Figure 2.5 Flow diagram of the RO sub-system utilizing three stage membrane array with the draw solution loop in orange and the permeate loop in blue. Conductivity (C), pressure (P), and flow rate (F) gauges are signified by circles.....	20
Figure 2.6 Steps for GC/MS and HPLC analysis of organic micropollutants at trace concentrations in aqueous solutions. Adapted from (Oldham 2008).....	25
Figure 3.1 Water flux as a function of draw solution concentration during bench-scale benchmark experiments. Experiments were conducted with DI water feed, feed and draw solution temperatures of 19 ± 0.1 °C, and feed and draw solution flow rates of 1.4 L/min.....	28

Figure 3.2 Water flux as a function of draw solution concentration for short-term bench-scale forward osmosis experiments with DI water, secondary effluent, nitrified effluent, or South Platte River water feeds. Experiments were conducted with feed and draw solution temperatures of 19 ± 0.1 °C and feed and draw solution flow rates of 1.4 L/min.....	29
Figure 3.3 Specific water flux as a function of draw solution concentration for short-term bench-scale forward osmosis experiments with deionized water feed, secondary effluent water feed, nitrified effluent water feed, or South Platte River water feed. Experiments were conducted at feed and draw solution temperatures of 19 ± 0.1 °C and feed and draw solution flow rates of 1.4 L/min	30
Figure 3.4 Water flux as a function of time during bench-scale experiments of different draw solution concentrations and secondary effluent feed solution. Experiments were conducted with feed and draw solution temperatures of 19 ± 0.1 °C and feed and draw solution flow rates of 1.4 L/min.....	31
Figure 3.5 Water flux as a function of time during the pilot-scale forward osmosis experiment with 35 g/L sea salt draw solution and secondary effluent feed solution. PC indicates physical cleaning and CC indicates chemical cleaning. The experiment was conducted with feed and draw solution temperatures of 22 ± 0.5 °C and flux data was corrected to 19 °C.....	32
Figure 3.6 Pilot-scale forward osmosis membrane cell (a) before experiment and (b) after seven-days of operation (before chemical cleaning). Experiment conducted with 35 g/L sea salt draw solution and secondary effluent feed solution. Feed and draw solution temperatures were 22 ± 0.5 °C. Feed and draw solution flow rates were 2.4 L/min. Nitrile rubber strips were used as spacers in the draw solution channel. No spacer was used in the feed solution channel	33
Figure 3.7 Water flux as a function of time for pilot-scale forward osmosis experiment with the feed channel of the membrane cell facing down. Experiment conducted with 35 g/L draw solution concentration and secondary effluent feed solution. Feed and draw solution temperatures were 22 ± 0.5 °C and flux data was corrected to 19 °C. Feed and draw solution flow rates were 2.4 L/min.....	34
Figure 3.8 Photograph showing the feed side of the inverted forward osmosis membrane cell after three days of operation with no cleaning (The feed channel of the membrane cell is under the membrane)	34

Figure 3.9 Water flux as a function of time for pilot-scale forward osmosis experiment with 20, 35, or 70 g/L sea salt draw solution and tertiary effluent feed solution. The experiment was conducted with feed and draw solution temperatures of 22 ± 0.5 °C and flux data was corrected to 19 °C. The feed solution channel is facing down.....	35
Figure 3.10 Reverse salt diffusion as a function of draw solution concentration for various feed and draw solutions during bench-scale forward osmosis experiments. Temperature of the feed and draw solution streams was 19 ± 0.1 °C, and feed and draw solution flow rates were 1.4 L/min.....	37
Figure 3.11 Ammonia concentrations as a function of time in the feed, draw solution, and RO permeate during pilot-scale forward osmosis experiment with 35 g/L sea salt draw solution and secondary effluent feed. The temperature of the feed and draw solutions was 22 ± 0.5 °C and the feed and draw solution flow rates were 2.4 L/min.	39
Figure 3.12 Nitrate concentrations as a function of time in the feed, draw solution and RO permeate streams during pilot-scale forward osmosis experiment with 35 g/L sea salt draw solution concentration and secondary effluent feed solution.	39
Figure 3.13 UV absorbance at 254 nm as a function of time in the feed, draw solution, and permeate streams for pilot-scale forward osmosis experiment with 35 g/L draw solution concentration and secondary effluent feed water.....	41
Figure 3.14 Rejection of micropollutants during pilot-scale forward osmosis experiment with 35 g/L draw solution concentration and secondary effluent feed by forward osmosis membrane, RO membrane, and total system. The temperature of the feed and draw solutions was 22 ± 0.5 °C and the feed and draw solution flow rates were 2.4 L/min.	43
Figure 3.15 Economic feasibility model schematic.....	45
Figure 3.16 Return on investment ratio and cumulative cost as a function of impaired water stream recovery. Energy cost and impaired water flow rate are (a) \$0.10/kWh – 200 m ³ /day (b) \$0.20/kWh – 200 m ³ /day (c) \$0.30/kWh – 200 m ³ /day (d) \$0.20/kWh – 150 m ³ /day (e) \$0.20/kWh – 200 m ³ /day (f) \$0.20/kWh – 300 m ³ /day.	47
Figure 3.17 Savings of forward osmosis over RO expansion to increase the capacity of an existing RO desalination plant and needed forward osmosis membrane area as a function of RO permeate production (above 100 m ³ /day).	48

FOREWORD

The Water Research Foundation is a nonprofit corporation that is dedicated to the implementation of a research effort to help utilities respond to regulatory requirements and traditional high-priority concerns of the drinking water community.

The Arsenic Water Technology Partnership (AWTP) program is a partnership between Water Research Foundation, Sandia National Laboratories (SNL) and WERC, a Consortium for Environmental Education and Technology Development at New Mexico State University that is funded by DOE and the Water Research Foundation. The goal of the program is to provide drinking water utilities, particularly those serving small and rural communities, with cost-effective solutions for complying with the new 10 ppb arsenic MCL. This goal is being met by accomplishing three tasks: 1) bench-scale research to minimize operating, energy and waste disposal costs; 2) demonstration of technologies in a range of water chemistries, geographic locales, and system sizes; and 3) cost effectiveness evaluations of these technologies and education, training, and technology transfer.

The AWTP program is designed to bring new and innovative technologies developed at the laboratory and bench-scale to full-scale implementation and to provide performance and economic information under actual operating conditions. Technology transfer of research and demonstration results will provide stakeholders with the information necessary to make sound decisions on cost-effective arsenic treatment.

The Foundation participates in the overall management of the program, helps to facilitate the program's oversight committees, and administer the laboratory/bench-scale studies. SNL conducts the pilot-scale demonstrations and WERC oversees the education, training, economic analysis, and outreach activities associated with this program.

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EXECUTIVE SUMMARY

INTRODUCTION

With dwindling supplies and a growing demand for fresh water, communities are increasingly motivated to recycle and reuse treated wastewater and/or desalinate seawater or brackish water. Seawater desalination with membrane treatment processes such as reverse osmosis and nanofiltration has become a common practice to supply the growing demand for water in areas with access to the ocean; however, the current methodologies for implementing these processes are energy-intensive and water recovery is often limited. In addition to energy concerns, membrane fouling, brine disposal, and environmental impacts are also critical aspects of desalination systems. Furthermore, in many coastal and inland areas, impaired waters and reclaimed wastewaters are often considered as new sources to alleviate short supplies of fresh water. However, negative public perception and recent concerns regarding the presence of organic micropollutants in recycled water have shed a negative light on potable reuse applications.

Forward osmosis (FO) is a membrane process that has been studied in recent years as novel technology for treatment of a wide variety of aqueous solutions. Forward osmosis utilizes the osmotic pressure differential across a semi-permeable membrane rather than hydraulic pressure differential (as in reverse osmosis) to extract clean water from impaired water. This results in concentration of a feed stream and dilution of a highly concentrated aqueous solution (referred to as the draw solution) that provides the driving force for separation in the process.

The focus of the current study was to investigate a forward osmosis – reverse osmosis hybrid process in which forward osmosis is being used to extract water from impaired aqueous solutions using seawater as a draw solution. By using this hybrid process, seawater can be diluted before desalination, hence reducing the energy cost of desalination, and simultaneously, contaminants present in the impaired water are prevented from migrating into the product water through two established barriers, the forward osmosis membrane and the reverse osmosis membrane.

RESEARCH OBJECTIVES

This study was funded to evaluate the technical and economic feasibilities of a forward osmosis and reverse osmosis hybrid process to co-treat saline water, such as seawater, and impaired water, such as secondary and tertiary treated wastewater or contaminated surface water. Reverse osmosis and nanofiltration membrane processes are commonly used for desalination of saline water and have been used since the late 1970s for advanced treatment of reclaimed water leading to indirect potable reuse. Yet, these processes are often energy intensive, very sensitive to membrane fouling, and the rejection of salts, nutrients, and organic micropollutants by many semi-permeable membranes is not complete. Thus, the main goal of the current study was to evaluate the performance and economics of the proposed hybrid process at both the bench- and pilot-scale. Specifically, this investigation focused on the following objectives:

1. Investigate the performance (e.g., water flux and solute and suspended solid rejections) and limitations of forward osmosis membranes for pretreatment of impaired/reclaimed water by examining the interactions between feed water quality

- (i.e., presence of particulate and dissolved constituents) and the forward osmosis membrane and the effect of operating conditions (i.e., brine concentration, hydraulics) on process performance
2. Investigate the performance of the combined forward osmosis pretreatment and reverse osmosis desalination hybrid system and specifically its effects on membrane fouling and overall solute rejection, with specific attention to organic micropollutants present in the impaired water, and
 3. Develop recommendations and cost estimates for a forward osmosis – reverse osmosis hybrid system for the simultaneous treatment of impaired and saline water.

APPROACH

This study was designed for a period of 12 months (January 2008 through December 2008) and was organized into three phases. The first phase consisted of comprehensive sets of bench-scale forward osmosis experiments. In that phase, a SCADA controlled forward osmosis system was designed and constructed that enabled precise control of experimental condition and data collection during the experiments. Forward osmosis experiments were conducted in the laboratory under various operating conditions with secondary and tertiary treated effluents and with river water from the South Platte River. In the second phase, a pilot-scale forward osmosis – reverse osmosis hybrid system was constructed, tested in the laboratory, and subsequently deployed at the Denver Water recycling plant. At this field site, the hybrid process was extensively tested with secondary effluent from the Denver Metro wastewater treatment plant and with tertiary effluent from Denver Water recycling plant while a synthetic sea salt mixture was used to mimic seawater. The final phase of the study involved development of an economic model to assist with evaluating the feasibility of the hybrid process under different operating conditions, system configuration, and material and energy costs.

CONCLUSIONS

Testing of the hybrid process was carried out on both bench- and pilot-scale systems and included characterization of water flux, membrane fouling propensity, solute transport across the forward osmosis and reverse osmosis membranes, and economic feasibility. Water flux was relatively low due to the weaker driving force induced by the seawater draw solution; approximately $5.6 \text{ L/m}^2\cdot\text{hr}$ were produced when draw solution concentration of 35 g/L sea salt was used. Additionally, specific flux, water flux normalized by osmotic pressure driving force, decreased at higher draw solution concentrations due to internal dilutive concentration polarization. Overall, feed water quality had a minimal effect on water flux through the forward osmosis membrane.

During short-term bench-scale batch experiments, minimal fouling of the forward osmosis membrane was observed. However, during the longer-term pilot-scale experiments fouling was more apparent. In the initial experiment, the forward osmosis membrane cell was configured with the feed channel on top of the membrane. Suspended solids were deposited on the membrane and contributed to moderate flux decline. On successive experiments, the forward osmosis membrane cell was inverted, so that the feed channel was oriented beneath the membrane. In this configuration, suspended solids settled away from the membrane, and water flux decline was minimal. Thus, configuration of the membrane cell has a substantial effect on

water flux decline due to fouling. Furthermore, physical and chemical cleaning of the forward osmosis membrane reversed water flux decline almost entirely.

To elucidate the effect of alternate feed water qualities, several experiments were conducted with tertiary treated effluent. Experiments with this alternate water showed water flux similar to other feed waters, but minimal water flux decline due to fouling.

Transport of solutes was studied at the pilot-scale, and the forward osmosis/reverse osmosis hybrid system successfully limited the flux of dissolved solids. Reverse diffusion of TDS through the forward osmosis membrane, while greater than through the RO membrane, was within the levels reported by other studies. Ammonia and nitrite were both rejected by the system in excess of 97 percent. Additionally, the select organic micropollutants studied were all well rejected by the system and most were undetectable in the RO permeate. Thus, the proposed hybrid system represents an effective multiple barrier approach to organic contaminant removal.

The data collected on the system were used to construct a mathematical model allowing an assessment of the economic feasibility of the process. The modeling results revealed that the process is feasible across a broad range of operating conditions. The forward osmosis process for energy reduction was economically feasible from 0 to almost 80 percent recovery of the impaired water source, significantly decreasing the cost of desalinated water.

Thus, the system was shown to be both economically and technically feasible over a broad range of operating conditions. Moreover, the cost of desalinated water can be substantially reduced with forward osmosis pretreatment, making desalination a more attractive alternative for utilities seeking to expand and diversify their source water portfolio into unconventional drinking water sources.

RECOMMENDATIONS

Forward osmosis is a simple and spontaneous process that was recently engineered and adapted to various water treatment applications. Specifically in the current project, it was successfully demonstrated that forward osmosis can be coupled with reverse osmosis processes to simultaneously protect the reverse osmosis membranes, recover purified water from a broad range of impaired waters, and to lower the energy required for desalination of seawater.

Due to the limited scope and funding of this study, only the feed (impaired water) side of the forward osmosis process was operated in an open loop, and the reverse osmosis system was operated in a closed loop, continuously reconcentrating the same seawater solution. Future work should be directed at testing the process at a larger scale and preferably at a coastal facility that can provide both seawater and impaired water (e.g., reclaimed water, runoff water, impaired river water, raw wastewater, etc.). In this demonstration-scale project, a large forward osmosis system should be tested that can be operated at high recovery and substantially diluted seawater (at least 50 percent dilution).

The forward osmosis hybrid concept that was tested in this study would be easily implementable in locations where the infrastructure provides a source of seawater and a source of impaired water at the same site/facility. Currently, not many coastal facilities in the U.S. can provide such infrastructure. It is recommended that future design and development of infrastructure in coastal locations will take into consideration hybrid processes like forward osmosis and reverse osmosis or pressure-retarded osmosis for harvesting of renewable chemical potential energy between seawater and any sources of impaired water.

Currently commercially available forward osmosis membranes are limited but already adequate for the tested application; yet, additional improvement can further enhance the efficiency of the hybrid process. Investment in development of forward osmosis membranes with higher solute rejection and higher water flux is strongly recommended. Furthermore, packaging of forward osmosis membrane modules is another area that must be further explored. Results in the current study demonstrated that membrane configuration plays a substantial role in preventing membrane fouling and maintaining process integrity and high performance.

CHAPTER 1

INTRODUCTION AND THEORY

INTRODUCTION

Increasing water demands and diminishing water supplies due to over allocation and contamination are forcing many water utilities to explore sustainable ways of producing water from unconventional water sources (Committee on Advancing Desalination Technology 2008). Two such options for augmenting water supply are water recycling and desalination. Non-potable water reuse is now widely accepted and potable water reuse is slowly gaining acceptance and will increasingly be applied in the future. However, potable water reuse creates a new set of challenges for the water treatment industry; most noticeably, the presence of organic micropollutants, such as pharmaceutical residues, personal care products, household chemicals, and endocrine disrupting chemicals (Kimura et al. 2004, Snyder et al. 2008).

Another unconventional source is saline water - either brackish groundwater or seawater. Some inland communities are now utilizing brackish water desalination technologies to augment their water resources by producing potable water from saline sources (Bond and Veerapaneni 2008), and seawater desalination is being rapidly implemented worldwide in many coastal areas to cope with increasing water demand (Khawaji, Kutubkhanah and Wie 2008). Most desalination processes, and especially membrane technologies such as reverse osmosis (RO) and nanofiltration (NF) are capable of producing high quality, drought resistant water supply, but most are energy intensive (Farooque et al. 2008).

Water Reuse

As compared to pristine water sources, the quality of reclaimed water is compromised, and although suitable for discharge into the environment, it is not fit for human consumption. Results from recent studies have shown that organic micropollutants at trace concentrations are not completely removed during wastewater treatment, and are constantly released into the environment (Kolpin et al. 2002, Clara et al. 2005, Oppenheimer, Stephenson and Burbano 2007, Snyder et al. 2008). The presence of micropollutants may pose a potential health risk to consumers and thus, recycled water requires high-level treatment to minimize human exposure in drinking water derived from recycled water.

A multiple barrier approach can be utilized for removal of various contaminants, utilizing both conventional and advanced water treatment processes. Common processes for removal of micropollutants include reverse osmosis, advanced oxidation processes, and adsorption to activated carbon (Barr 2007).

Desalination

Seawater and brackish water desalination have become common practices for augmentation of shrinking water supplies. From 2000 to 2004, the growth rate of installed desalination capacity grew at 7 percent per year to 35.6 million m³/day (Gleick, Cooley and Wolff 2006a). However, seawater desalination is still relatively limited to the Middle East, where

distillation is the preferred method of desalting. Brackish and river water desalination dominate the U.S. market, with seawater desalination being less than 10 percent of installed capacity.

Recent studies have shown that membrane desalination processes such as RO and NF are capable of rejecting the majority of organic micropollutants and producing high quality potable water from reclaimed water or from surface or ground water impacted by effluent from wastewater treatment plants (Drewes et al. 2005, Nghiem, Schafer and Elimelech 2005, Bellona and Drewes 2007, Bellona et al. 2008). Yet, public perception hinders the implementation of desalination of wastewater for potable reuse. However, providing multiple barriers to organic micropollutants may be increasing public trust and acceptance of potable reuse. Desalination is a proven technology that has been used for a few decades, but usually only in areas with inexpensive and abundant sources of energy (Thomas and Durham 2003). In order to enhance the sustainability of desalination, solutions must be found to decrease the cost, both monetarily and environmentally.

The FO/RO Hybrid Process

Forward osmosis is an engineered osmotically-driven membrane process that uses osmotic pressure of concentrated solutions, including seawater, to extract clean water from diluted solution. In a new approach investigated in this study, forward osmosis uses seawater or concentrated brackish water as a draw solution to extract clean water from impaired water streams. The driving force for water flux in forward osmosis is the difference in osmotic pressure between two water solutions, the saline water and the impaired water, and not hydrostatic pressure as in RO or NF. As such, the energy cost associated with forward osmosis is very low. The diluted seawater is then processed through an RO desalination system that provides high rejection of salts and dissolved contaminants that may have escaped the forward osmosis treatment, hence achieving a multi-barrier treatment system. A flow schematic of the hybrid process is illustrated in [Figure 1.1](#).

Additionally, because the seawater feed to the RO is being diluted during the forward osmosis process, the energy required for the RO desalination process can be substantially reduced. Thus, the energy demand of a desalination plant is diminished while two tight barriers are in place to reject contaminants present in the impaired stream.

Furthermore, a second forward osmosis stage can be installed between the RO concentrate stream and the concentrated impaired water to extract additional water from the impaired water stream, further reducing its volume. Consequently, the concentrated impaired water stream can be returned to a wastewater treatment plant for retreatment or can be used for beneficial purposes. In doing so, the RO concentrate is diluted, thus reducing the environmental impacts associated with discharging RO brine back to the ocean.

Therefore, with the addition of two passive membrane contactors, several problems associated with RO desalination can be mitigated; energy demand can be reduced, water recovery can be increased, and the environmental impact of seawater desalination can be diminished.

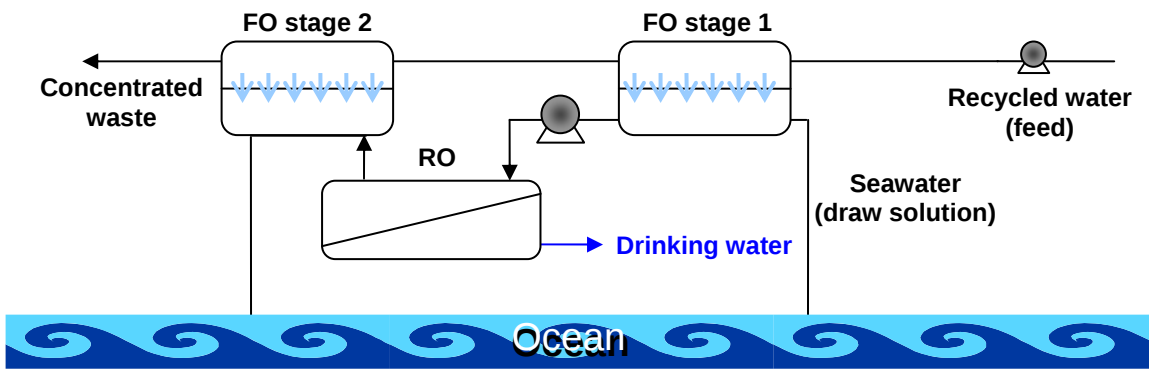


Figure 1.1 A schematic drawing of the novel hybrid FO/RO process for water augmentation

THEORY

Desalination and water reuse technologies can be utilized to augment drinking water supplies. However, both have drawbacks; most desalination technologies are energy intensive and reused water may contain pollutants that pose health risks to consumers. New processes are sought that can mitigate both of these drawbacks synergistically.

Energy Demand in Water Treatment Processes

While desalination can provide a secure, drought resistant source of drinking water, the high energy demand has consistently limited applications of desalination in many regions (Gleick, Cooley and Wolff 2006b). In order to expand the implementation of desalination, and especially seawater desalination, more efficient and lower energy demanding technologies must be developed.

Energy Recovery Devices and Ultra Low Pressure RO for Desalination

Membrane desalination of highly saline water is energy intensive because of the high osmotic pressure of this type of water. For example, in order to produce potable water from common seawater, an osmotic pressure of approximately 380 psi has to be overcome. A large portion of the energy used in the process is wasted when the concentrate stream is depressurized. Recent advances in RO technology have greatly reduced the energy required for desalination by implementing energy recovery devices. Early energy recovery devices, such as Pelton wheels, made use of turbines connected with a common shaft to a high-pressure pump or a motor/generator. These devices were only able to attain slightly greater than 50 percent efficiency (Harris 1999). Modern energy recovery devices typically make use of either a valve and piston assembly or a rotating cylinder and are capable of greater than 95 percent efficiency, reducing the total energy consumption of a seawater RO (SWRO) plants by more than 60 percent (Harris 1999, Stover 2007).

More efficient membranes, such as nanofiltration or ultra low-pressure RO (ULPRO) membranes have further decreased the energy demand of desalination. Energy savings between conventional RO and ULPRO could be more than a third (Nemeth 1998). Overall, the cost of

SWRO has declined 3 fold in the last 20 years (Karagiannis and Soldatos 2008). However, energy costs still contribute as much as 75 percent to the operating costs of a desalination plant, or between 30 and 50 percent of the produced water cost (Farooque et al. 2008).

Energy Reduction through Dilution with Forward Osmosis

Another way to reduce energy demand in desalination of highly saline water is by diluting the feed water and reducing its total dissolved solids (TDS) concentration. Most impaired waters have relatively low salinity and therefore can be used to dilute saline streams before desalination; however, direct dilution can substantially contaminate and complicate the chemistry of the feed stream of the desalination process and subsequently reduce the quality of the product water. A safer way to dilute saline water before desalination is by passing the water through a tight filter or membrane; yet, this can also be energy intensive. However, the chemical energy of the saline stream can be used as a driving force in specific applications.

Additionally, if a portion of the RO influent stream is provided from the impaired water stream, the flow rate of raw seawater is reduced, and energy costs associated with pre-treating the seawater influent are correspondingly reduced. While pretreatment may contribute more significantly to energy costs in brackish water desalination, it accounts for less than 2 percent of energy demand in seawater desalination (Cardona, Piacentino and Marchese 2005).

Osmotically Driven Membrane Processes

Osmosis is the diffusion of water across a semi-permeable membrane due to the difference in osmotic pressure of the solutions on the two sides of a semi-permeable membrane. The magnitude and direction of diffusion depends on the difference in osmotic pressure between the solutions. The osmotic pressure (π) of a solution depends on the concentration of dissolved ions in solution and the temperature of solution, and it can be calculated using the van't Hoff equation:

$$\pi = RT \sum iM \quad (1-1)$$

where i is the dimensionless van't Hoff factor for the specific ion, M is the molarity of the specific ion, R is the gas constant ($0.08206 \text{ L}\cdot\text{atm}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$), and T is the temperature in Kelvin. Water will diffuse across a semipermeable membrane from low to high osmotic pressure.

The major states of osmotically driven membrane processes are illustrated in [Figure 1.2](#). When two streams, one having high osmotic pressure and one having low osmotic pressure, are separated by a semi-permeable membrane, water will spontaneously diffuse from the diluted water into the brine to equilibrate the chemical potential of the water on both sides of the membrane. The osmotic pressure difference ($\Delta\pi$) between two solutions is defined as the hydrostatic pressure (ΔP) that if applied to the solution of higher osmotic pressure (the brine), would stop the net flux of water across the membrane. If the hydrostatic pressure applied to the brine is greater than the osmotic pressure, water flux is reversed.

In an osmotically driven membrane system, the theoretical water flux across the membrane (J_w) is calculated using a variation of Darcy's law:

$$J_w = A_w (\Delta P - \Delta\pi) \quad (1-2)$$

where ΔP is the applied hydrostatic pressure (or simply, pressure), $\Delta\pi$ is the differential osmotic pressure, and A_w is the pure water permeability coefficient of the membrane.

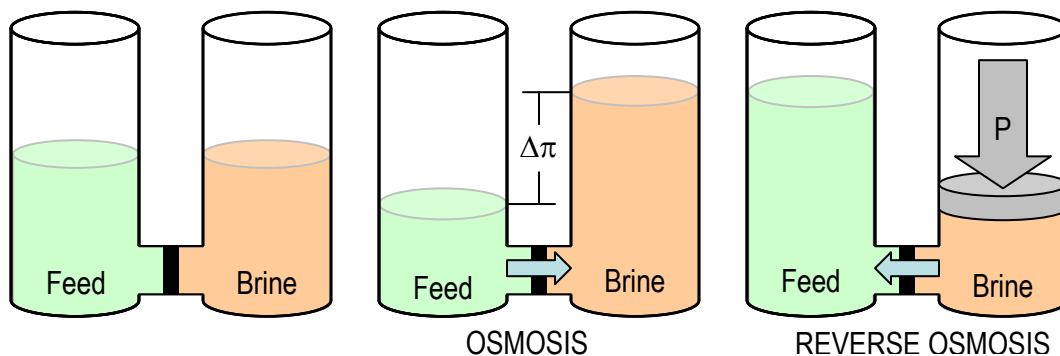


Figure 1.2 Osmotically-driven membrane processes. Feed solution on the left has lower osmotic pressure and the brine solution on the right is a hypertonic solution having high osmotic pressure.

Forward Osmosis

Forward osmosis is an engineered process utilizing natural osmosis with synthetic membranes. In forward osmosis, both sides of the membrane operate at equal pressure ($\Delta P=0$) and water diffuses through the membrane from the feed solution into a concentrated draw solution. Water flux is spontaneous and does not require energy input other than the chemical energy difference across the membrane. As the system is allowed to equilibrate, the low TDS in the feed side is concentrated and the high TDS in the brine is diluted to such a point that the system is at equilibrium (Figure 1.2).

Applications

Recently, forward osmosis has seen increased interest, and applications for the process have been steadily increasing. Cath et al. (2006) reviewed recent applications, including desalination, emergency relief, liquid food concentration, and RO pretreatment (Cath, Childress and Elimelech 2006).

Desalination

Because of the nature of forward osmosis, it is usually combined with other processes for desalination schemes. McCutcheon et al. (2005) have studied such a system. By using ammonium bicarbonate as a draw solution, it is possible to use forward osmosis to produce pure water from seawater feed. After drawing the water across the membrane, the draw solution is heated to recover ammonia and CO_2 , which is stripped from the water by distillation and reused (McCutcheon, McGinnis and Elimelech 2005).

RO Pretreatment

A recent study by Holloway et al. (2007) illustrated the ability of forward osmosis to concentrate sludge centrate from traditional water treatment processes using a sodium chloride draw solution. When concentrated, transportation and disposal of the liquid waste streams can be more easily accomplished. The sludge centrate contained high concentrations of nitrogen and phosphorus. The cellulose triacetate (CTA) forward osmosis membranes used in the study performed adequately and well rejected both phosphorus and nitrogen. It has also been shown that the concentrated centrate can be used as a high grade fertilizer (Holloway et al. 2007).

NASA has explored the use of forward osmosis coupled with reverse osmosis and membrane distillation (MD) for the treatment of wastewater on long-term space missions (Cath et al. 2005). The forward osmosis contactor extracted water from the humidity condensate and hygiene wastewater, and the concentrate was combined with urine and was treated with an FO/MD membrane for complete rejection of urea. Both of the forward osmosis membranes were fed by a common draw solution loop, which was reconcentrated by an RO subsystem. This hybrid membrane system demonstrated the ability to accomplish direct potable reuse of wastewater for life support systems (Cath et al. 2005).

Similarly, a waste company in Corvallis, OR, evaluated forward osmosis as a pre-treatment for RO treatment of the leachate from their landfill (York, Thiel and Beaudry 1999). The FO/RO system utilized plate and frame forward osmosis membrane cells and an RO reconcentration system. With this system, consistently high quality effluent was produced despite the large variability in feed water characteristics. The system did especially well in removing metals from the leachate; keeping ammonia and BOD well below discharge permit limits (York, Thiel and Beaudry 1999).

Pressure Retarded Osmosis

Another osmotic process is pressure retarded osmosis (PRO). In PRO, the osmotic pressure ($\Delta\pi$) is partially offset by a higher hydraulic pressure ($\Delta P < \Delta\pi$) on the brine side, induced by the flux of water across the membrane from the feed into the brine. The system produces a stream of pressurized diluted brine that can be converted into useful energy. In this way, energy can be realized from the difference in osmotic pressure between two solutions (Loeb 1974, 1995, 2002). The PRO process is beyond the scope of this study.

Reverse Osmosis

Perhaps the most familiar osmotic process is reverse osmosis (RO) in which the osmotic pressure difference ($\Delta\pi$) is exceeded by an applied pressure on the brine stream ($\Delta P > \Delta\pi$), reversing the flux across the membrane and producing pure water from saline water. In RO, the high TDS of the brine is concentrated and the low TDS of the feed is diluted. The high pressure needed for overcoming the osmotic pressure of the brine solutions is the source for the high energy demand of most membrane-based desalination processes.

Flux-Pressure Curves

Forward osmosis can be combined with reverse osmosis to safely dilute concentrated brines with impaired waters before desalination. In order to visualize the process dynamics, a simplistic example of an osmotic process, with a theoretically perfect membrane, can be illustrated. For a given set of solutions, a curve can be generated relating the applied pressure on the brine side of the membrane to the water flux across the membrane. Such curves of water flux as a function of ΔP are illustrated in Figure 1.3. In Figure 1.3a, when $\Delta P=0$, the water flux is negative. Water diffuses from the diluted feed into the brine in a forward osmosis mode. As pressure increases, the water flux becomes less negative and the system operates in PRO mode. At the flux reversal point, the osmotic pressure difference equals the applied pressure ($\Delta P=\Delta\pi$). When the pressure is further increased, the system operates in RO mode, the water flux becomes positive, and pure water diffuses from the concentrated brine to the diluted stream.

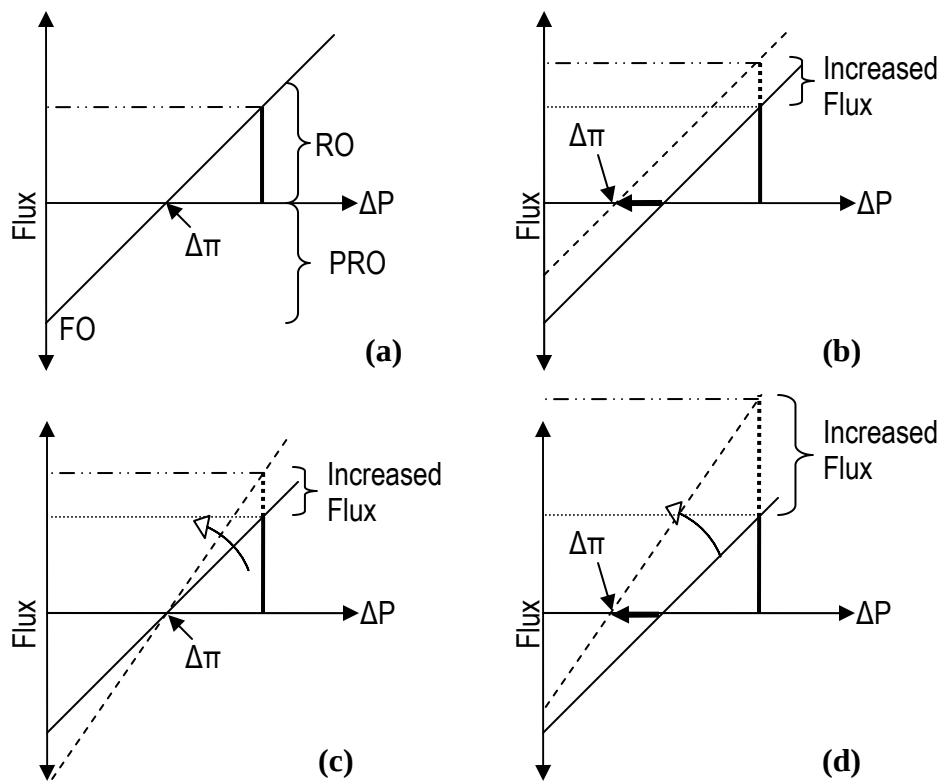


Figure 1.3 Changes in the water flux/pressure curves for feed solution dilution and/or increased membrane permeability. (a) osmotic process regions; FO, PRO, and RO, (b) effect of dilution of brine stream on flux curve, (c) effect of increased membrane permeability on flux curve, and (d) combined effects of diluted brine stream and increased membrane permeability.

Each curve in Figure 1.3 is valid only for a single set of solution chemistries. For example, if the brine is diluted, the curve shifts up, as illustrated in Figure 1.3b. Consequently, the flux reversal point occurs at lower applied pressure, which indicates that $\Delta\pi$ for the new

condition is lower. Also, at a given pressure, the flux is higher in RO mode; or alternatively, at a constant flux the needed pressure is reduced, reducing the energy demand proportionally.

Membranes for Forward Osmosis

Since the 1990's, the only available forward osmosis membrane has been provided by Hydration Technologies, Inc. (HTI, Albany, OR). Although the materials used for HTI's membranes are similar to those used for some RO membranes (i.e., cellulose acetate based), the structure of the HTI forward osmosis membrane is very different. The membrane consists of a dense cellulose triacetate polymer cast onto a polyester mesh for mechanical support. The membrane is also very thin, having a total thickness on the order of 50 μm . Typical asymmetric RO membranes consist of a thin dense active layer cast on a thick porous support layer. However, in a forward osmosis, the porous support layer contributes to internal concentration polarization (Loeb 1976, McCutcheon and Elimelech 2006) that reduces the performance of the process. It has been shown that the HTI membrane far outperforms commercially available RO membranes operated in forward osmosis mode (Cath et al. 2005).

If improved membranes were available, the efficiency of the forward osmosis process could be enhanced. Referring to [Figure 1.3c](#), if the permeability of a forward osmosis membrane increases, the flux-pressure curve rotates around the flux reversal point (in this case, counterclockwise) and water flux increases at a specific applied pressure. This is the effect that would be expected by changing from a conventional RO membrane to an ultra low pressure RO (ULPRO) membrane. The combined effects of both diluting the brine and increasing membrane permeability are illustrated in [Figure 1.3d](#).

Concentration Polarization

Equation 2-2 provides a simplistic view of mass transport in semi-permeable membranes, and it is applicable mainly when the applied pressure is higher than the osmotic pressure difference across the membrane. Water flux in osmotic processes deviates from this theoretical water flux due to concentration polarization (CP) (McCutcheon and Elimelech 2006). CP occurs when the difference in concentration across the active later of the membrane is different than the difference in concentration in the bulk solutions, and can occur both within the porous support layer of the membrane (internal CP (ICP)) and near the active layer of the membrane (external CP (ECP)) ([Figure 1.4](#)). ECP is common to all membrane processes (including RO) and involves the increased or decreased concentration of solutes near the membrane. ECP can be mitigated by improving turbulence in the flow channels of the membrane cell. However, ICP is unique to forward osmosis and PRO and is the result of brine dilution in the porous support layer of the membrane. ICP depends on the diffusion coefficient of the solute and on the properties of the membrane support layer, including porosity, tortuosity, and thickness. ICP is very minimally affected by changing the hydraulic conditions in the membrane cell (McCutcheon and Elimelech 2006).

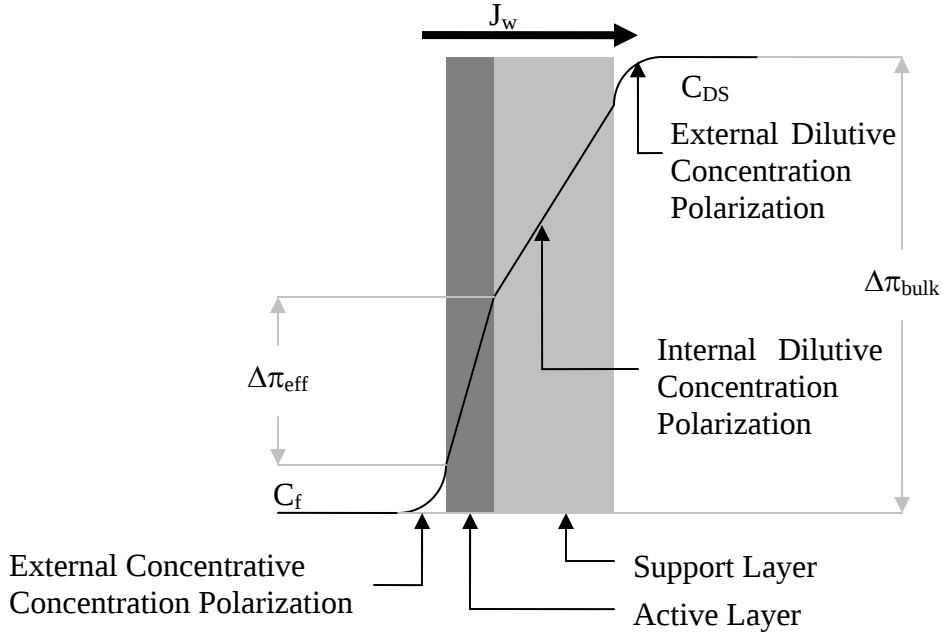


Figure 1.4 Areas of concentration polarization during forward osmosis

In forward osmosis mode, the solvent (water) flux across a forward osmosis membrane can be calculated using a modified equation that considers the effects of concentration polarization (McCutcheon and Elimelech 2006):

$$J_w = A_w \sigma \left[\Delta P - \pi_D \exp(-J_w K) + \pi_F \exp\left(\frac{J_w}{k}\right) \right] \quad (1-3)$$

where σ is the reflection coefficient, π_D is the osmotic pressure of the draw solution, π_F is the osmotic pressure of the feed solution, K is the solutes resistivity to diffusion in the porous support layer, and k is the feed solute's mass transfer coefficient (McCutcheon and Elimelech 2006). Alternatively, if pure water is used as the feed solution, external concentrative concentration polarization resistance ($1/k$) can be assumed to be zero. Assuming perfect rejection of salt ($\sigma=1$), the equation can be simplified to:

$$J_w = A_w [\Delta P - \pi_D \exp(-J_w K) + \pi_F] \quad (1-4)$$

and the internal dilutive concentration polarization factor (K) can be solved for empirically. This modified flux equation will allow the pure water permeability coefficient to be calculated from the experimental results that will be obtained in this study.

Water Quality

In any application using recycled water for potable reuse, removal and elimination of traditional and emerging contaminants are of a great importance and concern to regulators, utilities, and the general public.

Solute Transport

The transport of organic and inorganic solutes through a membrane can pose substantial limitation to implementation of forward osmosis processes. For example, in forward osmosis processes that utilize a closed draw solution loop with RO reconcentration, loss of the osmotic agent (e.g., sodium chloride) into the feed solution and into the RO permeate can make the process uneconomical, or require treatment of the feed solution before discharge. Additionally, because solutes exist on both sides of the forward osmosis membrane, bi-directional diffusion of solutes must be considered.

The HTI forward osmosis membranes used in many forward osmosis studies are semi-permeable and reject salts very well. Chloride rejection can be greater than 98 percent with these membranes (York, Thiel and Beaudry 1999). The membrane also rejects phosphate very well (>99%); however, only moderate rejection of ammonia and nitrate (80-90%) can be achieved with this membrane (Holloway et al. 2007). This can be a potential problem during treatment of impaired water that is elevated in nitrogen species.

An important part of any membrane treatment system is its ability to reject organic micropollutants, even more so when treating impaired water sources. To date, there are few studies in the literature regarding the rejection of organic micropollutants by forward osmosis (Cartinella et al. 2006). However, extensive research has been conducted regarding the transport and rejection mechanisms of organic micropollutants by RO and NF (Drewes et al. 2005, Xu et al. 2005, Kim et al. 2007, Bellona et al. 2008). While specific rejection characteristics may not carry over from RO to forward osmosis, it is likely that because the membranes are similar, many of the same mechanisms are still involved. Therefore, it is important to examine the mechanisms by which micropollutants are rejected by RO.

Bellona et al. (Bellona et al. 2004) conducted an in-depth literature review on rejection mechanisms of organic solutes in high-pressure membrane processes. Some of the important characteristics of the compounds that influence the level of rejection by RO and NF membranes include charge, size, molecular weight, and hydrophobicity of the compounds. The review identified some of the key mechanisms for rejection as being electro-static repulsion, size exclusion, adsorption, and steric hindrance. The study concluded that small, neutral, hydrophilic compounds would be poorly rejected and compounds that are large, charged, or hydrophobic should be better rejected. These findings are supported in the literature (Bellona et al. 2004). Whether these mechanisms govern the organic solute rejection for forward osmosis membrane processes is unknown and will require additional research.

Xu et al. (2005) found that other factors affect the rejection of organic contaminants; the hydraulic operating conditions and feed water matrix both have a substantial effect on rejection behavior. Similarly, Kim et al. (Kim et al. 2007) demonstrated that the operating conditions of the membrane determine which transport mechanism is dominant. It has been also established that surrogates can be used as a proxy for the rejection of other similar compounds. In this way

compounds that have established analytical methods can be used to determine how other compounds may be rejected (Drewes et al. 2005, Bellona and Drewes 2007).

In this study, several compounds were chosen to provide insight on how organic trace contaminants with different characteristics are rejected by forward osmosis membranes and osmotically-driven hybrid membrane processes.

Multiple Barriers to Contaminants

Because of the uncertainty regarding the transport of solutes through semi-permeable membranes, having multiple barriers in place to reject potential contaminants is important. While it was previously shown that RO and NF membranes can reject a major portion of solutes present in impaired water, it is unknown to what extent the rejection mechanisms will remain valid for forward osmosis. However, because forward osmosis membranes are dense, semi-permeable membranes and are made of similar polymers used in the manufacturing of RO membranes, it is expected that the addition of the forward osmosis process will provide an additional level of rejection of solutes. Additionally, because the forward osmosis operates at very minimal applied pressure, and compression of a cake layer is negligible, it is likely that some compounds will be rejected differently, increasing the overall system rejection.

Membrane Fouling

Membrane fouling and its prevention are of great importance and concern in operation of any membrane type and system. Fouling can change the characteristics of the membrane and therefore it can affect water flux and contaminant rejection. Furthermore, severe fouling can permanently damage the membrane and reduce the overall productivity of a membrane system, both of which can reduce compromise the economic feasibility of a water treatment process and treatment facility.

Effect of Membrane Fouling on Water Flux

Fouling has a strong influence on flux decline in membranes, and many organic contaminants commonly present in wastewater effluent can foul membranes severely; Yiantsios (Yiantsios, Sioutopoulos and Karabelas 2005) showed that flux decline is more severe at higher operating pressures. Due to the relatively high fouling propensity of some impaired water feed solutions, membrane fouling should be severe. However, it has been shown that because forward osmosis operates with negligible applied pressure, water flux due to fouling is minimal, even with waste streams of high fouling propensity (Holloway et al. 2007).

Effect of Fouling on Micropollutant Rejection

Membrane characteristics (i.e., molecular weight cut-off, surface charge, and hydrophobicity) affect the rejection of contaminants (Bellona et al. 2004). When a membrane is fouled, membrane surface characteristics can change drastically (Xu et al. 2006). These changing characteristics can either improve or degrade the rejection capability and flux behavior of a membrane.

Xu et al. (Xu et al. 2006) studied several membranes, both NF and RO, for changes in rejection and membrane characteristics after fouling with micro-filtered secondary effluent. It was found that fouling made the membrane more hydrophilic and increased the negative surface charge. The increased charge on the CTA membrane probably led to membrane swelling, which reduced the rejection of almost all of the tested solutes. The CTA membrane was more susceptible than other membranes tested to decreasing rejection of various solutes tested, including primidone, bromoform, chloroform, and trichloroethylene. A polyamide membranes tested in that study did show a decline in rejection, though not as severe as the CTA membrane (Xu et al. 2006).

Agenson et al. (Agenson and Urase 2007) showed decreased rejection of organic solutes with tight polyamide RO membranes, and increased rejection through looser polyamide NF membranes (Agenson and Urase 2007). Similarly, a study by Drewes et al. (2005) found that rejection of many organic pollutants at trace concentrations increased with fouling of NF membranes when used in a reuse application. Bellona et al. supported these observations through findings derived during rejection studies at pilot scale (Bellona and Drewes 2007).

Project Objectives

The overall goal of the current study was to evaluate the technical and economic feasibilities of an FO/RO hybrid processes to co-treat saline water (e.g., seawater or concentrated brackish water) with impaired water, thereby increasing water recovery, protecting desalination membranes, and reducing the overall cost of seawater desalination. Specifically, this investigation focused on the following questions:

1. What are the fouling and flux characteristics of a forward osmosis membrane operated at low driving force and minimal hydrostatic pressure
2. How does feed water quality affect membrane fouling and water flux in forward osmosis of impaired water?
3. At what level will organic and inorganic solutes be rejected by the FO/RO hybrid system?
4. What level of water augmentation is economically feasible and what are the associated energy savings?

CHAPTER 2

MATERIALS AND METHODS

Experiments were designed to answer the research questions; specifically, the study was divided into sets of bench-scale and pilot-scale experiments. The bench scale experiments were used to determine the short-term performance (e.g., water flux, solute rejection, and fouling potential) of the hybrid process. Both deionized (DI) water and impaired water were used as feed solutions in the bench-scale experiments to determine the effect of feed water quality on water flux, the onset of short-term water flux decline due to fouling, and the rejection of organic and inorganic solutes. Experiments were conducted with various draw solution sea salt concentrations to elucidate the driving force – flux relationship.

Pilot-scale experiments were conducted to determine the long-term water flux and fouling rates of both the forward osmosis and RO membranes. In addition, the effect of membrane fouling on rejection of organic solutes was studied. Because pilot-scale tests were much longer than bench-scale experiments, not all draw solution concentrations were tested in each experimental set. [Table 2.1](#) summarizes the matrix of draw solution concentrations and feed waters tested at each stage.

Table 2.1
Summary of experiments conducted showing combinations of draw solution concentrations and feed water types tested on bench and pilot scales

Synthetic seawater draw solution concentrations (g/L)	Bench-scale				Pilot-scale	
	DI water feed	Secondary effluent feed	Tertiary effluent feed	Impaired river water feed	Secondary effluent feed	Tertiary effluent feed
5	+	+	+	+		
10	+	+	+	+		
15	+	+	+	+		
20	+	+	+	+		+
25	+	+	+	+		
30	+	+	+	+		
35	+	+	+	+	+	+
70	+	+	+	+		+

Bench-Scale Experiments

In the first phase of the investigation, baseline performance and the effect of feed water quality on water flux through the forward osmosis membrane were determined. Experiments were conducted in the laboratory with forward osmosis membranes only and with different feed waters that were brought from the field.

Experimental Setup

A bench-scale test system was designed and constructed for this study. A schematic drawing of the system is illustrated in Figure 2.1. Feed water was circulated from a 12 L PVC feed tank through the forward osmosis membrane cell and back to the feed tank using a constant speed rotary vane pump (Procon, Murfreesboro, TN). Feed flow rate was measured with a rotameter and maintained at 1.5 L/min by adjusting a bypass valve that returned a portion of the water from the pump outlet to the pump inlet. The feed water tank was constructed from a 36" long, 6" diameter PVC pipe that was capped at the bottom end. The tank was designed with a minimal cross-sectional area to produce large changes in water level with small changes in volume, thereby allowing more accurate volume measurement. A lid was constructed from a 1/4" thick clear acrylic plastic.

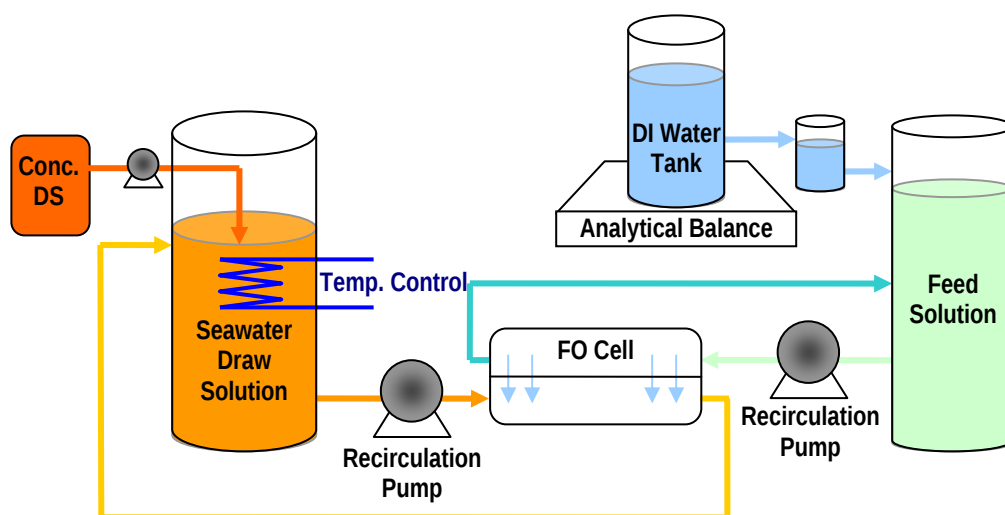


Figure 2.1 Schematic drawing of the closed-loop bench-scale forward osmosis experimental setup with the draw solution loop in orange, and the feed solution loop in blue.

Feed water was kept at constant concentration by continuously adding DI water to the feed tank to replace water that diffused through the membrane from the feed solution into the draw solution. A 6 L acrylic plastic tank was used to hold DI water and the tank was placed on an analytical balance that was connected to a supervisory control and data acquisition (SCADA) system. DI water first flowed into a small (<500 mL) buffer tank through a float valve, and then flowed through another float valve into the feed tank. The buffer tank and additional float valve were used because the mechanical float valves in the feed tank depend on water pressure behind the valve for proper operation. The float valve in the feed tank was installed on an adjustable height mechanism to allow operation with different feed volumes in the system.

Water flux across the forward osmosis membrane was calculated from the change in weight of the DI water tank on the analytical balance; the weight decreased as DI water flowed into the feed tank. In-line sensors were used to measure and record feed solution conductivity and pH. Both analog and digital pressure gauges were used to monitor pressure differentials across the membrane and along the membrane cell. Sodium hydroxide and hydrochloric acid

(Fisher Scientific, Waltham, MA) were used to maintain the pH of the feed solution between 7.0 and 7.5.

A rotary vane pump, similar to the one used for circulation of the feed solution, was used for circulation of the draw solution from the draw solution tank through the membrane cell. A bypass valve was used to return a portion of the draw solution from the pump outlet to the inlet, maintaining a flow rate of 1.5 L/min. The draw solution tank was constructed of 6" diameter PVC pipe and had a capacity of 5 L. Conductivity and temperature were measured in-line by electronic probes. Temperature was measured, recorded, and maintained at 19.0 ± 0.1 °C using the SCADA system. A stainless steel cooling coil was installed in the draw solution tank and a valve controlled by the SCADA system regulated chilled water through the coil.

Synthetic seawater salt (Instant Ocean, Mentor, OH) was used to prepare the draw solution. The composition of the synthetic sea salt was calculated from the data provided by the manufacturer and is summarized in Table 2.2. The concentration of the draw solution was maintained constant within ± 0.25 mS/cm of the predetermined experimental value by intermittently dosing a highly concentrated synthetic sea salt solution into the draw solution tank. This was accomplished with a SCADA-controlled peristaltic pump. Samples were taken from a port placed before the membrane cell in the draw solution line.

Table 2.2
Instant Ocean synthetic sea salt composition at 35 g/L concentration

Ion	Instant Ocean (@ 35 g/L TDS) (mg/L)
Chloride	19,290
Sodium	10,780
Sulfate	2,660
Magnesium	1,320
Potassium	420
Calcium	400
Carbonate/bicarbonate	200
Bromide	56
Strontium	8.8
Boron	5.6
Fluoride	1

Membrane and Bench-Scale Membrane Cell

Because the expected water flux was relatively low, large membrane cells were designed and constructed to produce the required volumes of water for analysis within reasonable time frames. A custom designed membrane cell with an effective surface area of 0.062 m^2 was fabricated from two 1" thick acrylic plastic boards and was designed to have solutions circulated through both channels of the membrane cell. The two halves of the cell were assembled with bolts threaded into one half of the cell (Figure 2.2). This method of closure eliminated the need for compression plates and enabled observation of the membrane surface through the clear acrylic during the experiments.

Initial experiments were conducted with mesh spacers installed in the feed and draw solution channels of the membrane cell. The spacers were utilized to hold the membrane tight in the cell and to promote turbulence, which reduces fouling and external concentration polarization. During operation, the spacers produced a considerable pressure drop along the flow channels (~0.35 bar, 5 psi). In order to reduce pressure drop and better detect the onset of membrane fouling, several experiments were conducted without a spacer in the forward osmosis feed channel. However, without the spacer in the feed channel, the system was unstable; resulting in differential pressure between the feed and draw solution and pulsing of the membrane. To resolve the hydraulic problems, custom made 1/4" wide spacers were fabricated from 3/16" thick nitrile rubber, holding the membrane in place and creating a very small pressure differential (<0.1 bar, 1 psi) both across the membrane and along the flow channels in the membrane cell. The new spacers in the bench-scale forward osmosis membrane cell are shown in [Figure 2.2](#).

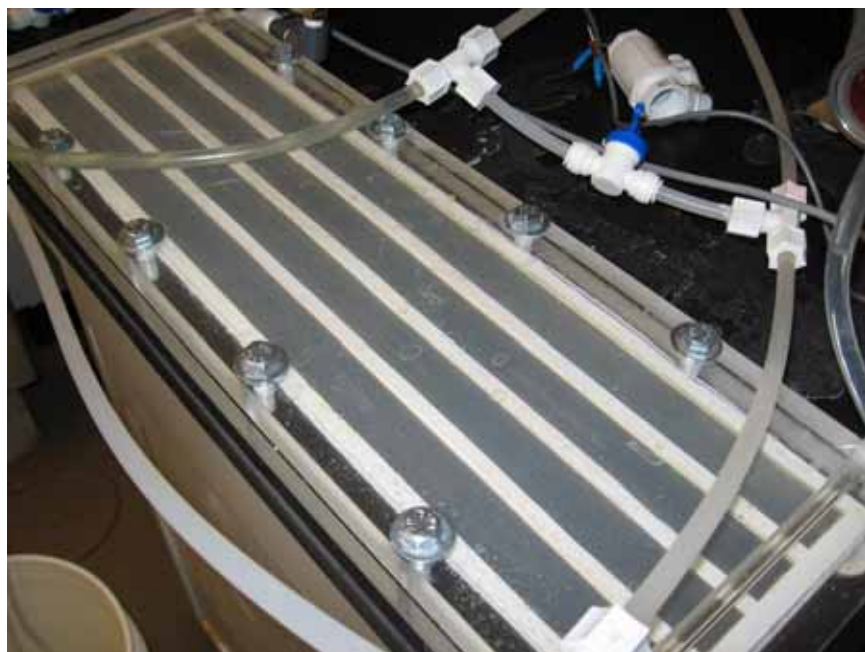


Figure 2.2 Feed and draw solution spacers in the bench-scale forward osmosis membrane cell (with membrane installed)

An environmental scanning electron microscope (ESEM) micrograph of a virgin forward osmosis membrane specimen is shown in [Figure 2.3](#). Membrane was provided for this study from a single production cast, minimizing errors due to membrane variability.

Table 2.3
Forward and reverse osmosis membrane properties

	HTI forward osmosis	Dow Filmtec SW30
Selective material	Cellulose tri-acetate	Polyamide
NaCl rejection	95-99%	99.4%

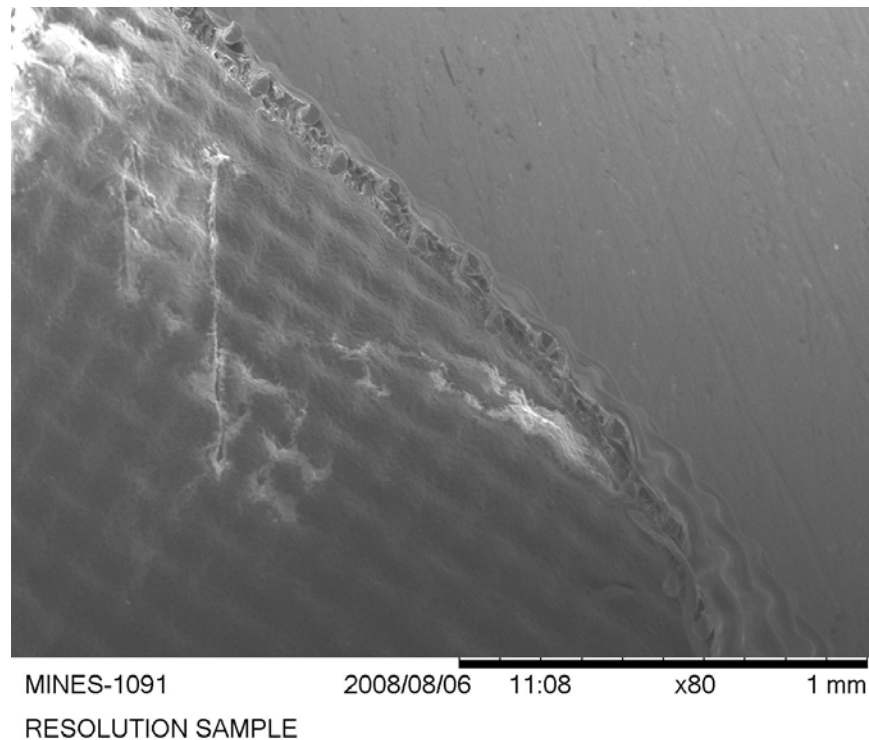


Figure 2.3 Environmental scanning electron microscope (ESEM) micrograph of the HTI CTA forward osmosis membrane with the dense, non-porous, side up

Supervisory Control and Data Acquisition (SCADA)

A SCADA system was developed and utilized to control draw solution concentration and temperature in the bench-scale system. In addition, signals from conductivity, pH, temperature, and pressure sensors, as well as readings from an analytical balance were acquired and recorded by the SCADA system.

To maintain a constant draw solution concentration, the bench-scale forward osmosis system was initially coupled with a bench-scale RO system, similar in configuration to a potential full-scale hybrid process. The water that diffuses through the forward osmosis membrane and diluted the draw solution was removed from the system by the bench-scale RO process, simultaneously re-concentrating the salt in the draw solution loop. To make this possible, the SCADA system was developed to monitor and control the concentration of salt in the draw solution by adjusting the pressure of the bench-scale RO system, producing water through a tight RO membrane at the same rate as the flux through the forward osmosis membrane. However, after preliminary system performance tests, it was evident that even with the improved control provided by the SCADA system, the RO system was not flexible enough to adjust to the forward osmosis operating conditions. Consequently, a new control strategy was developed in which a highly concentrated salt solution was dosed into the draw solution tank to maintain constant draw solution concentration. The SCADA system was modified to monitor the concentration of the draw solution and correct the conductivity by intermittently (several times each minute) operating a peristaltic pump that dispensed concentrated sea salt solution into the draw solution tank. A screen capture of the modified SCADA system is shown in [Figure 2.4](#).

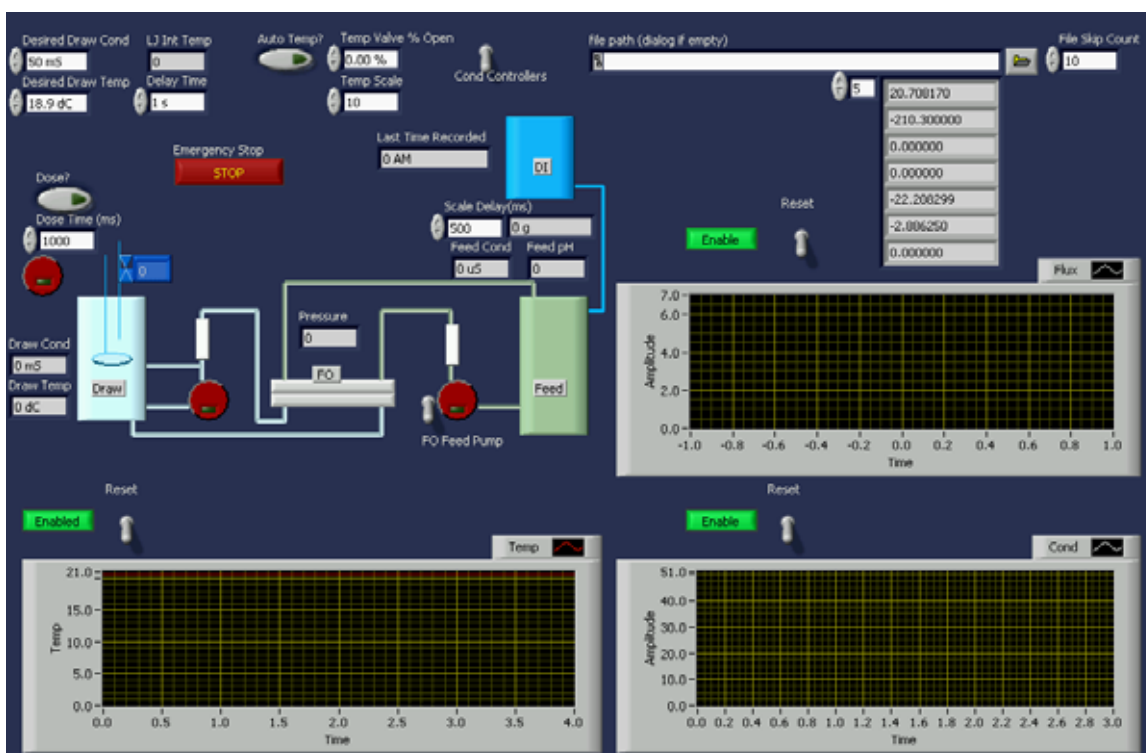


Figure 2.4 Control panel of the SCADA system used to maintain draw solution concentration and temperature, and record experimental data

Benchmark Forward Osmosis Experiments

Benchmark forward osmosis experiments were conducted to determine the pure water permeability and to obtain data on the rates of reverse diffusion of salts from the draw solution into the feed. DI water was used as feed solution and for preparation of synthetic seawater draw solution.

At the beginning of each experiment, 4-L of DI water was mixed with synthetic sea salt to a predetermined concentration. The draw solution loop was rinsed twice with 1-L of seawater, and the remaining 2-L of seawater were used as the initial draw solution for the experiment. Each experiment with different draw solution concentration was performed over approximately 4-hours, or until steady state water flux was achieved. At the end of each experiment the draw solution loop was rinsed four times, each with 5-L DI water. The feed loop was drained and rinsed four times, each with 5-L DI water, and the DI water tank was fully refilled (6-L). The experiments were conducted from low draw solution concentration to high draw solution concentration ([Table 2.1](#)) to minimize errors due to salt carryover between experiments. Feed and draw solution samples of 40 mL each were collected for analysis before and after each experiment to determine the rate of reverse diffusion of specific ions across the membrane.

Forward Osmosis Experiments with Impaired Water Feed

Bench-scale forward osmosis experiments were conducted with different feed waters, including secondary and nitrified effluent from the Denver Water Recycling Plant (DWRP, Denver, CO) and effluent impacted surface water from the South Platte River, just downstream of Denver, CO. The focus of the experiments was to determine the effect of feed water quality on process performance (i.e., water flux, fouling, and rejection). Each experiment was conducted with a virgin membrane for approximately 4 hours, or until steady state water flux was reached. All experiments were conducted on the same bench scale system that was used for the benchmark performance experiments using the same procedures.

Benchmark Organic Micropollutant Rejection Experiments

Rejection of organic micropollutants by virgin forward osmosis membrane was studied at the bench-scale to determine baseline micropollutant rejection in the absence of fouling. Feed solution was DI water spiked with select organic micropollutants, including diclofenac, gemfibrozil, mecoprop, naproxen, and salicylic acid, each at concentrations of 500 ng/L. Synthetic seawater (35 g/L sea salt) was used as a draw solution. The system was operated for 48 hours to allow sufficient time for potential accumulation of organic micropollutants in the draw solution and sufficient volume to produce samples for analysis of organic micropollutants.

Pilot Scale Experiments

A pilot scale system was constructed and tested at DWRP. The system consisted of a pilot-scale RO sub-system and a forward osmosis sub-system. The pilot system was deployed in the biologically active filter building at DWRP, where access to both secondary and tertiary effluent exists. The secondary effluent stream was drawn from a pipeline that transfers water from the Metropolitan Water Reclamation District's (MWRD, Denver, CO) wastewater treatment plant to DWRP. Tertiary treated water was the DWRP effluent before chlorine disinfection.

RO Sub-system

The RO sub-system is a three-stage array of 2.5" diameter/40" long membrane elements connected in series. Depending on the operational settings, the system is capable of producing up to 2 L/min permeate from stage 1 and up to 3 L/min of final concentrate (i.e., draw solution). For the pilot study, permeate from the first stage only was collected as the final permeate of the pilot system. Stages 2 and 3 were used to further concentrate the brine for use as draw solution in the forward osmosis process, and permeate was returned to the brine tank. The membranes in the RO sub-system are seawater RO membrane elements (SW30-2540, Dow Filmtec, Edina, MN). These membranes were chosen for their high salt rejection and high operating pressure that enable production of high draw solution concentrations. A schematic drawing of the RO sub-system is illustrated in [Figure 2.5](#).

The RO system was constructed inside a steel frame with permeate and brine tanks installed inside the frame. The pressure vessels are mounted on the outside of the frame for ease of membrane replacement. A high-pressure positive displacement pump (HydraCell M03,

Wanner Engineering, Inc., Minneapolis, MN) is used in the system and is capable of producing high pressure at low and variable flow rates. All high-pressure lines are constructed with stainless steel tubing and fittings while low-pressure lines are made of polyethylene or PVC tubing and nylon or PVC fittings. The tanks are made of either PVC or acrylic plastic.

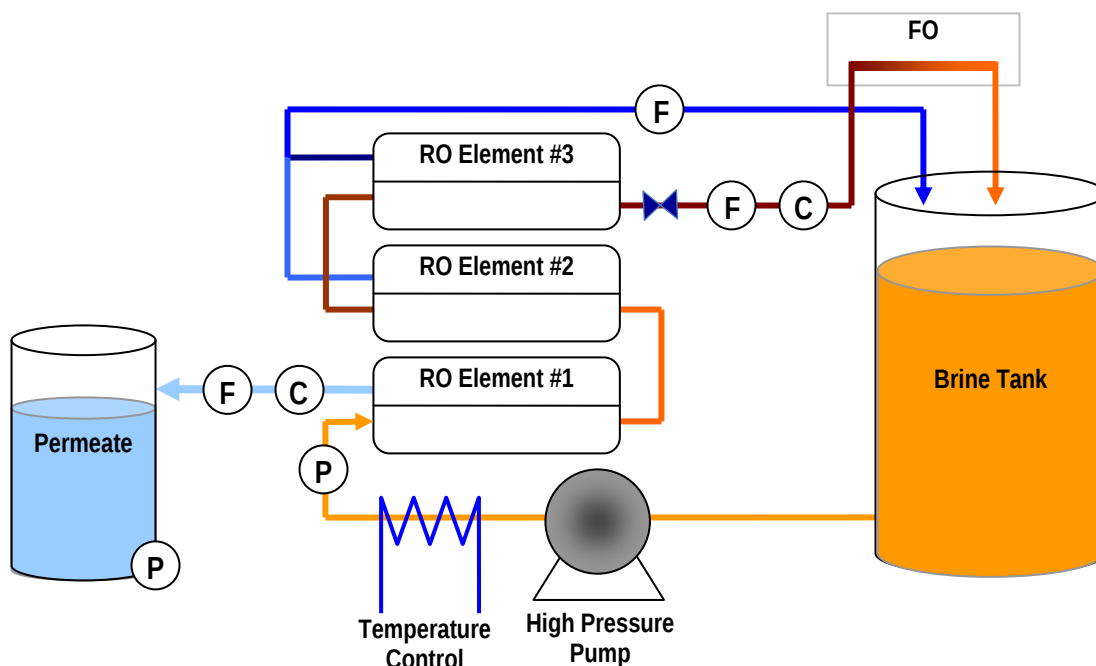


Figure 2.5 Flow diagram of the RO sub-system utilizing three stage membrane array with the draw solution loop in orange and the permeate loop in blue. Conductivity (C), pressure (P), and flow rate (F) gauges are signified by circles

Various sensors were installed in the RO sub-system that measure stage 1 permeate and final concentrate conductivities, flow rates of all streams, and operating pressures. Information from these sensors was not recorded with the forward osmosis SCADA system due to integration complexities. Conductivities are measured with two conductivity probes; $K=1 \text{ cm}^{-1}$ for the permeate stream and $K=10 \text{ cm}^{-1}$ for the concentrate (draw solution) stream (Cole-Parmer, Vernon Hills, IL), and the probes are connected to a two-channel conductivity controller (+GF+ SIGNET 8860, El Monte, CA). Permeate and concentrate flow rates and concentrate pressure are measured manually using rotameters and analog pressure gauges, respectively. The operation of the RO sub-system was stable enough throughout the experiments and therefore did not require any control system. Flows and pressures during the long-term pilot tests were slightly adjusted every other day. Operating parameters for the pilot-scale RO system are summarized in [Table 2.4](#).

Table 2.4		
Pilot-scale RO sub-system operating parameters		
Parameter	Unit	Value
Feed flow rate	L/min	4.4
First permeate flow rate	L/min	1.0
Concentrate flow rate	L/min	2.4
Water flux	LMH (gfd)	21.4 (13.1)

Pilot Forward Osmosis Membrane Cell

For the pilot scale study, an additional membrane cell was fabricated for the forward osmosis flat sheet membrane. This cell was similar to the bench scale membrane cell, but much larger; the total membrane surface area was 0.266 m². The larger cell made use of both types of spacers used in the bench scale, with nitrile rubber strips used on the feed solution side and typical turbulence enhancing mesh spacers on the draw solution side. Two cells were constructed for redundancy.

Pilot System Operation

The continuous supply of treated wastewater at DWRP for use as feed solution allowed for experiments over longer time frames. The location of the pilot system allowed access to both secondary effluent from the MWRD, as well as tertiary effluent from the DWRP. Average water properties for the secondary and tertiary effluent are summarized in [Table 2.5](#).

Table 2.5
Summary of average properties of impaired water streams used as feed solutions in pilot scale experiments at DWRP

	Secondary Effluent, MWRD	Tertiary Effluent, DWRP
pH	7.5	7.5
TDS, mg/L	400	400
UVA 254 nm, cm ⁻¹	0.2	0.1
Nitrate, mg/L NO ₃ -N	5	10
Ammonia, mg/L NH ₃ -N	5	0

Reclaimed water from the DWRP sampling lines fed a 20 L buffer tank at a rate of approximately 3 L/min and a constant speed rotary vane pump (Procon, Murfreesboro, TN) was used to draw water from the buffer tank. The pump was operated with a bypass that directed 2.4 L/min feed water to the forward osmosis membrane cell and the rest returned back to the buffer tank. After passing through the membrane cell, the feed solution was wasted.

Synthetic sea salt was dissolved into DI water to make the brine for the RO system. The brine was concentrated in the RO system and the concentrate became the draw solution for the forward osmosis process. A portion of the permeate stream from stage 1 of the RO subsystem was removed from the system; the flow rate of this stream was equivalent to the flux of water through the forward osmosis membrane. The remaining permeate stream was returned to the

brine tank; therefore, stage 1 permeate flow rate had to be greater than the flow rate of water diffusing through the forward osmosis membrane and had to be maintained without over concentrating the brine. To do so, the brine was mixed at a concentration of approximately 5 g/L below the desired draw solution concentration and then concentrated in the RO system to the desired draw solution concentration. Water flux through the forward osmosis membrane was calculated from the rate of accumulation of RO permeate in the permeate tank. The volume of liquid in the RO system was set to 50 L, of which 40 L was stored in the brine tank. The brine was pumped from the brine tank to the RO system, flowing through the RO membrane elements and concentrated to the desired draw solution concentration. The draw solution then flowed through the forward osmosis membrane cell on the draw solution side of the membrane, was diluted by water diffusing from the feed stream, and returned to the brine tank to be concentrated again.

Pilot-scale Experiments

Pilot-scale experiments were conducted with either secondary or tertiary treated feed water for durations of between 4 and 14 days. All experiments with secondary effluent were conducted with a draw solution concentration of 35 g/L synthetic sea salt. Experiments with tertiary effluent were conducted with draw solution concentrations of 20, 35, or 70 g/L sea salt. The effect of draw solution concentration on water flux was examined using tertiary treated water feed solution to isolate driving force effects on flux. The forward osmosis membrane was replaced and the system was rinsed with RO permeate before each experiment.

Sampling

Samples were collected throughout the course of each experiment. For all experiments, 40 mL samples were collected for analysis from the feed, draw solution, and permeate on the first day and every other day thereafter until the experiment was terminated. Feed samples were drawn directly from the feed line. During operation, a large portion of the salt and other constituents in the draw solution loop were concentrated in the feed channels of the RO membrane elements. Therefore, the RO system was depressurized while brine flow was maintained at 2.4 L/min for approximately 5 minutes before each draw solution sample was collected. Due to the lower pressure in the feed channels, the RO membranes were most likely osmotically-backwashed when purified water that remained in the permeate spacers of the membranes was drawn back through the membrane into the brine. This helped to flush salts and contaminants back into the bulk solution. Samples were cooled to 4 °C and analyzed within 2 days.

Analysis of organic micropollutants required 2-L samples. The feed and permeate samples were drawn without affecting the system, but when draw solution samples were collected, a large amount of salt was removed from the draw solution loop. To balance the loss of salt, 2-L of stock draw solution was added to the system following sample withdrawal. The loss of other constituents, however, did have to be taken into consideration. Samples for micropollutant analysis were preserved on ice and extracted using solid phase extraction (SPE) shortly after they were collected.

Analytical Methods

Aqueous samples were analyzed for several different classes of solutes including inorganic ions and organic micropollutants. General properties such as ultra-violet absorbance and total organic carbon were also quantified.

Analysis of Inorganic Ions

Inorganic ion analysis was conducted using a Dionex DC80 ion chromatography (IC) system (Dionex, Sunnyvale, CA) for anions, and Optima 3000 inductive coupled plasma (ICP) spectrophotometer (Perkin Elmer, Norwalk, CT) for cations. IC analysis is limited to chloride concentrations below 300 mg/L, therefore draw solution samples were diluted prior to analysis. ICP samples were acidified with nitric acid to a pH of less than 2, and similarly diluted to less than 300 mg/L sodium. TDS was measured according to Standard Method 2540c (APHA, AWWA and WEF 2005).

Ammonia and nitrate were both analyzed using a Hach 5000 spectrophotometer (Hach Company, Loveland, CO). Ammonia was tested using the salicylate method (10031, 0.4-50 mg/L), and nitrate was analyzed with the chromotropic acid method (10020, 0.2-30 mg/L). Nitrate samples were diluted to a chloride concentration of less than 1,000 mg/L due to interference. A 2,000 mg/L sea salt blank was analyzed and found to have insignificant interference.

Analysis of Organic Micropollutants

It was anticipated that analysis of organic micropollutants at trace concentrations would be difficult because of the relatively higher concentration of ions in the draw solution. High concentrations of salt can damage analytical equipment and mask the signals of the compounds of interest. Therefore, micropollutants either had to be removed from the salty matrix or the samples had to be diluted so that salt concentrations were within acceptable levels.

Analysis of Organic Properties

Ultra-violet absorbance (UVA) was measured as a surrogate for total organic carbon (TOC) because TOC at low concentrations is difficult to measure in the salty matrix of the draw solution. UVA was measured at a wavelength of 254 nm using a UV/VIS spectrophotometer (DU 800, Beckman-Coulter, Fullerton, CA) and a 1 cm quartz cell (SM 5910 B). In samples from selected experiments, TOC was measured directly with the combustion/NDIR method using a carbon analyzer (TOC-5000A, Shimadzu Scientific Instruments, Columbia, MD).

Analysis of Micropollutants

Organic micropollutants can be quantified by different methods. For samples containing micropollutants in the $\mu\text{g/L}$ range, high performance liquid chromatography (HPLC) can be used, usually without sample preparation. If micropollutants are present in a sample that contains high concentrations of total dissolved solids, HPLC analysis can be performed only if the sample is properly prepared and TDS is removed prior to analysis. For samples containing

micropollutants at concentrations in the ng/L range, gas chromatography/mass spectroscopy (GC/MS) can be used. However, GC/MS requires thorough sample preparation; including extraction, elution, and derivatization. In this study, both methods were tested and subsequently, only GC/MS method was used for analysis of organic micropollutants.

Solid Phase Extraction (SPE)

SPE is commonly used to concentrate organic micropollutants from aqueous solutions before GC/MS analysis. SPE can also be used very effectively to separate micropollutants from aqueous solutions containing high TDS concentrations. Therefore, all samples for organic micropollutant analysis in this study were extracted with SPE.

In SPE, 1-L of water sample is acidified to a pH of less than 2 and 1 percent methanol is added along with two 100 ng internal standards (diclofenac-d4 and ibuprofen-13C3). SPE cartridges are prepared by adding 1-g of RP-C-18 resin (Bakerbond Polar Plus, Mallinckrodt-Baker, Phillipsburg, NJ) to each 6 mL polyethylene filter cartridge. The cartridges are placed on a 12-port vacuum manifold (Fisher Scientific, Pittsburgh, PA) and conditioned with 5 mL of acetone, 10 mL of methanol, and 10 mL of DI water at pH of less than 2. The conditioning solutions are flushed through the resin one after the other in the above order while ensuring that air does not come in contact with the resin. After conditioning, the water sample is drawn through the cartridge at a flow rate of 3-5 mL/min by vacuum. Hydrophilic ions remain in the aqueous phase and are flushed through the column to waste. After extraction, 50 mL of DI water at a pH of less than 2 is used to rinse any remaining salts off the resin in the cartridge. The cartridge is then dried overnight under a stream of medical-grade nitrogen.

Gas Chromatograph / Mass Spectroscopy (GC/MS)

The GC/MS method used in this study was developed for several different micropollutants, but varies from the HPLC method. The GC/MS compounds, along with some compound properties are summarized in [Table 2.6](#).

Analysis of organic micropollutant with GC/MS requires several additional preparation steps after extraction. As with the HPLC method, the C-18 resin must be eluted to desorb the micropollutants; for GC/MS analysis, samples must also be derivatized to make the micropollutants amenable to gas chromatography.

Table 2.6
Properties of micropollutants studied (Kimura et al. 2003, Drewes et al. 2005)

Compound	Classification	Molecular Weight (g/mol)	Molecular Width (Å)	Log K _{ow}
Diclofenac	Analgesic	296.2	5.95	4.51
Gemfibrozil	Blood lipid regulator	250.3	6.65	4.39
Ibuprofen	Analgesic	206.3	5.23	3.97
Naproxen	Analgesic	230.3	5.22	3.18
Salicylic Acid	Skin medication	138.1	n/a	2.26
TCEP	Flame retardant	285.5	5.95	0.48

Organic compounds were eluted once with acetone into 2 mL GC/MS vials. The vials were dried, and 100 μ L of a pentafluorobenzyl bromide (PFBBBr) derivatization solution (2% in toluene) was added along with 4 μ L of triethylamine catalyst. The vials were heated in an oven at 100 °C for 1 hour. After cooling, the vials were dried again and dissolved in 100 μ L of toluene and transferred into a 200 μ L glass insert. The samples were then analyzed on an HP6890 gas chromatograph and a HP5973 quadrupole mass spectrometer (Agilent Technologies, Palo Alto, CA). [Figure 2.6](#) summarizes the steps required for sample preparation for HPLC or GC/MS analysis.

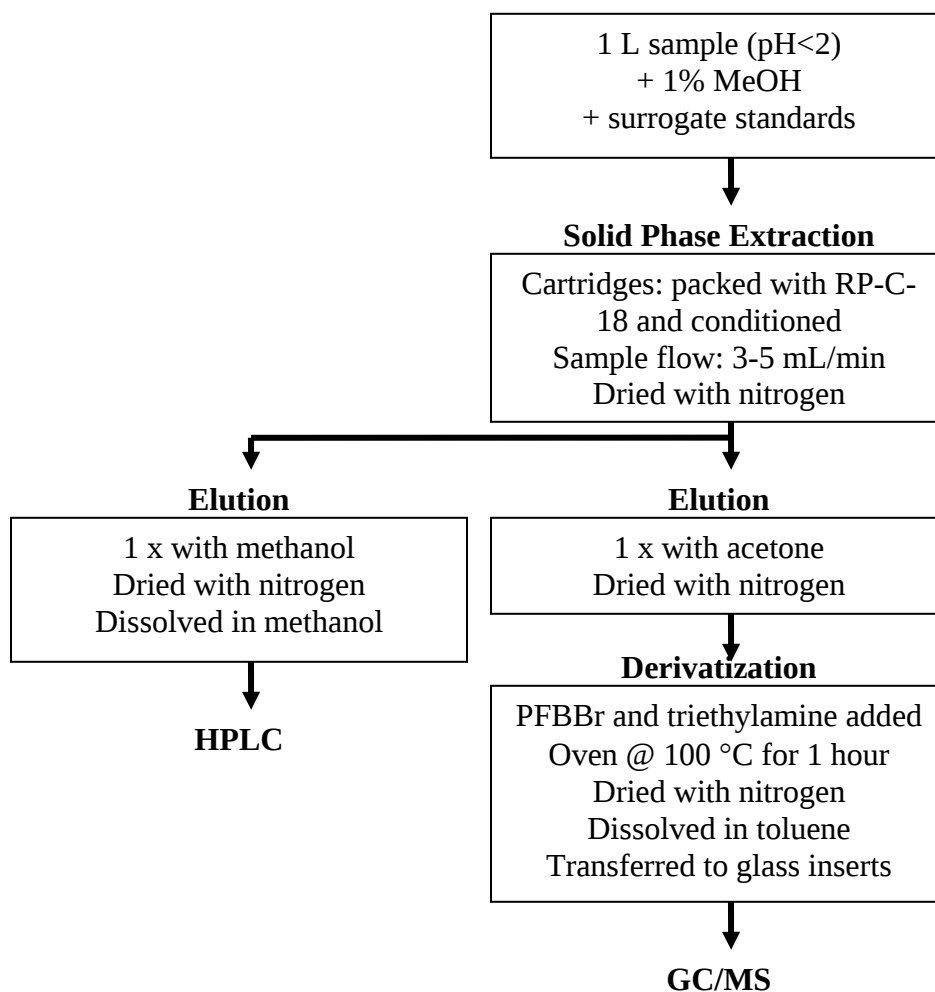


Figure 2.6 Steps for GC/MS and HPLC analysis of organic micropollutants at trace concentrations in aqueous solutions. Adapted from (Oldham 2008)

CHAPTER 3

RESULTS AND DISCUSSION

WATER FLUX

Benchmark forward osmosis experiments were conducted with DI water to determine the water flux and reverse salt transport across a virgin forward osmosis membrane. Experiments were conducted with seawater draw solution at various concentrations to elucidate the relationship between water flux and driving force. Water flux data were used to determine the baseline pure water permeability of the forward osmosis membrane and the effect of concentration polarization on the performance of the process. Experiments were also conducted with seawater draw solution and different impaired feed solutions, including secondary and nitrified effluents from domestic wastewater treatment plant and river water collected downstream from a wastewater treatment plant discharge. These experiments were conducted to determine the effect of feed water quality on water flux during forward osmosis of impaired water.

Pure Water Permeability

Pure water permeability experiments were conducted on the forward osmosis bench-scale test unit. The water temperature for all experiments was maintained constant at 19.0 ± 0.1 °C and the conductivity of the draw solution was constantly adjusted to be within ± 0.25 mS/cm of the predetermined experimental value. Results from the water permeability experiments are summarized in [Table 3.1](#) and water flux as a function of draw solution concentration is illustrated in [Figure 3.1](#). Experiments were conducted with concentrated and dilute draw solutions to determine the water flux across the entire range of draw solution concentrations that may be encountered when the draw solution is becoming diluted during the process. Results presented in [Table 3.1](#) and [Figure 3.1](#) illustrate that water flux is relatively low when the draw solution concentrations, and thus the driving forces, are low. At higher draw solution concentrations the flux is relatively higher, but still lower than fluxes usually observed in most pressure-driven membrane processes. Water flux also deviates from linearity at higher draw solution concentrations. This effect is due to dilutive internal concentration polarization, where the salt in the porous support layer of the membrane is diluted by pure water flowing from the feed into the draw solution. This phenomenon is unique to FO and is not observed in pressure-driven membrane processes like RO and NF (McCutcheon and Elimelech 2006). Based on results from this set of experiments, the average pure water permeability of the FO membrane used in this study was determined to be 0.365 LMH/bar ($1.014 \cdot 10^{-7}$ m/sec·bar).

The effect of concentration polarization can be seen in the divergence of the specific water flux and the permeability coefficient, as observed from the data summarized in [Table 3.1](#). Specific flux is calculated from the water flux across the membrane divided by the osmotic pressure difference across the membrane ($\Delta\pi$). However, the permeability coefficient (A) depends on an additional concentration polarization term (Eq. 2-4) and is calculated for each of the experiments using an iterative solver, solving for the concentration polarization factor (K) such that the permeability coefficient is constant across all draw solution concentrations. Thus, specific water flux decreases as the permeability coefficient remains unchanged. This analysis

yielded a concentration polarization term (K) value of 0.09 LMH^{-1} ($324,000 \text{ sec/m}$) which is similar to values published in the literature (McCutcheon and Elimelech 2006). As such, the declining value of specific flux at higher draw solution concentrations is due to an increased concentration polarization effect.

Table 3.1
Results from bench-scale experiments using DI water as a feed solution and increasing concentrations of sea salt draw solution. Feed and draw solution flow rates were 1.4 L/min.

Draw Solution Concentration (g/L sea salt)	Draw Solution Conductivity (mS/cm)	Water Flux (L/m ² -hr)	Temperature (°C)	Δ Osmotic Pressure (Bar)	Specific Water Flux (LMH/bar)	Permeability Coefficient: A (LMH/bar)
5	10.19	1.13	19.0	3.49	0.326	0.361
10	20.15	2.13	19.0	7.03	0.304	0.369
15	30.21	2.95	19.0	10.47	0.283	0.369
20	39.06	3.55	19.0	13.93	0.255	0.352
25	47.30	4.21	19.0	17.42	0.242	0.354
30	57.13	4.94	19.0	20.94	0.236	0.369
35	64.15	5.65	19.0	24.51	0.231	0.385
70	116.14	8.29	19.0	49.00	0.169	0.359

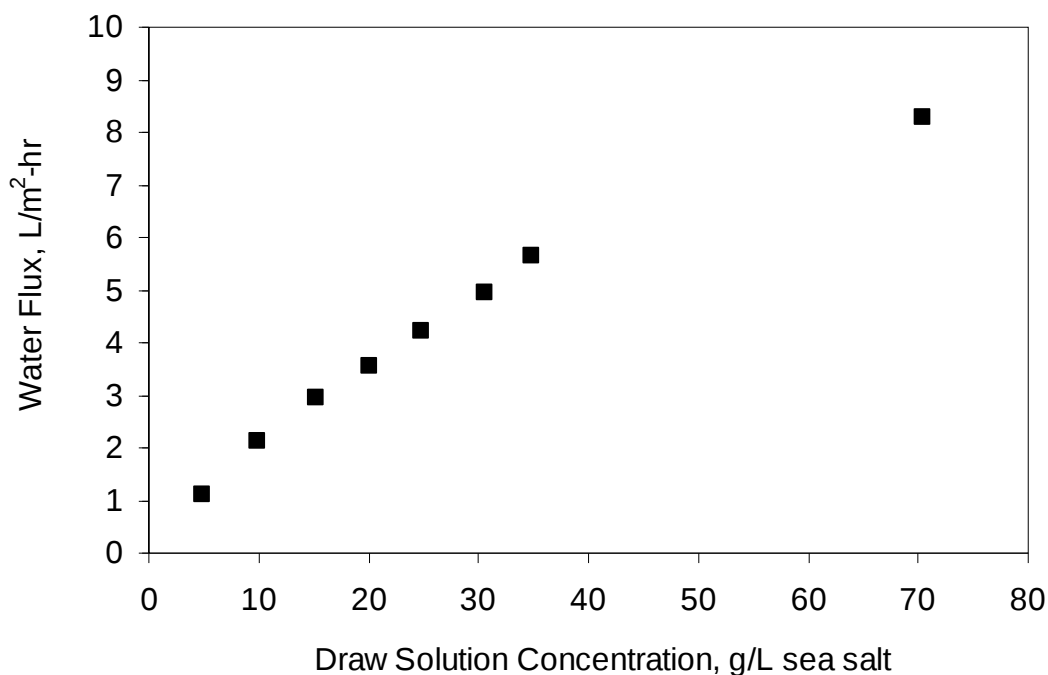


Figure 3.1 Water flux as a function of draw solution concentration during bench-scale benchmark experiments. Experiments were conducted with DI water feed, feed and draw solution temperatures of $19 \pm 0.1^\circ\text{C}$, and feed and draw solution flow rates of 1.4 L/min

Effect of Feed Water Quality on Water Flux

Following experiments with DI water feed, three sets of experiments were conducted with different feed solutions and with seawater draw solutions at different concentrations. Secondary and nitrified wastewater effluents from the Denver Water Recycling Plant and water from the South Platte River (Denver, CO) were used as feed solutions in these experiments.

Water flux as a function of draw solution concentration for the different feed solutions is illustrated in Figure 3.2. Each 4-hour experiment is represented as a single data point. Full data from a single set of experiments is illustrated in Figure 3.4. Very little difference in water flux was observed between the different feed waters. This is likely due to the low TDS concentration of the feed waters as compared to the draw solution. Even at the higher feed TDS concentration of the secondary and nitrified effluents (800 $\mu\text{S}/\text{cm}$), the draw solution concentration is much more dominant and limits the influence of feed solution osmotic pressure on water flux. More importantly, unlike in pressure-driven membrane processes, short-term, initial flux decline was not observed in these experiments even though the feed streams contained elevated concentrations of suspended solids and other contaminants that can foul membranes relatively quickly.

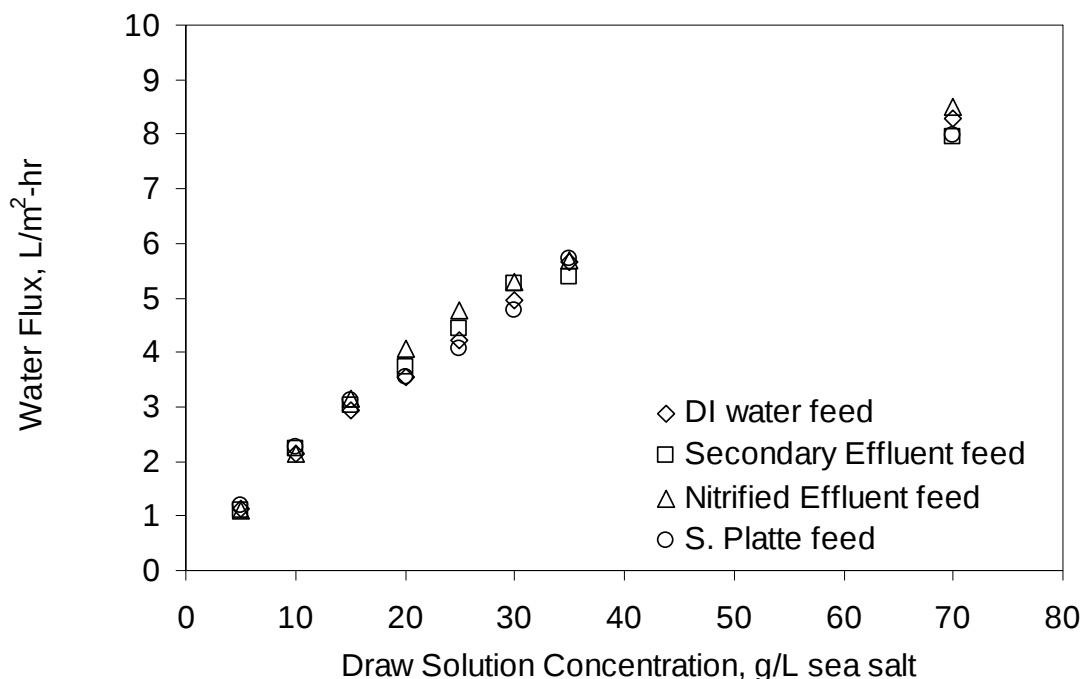


Figure 3.2 Water flux as a function of draw solution concentration for short-term bench-scale forward osmosis experiments with DI water, secondary effluent, nitrified effluent, or South Platte River water feeds. Experiments were conducted with feed and draw solution temperatures of 19 ± 0.1 °C and feed and draw solution flow rates of 1.4 L/min

Specific water flux as a function of draw solution concentration is illustrated in Figure 3.3 for the same data. As anticipated, specific flux declines at higher draw solution concentrations due to concentration polarization. Specific flux is consistently lower for the DI

water feed than the other feed solutions. This is likely because the low TDS of the DI water contributes to a relatively higher driving force. Complete data from these experiments is included in Appendix A.

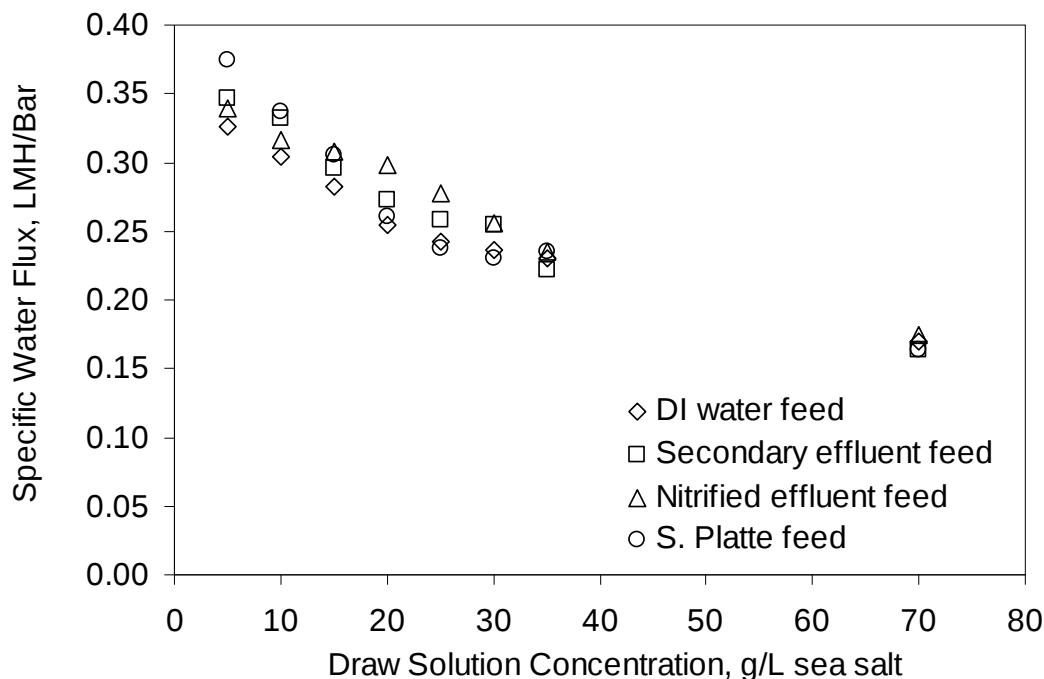


Figure 3.3 Specific water flux as a function of draw solution concentration for short-term bench-scale forward osmosis experiments with deionized water feed, secondary effluent water feed, nitrified effluent water feed, or South Platte River water feed. Experiments were conducted at feed and draw solution temperatures of 19 ± 0.1 °C and feed and draw solution flow rates of 1.4 L/min

Results indicate that under the conditions tested in the laboratory, water flux is highly dependant on driving force and draw solution concentration. Additionally, concentration polarization has an increasing effect on water flux when the driving force increases. Therefore, there is a diminishing return on additional driving force, and the process becomes increasingly inefficient at higher draw solution concentrations. However, in the application tested in this study, where seawater or concentrated brine from seawater desalination is used as draw solution, this has limited importance because no additional energy is directly needed to concentrate or reconcentrate the draw solution; it is a natural resource or a by-product of desalination processes.

FORWARD OSMOSIS MEMBRANE FOULING

During the short bench-scale FO experiments, water flux remained relatively constant (Figure 3.4) and therefore, membrane fouling was most likely very minimal. This can be attributed to several factors including low osmotic pressure of the feed solution and limited transport of foulants to membrane due to lower water flux. Yet, it is likely that the combination of a very hydrophilic membrane, low operating pressure process, and low fowling potential in

the feed water played a more important role in maintaining low membrane fouling during the short-term bench-scale experiments. It is known that pressure-driven membrane processes (specifically NF and RO) under similar experimental conditions (e.g., flux, temperature, and feed characteristics) experience more substantial flux decline and membrane fouling (Agenson and Urase 2007).

Because, in the current application, a combined FO/RO process will be used in conjunction with impaired water sources, the effect of membrane fouling on water flux is critical for process longevity and feasibility, especially because water flux through forward osmosis membrane is relatively low. Therefore, longer-term experiments with typical impaired feed water were needed to determine the fouling propensity of the various feed streams.

The pilot-scale combined FO/RO system was deployed at the DWRP. Initially, the forward osmosis membrane cell was installed with the feed solution flow channel on top and the draw solution flow channel on the bottom; thus, the diffusion of water through the membrane was downward. The forward osmosis membrane was oriented with the dense side facing upward in contact with the feed solution, and the porous support side of the membrane faced the draw solution.

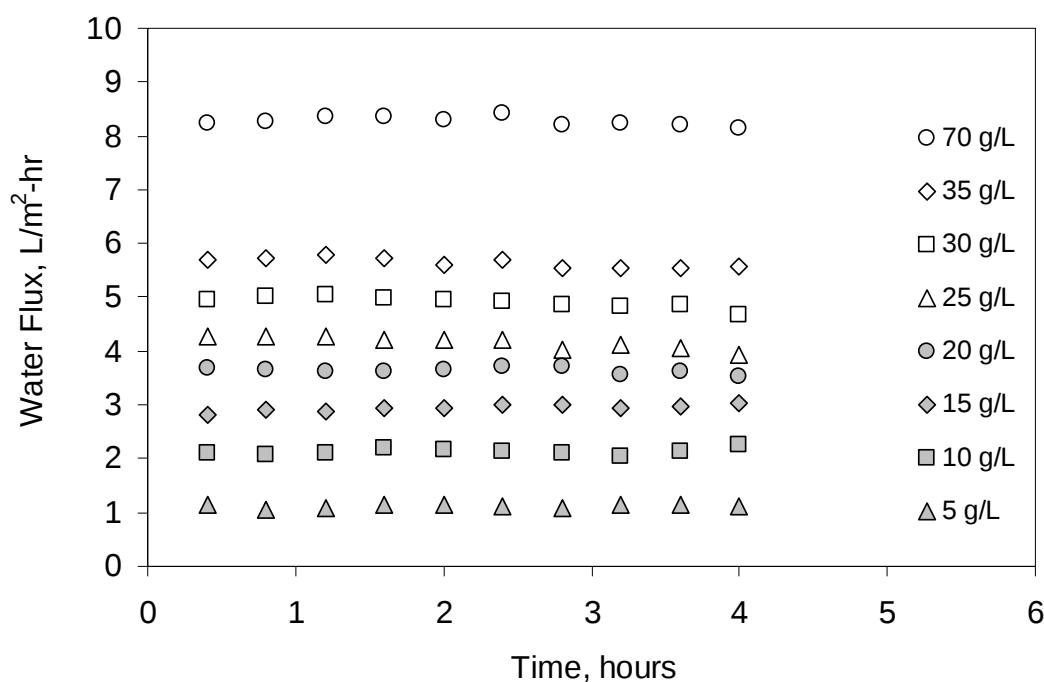


Figure 3.4 Water flux as a function of time during bench-scale experiments of different draw solution concentrations and secondary effluent feed solution. Experiments were conducted with feed and draw solution temperatures of 19 ± 0.1 °C and feed and draw solution flow rates of 1.4 L/min.

Initial experiments were conducted with secondary effluent feed from the MWRD, in Denver, CO, and the draw solution was maintained at a constant concentration of 35 g/L sea salt. The feed flow rate was initially regulated with a valve to maintain 2.4 L/min. Water flux as a function of time for the seven-day experiment is illustrated in [Figure 3.5](#). During the first day,

the feed flow rate was unstable and changed when the pressure in the plant's influent pipeline changed. Due to variability in the feed flow rate to the forward osmosis membrane cell, water flux through the forward osmosis membrane was low and fluctuated over the first 24 hours (Figure 3.5). Consequently, a pump was installed to maintain a constant feed flow rate.

During operation over the following days, it was observed that suspended solids broke through the 50-mesh (279 micron) strainer installed on the feed line and started to accumulate on the feed side of the forward osmosis membrane. The membrane cell with accumulated solids is shown in Figure 3.6. With the thick layer of solids on the membrane, flux decline was moderate (Figure 3.5).

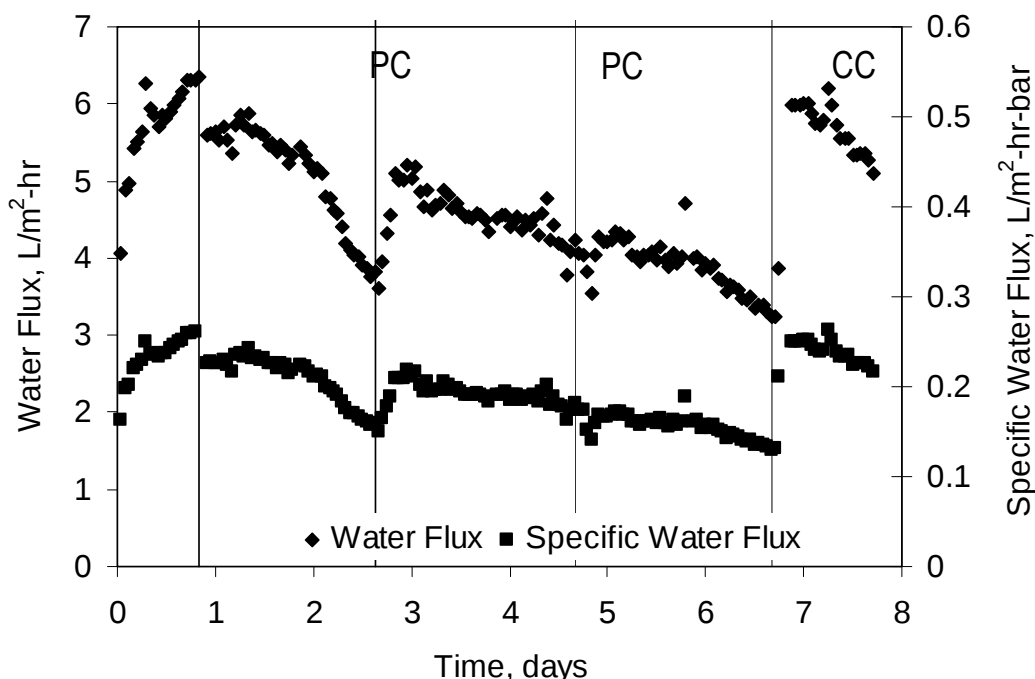


Figure 3.5 Water flux as a function of time during the pilot-scale forward osmosis experiment with 35 g/L sea salt draw solution and secondary effluent feed solution. PC indicates physical cleaning and CC indicates chemical cleaning. The experiment was conducted with feed and draw solution temperatures of 22 ± 0.5 °C and flux data was corrected to 19 °C

On the third and fifth days of testing, physical cleaning of the membrane was performed. This procedure involved increasing the feed flow rate to 4 L/min for approximately three minutes, and thus flushing solids that accumulated on the forward osmosis membrane out of the membrane cell. On the seventh day, a short chemical cleaning was performed with a surfactant (Citranox, Alconox, Inc., White Plains, NY) that was diluted to a pH of 3. The cleaning solution was recirculated through the feed channel of the forward osmosis membrane cell for approximately 30 minutes at 2.4 L/min. The pH was then increased to 8 with sodium hydroxide (Fisher Scientific, Waltham, MA), and circulated through the feed solution channel of the forward osmosis membrane cell for another 30 minutes, after which the feed channel was rinsed with 20 L of DI water before being returned to service. Results in Figure 3.5 show that physical

cleaning restored much of the water flux that was lost due to fouling on the membrane and chemical cleaning completely restored the water flux to its initial level.

While initial water flux values for the bench-scale and pilot-scale experiments were similar, in the longer-term pilot-scale experiment, flux declined more rapidly when solids accumulated on the forward osmosis membrane. Prior to chemical cleaning, water flux declined to approximately 50 percent of its initial level. Similar to the bench-scale results, there was minimal flux decline early in the experiment until approximately the middle of the second day. Specific flux (flux normalized to the instantaneous driving force) is also shown in Figure 3.5 and increases slightly relative to water flux due to a small loss of driving force over the course of the experiment.

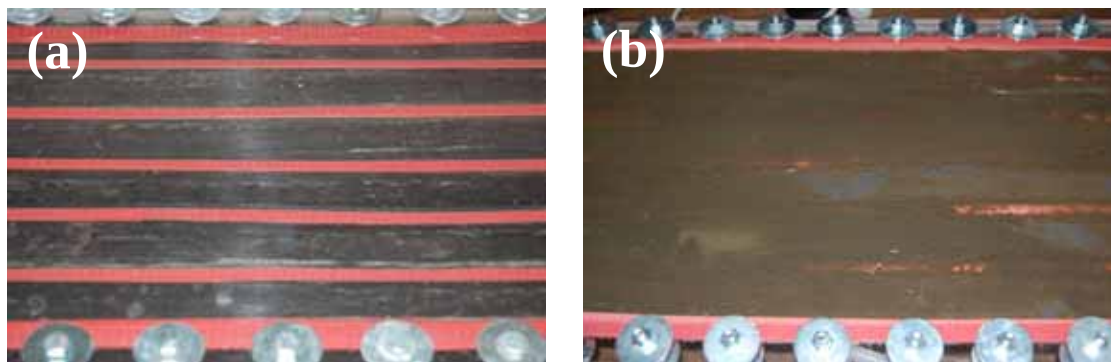


Figure 3.6 Pilot-scale forward osmosis membrane cell (a) before experiment and (b) after seven-days of operation (before chemical cleaning). Experiment conducted with 35 g/L sea salt draw solution and secondary effluent feed solution. Feed and draw solution temperatures were 22 ± 0.5 °C. Feed and draw solution flow rates were 2.4 L/min. Nitrile rubber strips were used as spacers in the draw solution channel. No spacer was used in the feed solution channel

Effect of Feed Water Quality on Membrane Fouling

A shorter-term experiment was conducted with the forward osmosis membrane cell oriented with the feed side facing down. All other operating conditions were maintained constant. It was expected that flow and gravity would prevent accumulation of solids on the membrane surface and in the feed channels, possibly eliminating flux decline due to membrane fouling. The experiment was conducted for three days without membrane cleaning. Water flux as a function of time for this experiment is illustrated in Figure 3.7. Results revealed that with the new configuration, water flux declined very minimally as compared to the flux decline observed when the feed channel was facing up; likely because of a decrease in membrane fouling. Comparing Figure 3.6 and Figure 3.8, it can be seen that much fewer solids accumulated in the feed channels of the membrane cell when oriented with the feed channel on the bottom. Solids that did accumulate in the feed channel settled onto the side plate of the membrane cell, not the membrane itself.

During experiments with the membrane cell oriented with the feed channel down, spacers were needed in the feed channel due to sagging of the membrane. With the addition of the nitrile rubber spacers in the feed channel, the flow in the forward osmosis cell once again became

hydraulically unstable. Vibration of the membrane was observed similar to the initial bench-scale experimentation. To hold the membrane tight and to determine the effects of dilutive external concentration polarization, turbulence enhancing mesh spacers were also installed in the draw solution channel of the forward osmosis membrane cell.

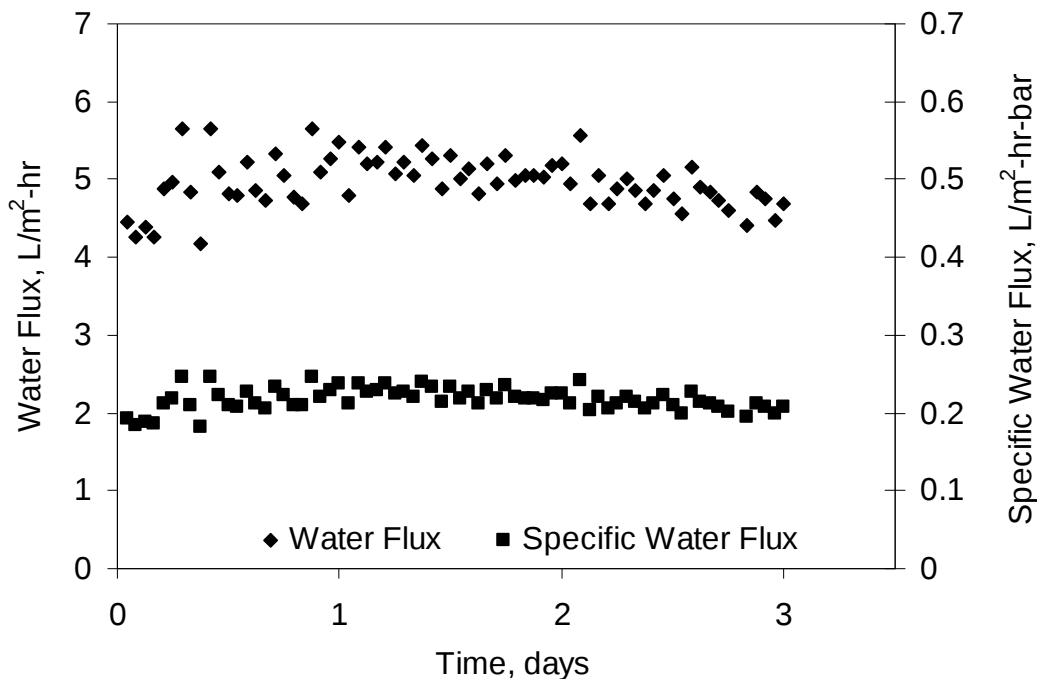


Figure 3.7 Water flux as a function of time for pilot-scale forward osmosis experiment with the feed channel of the membrane cell facing down. Experiment conducted with 35 g/L draw solution concentration and secondary effluent feed solution. Feed and draw solution temperatures were 22 ± 0.5 °C and flux data was corrected to 19°C. Feed and draw solution flow rates were 2.4 L/min.



Figure 3.8 Photograph showing the feed side of the inverted forward osmosis membrane cell after three days of operation with no cleaning (The feed channel of the membrane cell is under the membrane)

To elucidate the effect of suspended solids on flux decline, experiments were conducted with tertiary effluent feed water and several draw solution concentrations, including 20, 35, or 70 g/L sea salt. Water flux as a function of time is illustrated in Figure 3.9 for the three experiments. All three experiments were conducted with the feed channel under the membrane. The experiment with 35 g/L draw solution was operated continuously for almost 14 days without any cleaning at an average water flux of 7.2 LMH ($2.0 \cdot 10^{-6}$ m/sec). Flux decline was minimal for the entire 14 days. Experiments with 20 g/L and 70 g/L draw solution concentrations were conducted for a shorter time; these experiments were operated until approximately 250 L of water were produced. As illustrated in Figure 3.9, average flux was approximately 4.3 LMH ($1.19 \cdot 10^{-6}$ m/s) for the experiment conducted with 20 g/L draw solution concentration and approximately 8.7 LMH ($2.42 \cdot 10^{-6}$ m/s) for the experiment with 70 g/L draw solution concentration. A slight flux decline was observed during the experiment with 70 g/L draw solution, likely due to the increased draft of foulants towards the membrane at higher water flux. These relatively long-term experiments illustrate the extremely low fouling propensity of the forward osmosis process, and the ability of the forward osmosis membrane to treat large volumes of water with virtually no need for flux recovery.

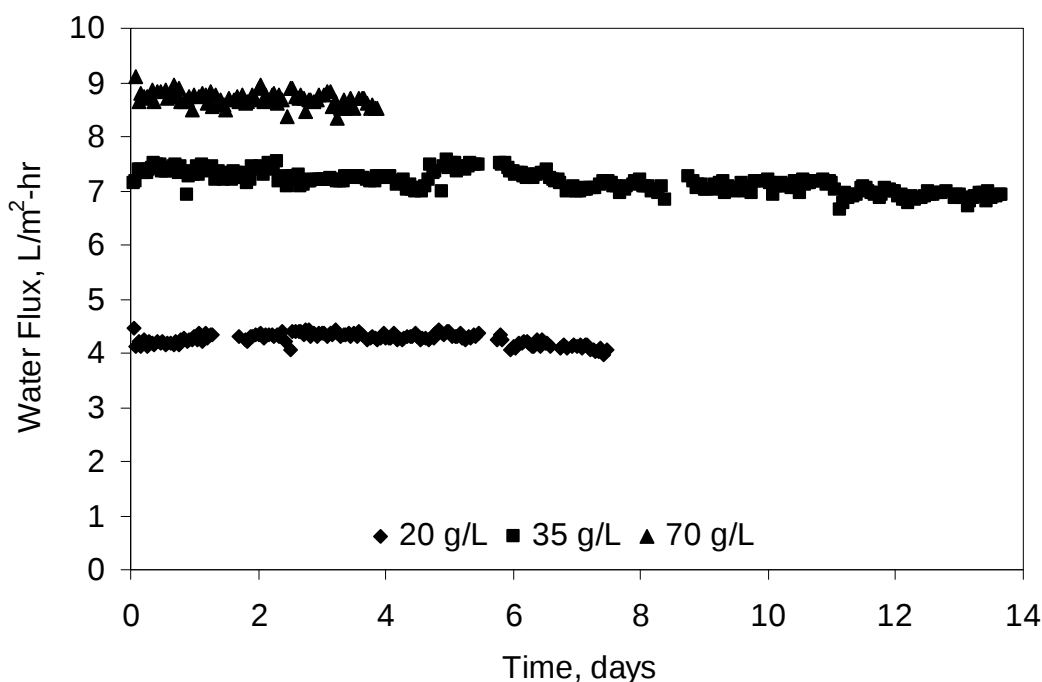


Figure 3.9 Water flux as a function of time for pilot-scale forward osmosis experiment with 20, 35, or 70 g/L sea salt draw solution and tertiary effluent feed solution. The experiment was conducted with feed and draw solution temperatures of 22 ± 0.5 °C and flux data was corrected to 19 °C. The feed solution channel is facing down.

Water flux during the pilot-scale experiment with draw solution concentration of 35 g/L was consistently higher than the bench-scale results. This is likely due to improved turbulence in the draw solution channel of the forward osmosis membrane decreasing concentration polarization. Variances in the specific sample of membrane used, the area of the membrane

which is fully effective, as well as slight hydraulic differences in the membrane cell may also play a role in the water flux discrepancy.

SOLUTE TRANSPORT IN FORWARD OSMOSIS AND THE COMBINED FO/RO PROCESS

In addition to studying water flux and fouling rates in forward osmosis of impaired water, solute transport was investigated to determine the capability of the dual barrier membrane system to reject both organic and inorganic constituents.

Inorganic Solute Transport in the FO/RO System

Transport of inorganic solutes across forward osmosis membranes is very important and in specific cases may determine the feasibility of the hybrid FO/RO process. Unlike transport of solutes in pressure driven membrane processes, solutes in forward osmosis diffuse in both directions, from the feed to the draw solution and from the draw solution to the feed. Due to the high concentration of solutes in the draw solution, more ions diffuse from the draw solution into the feed solution (i.e., reverse diffuse); thus, the transport of ions both decreases the osmotic pressure of the draw solution and potentially contaminates the feed solution.

The reverse diffusion of TDS was measured during the experiments in this study both to test membrane integrity and to evaluate process longevity. In this study, reverse salt flux, or TDS flux, is defined as the flux of salts through the membrane in the reverse direction divided by the flux of water through the membrane in the forward direction. This yields a transport unit of milligrams of salt (crossing the membrane from the draw solution to the feed solution) per liter of water being produced (from feed solution to draw solution).

TDS flux as a function of draw solution concentration is illustrated in [Figure 3.10](#) for bench-scale experiments conducted with different feed solutions and various concentrations of seawater draw solution. TDS flux across the forward osmosis membrane that was used in this study ranged from 400 to 600 mg/L; these values are within the range of results obtained in previous studies (Cath et al. 2005) and confirm that membrane integrity was not compromised.

Results in [Figure 3.10](#) indicate that feed solution chemistry affects solute flux at lower draw solution concentrations, and that TDS flux for the different feed solutions converges at higher draw solution concentrations. This is likely because, as the water flux through the membrane increases, the faster diffusion of water hinders the reverse diffusion of salts through the membrane.

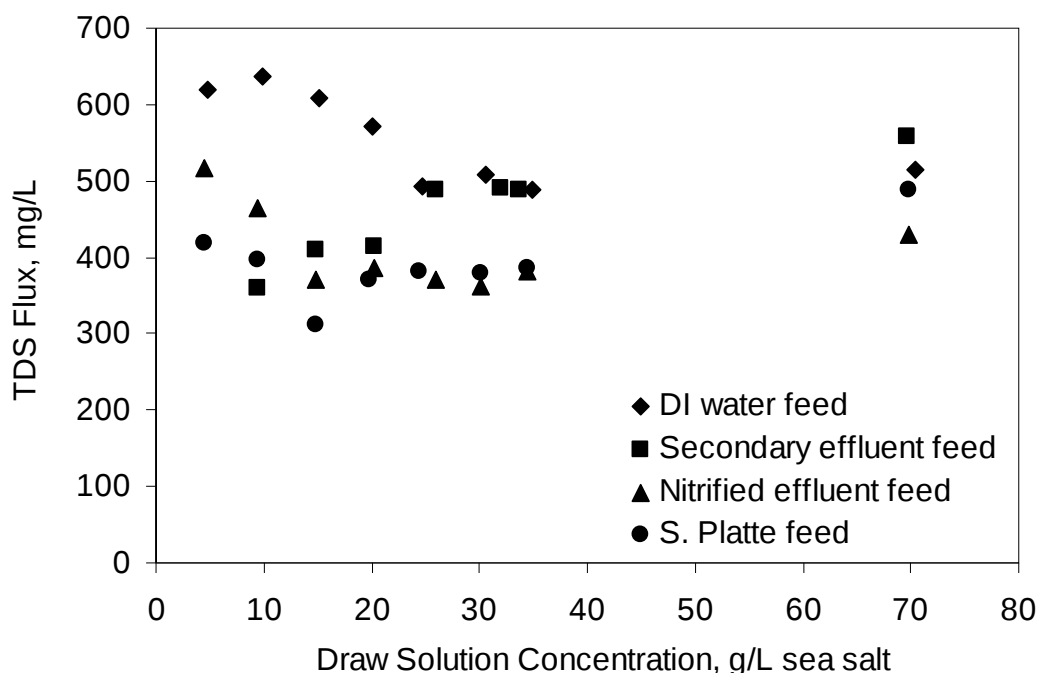


Figure 3.10 Reverse salt diffusion as a function of draw solution concentration for various feed and draw solutions during bench-scale forward osmosis experiments. Temperature of the feed and draw solution streams was $19 \pm 0.1^\circ\text{C}$, and feed and draw solution flow rates were 1.4 L/min

Reverse diffusion of the major ions is summarized in [Table 3.2](#) for the bench-scale experiment conducted with 35 g/L sea salt draw solution and DI water as the feed solution. Chloride and sodium account for a large fraction of the diffusing TDS; this is due to sodium and chloride being the major ions in the draw solution. The data for specific ion diffusion show that chloride and sodium diffusion are approximately equal, on a molar basis. Thus, transport did maintain electro-neutrality of the solutions. Conversely, due to an opposite chemical concentration gradient, several ions diffused from the feed solution into the draw solution; most notably sulfate. The higher concentration of sulfate in the feed solution was due to the sodium meta-bisulfate that was used to reduce residual chlorine that may have been present in the DI water. While TDS diffusion gives a rough estimate of how ions are transported through the membrane, specific ion transport is much more complicated and can involve many different diffusion mechanisms. Research is ongoing on the mechanisms of specific ion diffusion during forward osmosis (Hancock and Cath 2008).

Transport of other inorganic constituents was also analyzed on samples collected during the pilot-scale experiments. Ammonia and nitrate are relatively difficult to remove from impaired water sources with membrane treatment; therefore, transport of both contaminants was specifically studied at the pilot scale.

Table 3.2

Reverse ion diffusion for bench-scale experiment with 35 g/L sea salt draw solution and deionized water feed solution. Experiment was conducted at 19±0.1 °C and 1.4 L/min feed and draw solution flow rates (Note that mass values are for the entire 12 L feed solution loop)

Ion	Initial mass in feed loop	Final mass in feed loop	Change in mass in feed loop	Mass of ion per volume of water produced
	(mg)	(mg)	(mg)	(mg/L)
F ⁻	0.4	0.3	-0.1	-0.09
Cl ⁻	44.1	217.8	173.6	270
Br ⁻	0.4	1.3	0.9	1.4
NO ₃ ³⁻	0.7	0.7	0.0	-0.04
PO ₄	n.d.	n.d.	n/a	n/a
SO ₄	82.1	76.9	-5.3	-8.2
B	0.4	1.2	0.8	1.24
Ca ²⁺	2.8	3.7	0.9	1.4
K ⁺	10.2	15.6	5.4	8.4
Mg ⁺	1.0	2.9	1.8	2.9
Na ⁺	50.8	149.2	98.4	153

At DWRP, ammonia and nitrate were both present in the secondary effluent feed water at concentrations of approximately 5 mg/L-N. Water samples were collected during the 13-day experiment from the feed stream, draw solution, and RO permeate of the FO/RO system. The concentrations of ammonia and nitrate are summarized in [Figure 3.11](#) and [Figure 3.12](#), respectively. Ammonia was present at relatively stable levels in the feed stream and slowly diffused through the forward osmosis membrane into the draw solution. However, ammonia was moderately rejected by the RO membrane and, consequently, was accumulated in the draw solution closed loop. Yet, results in [Figure 3.11](#) show that the ammonia level in the draw solution stabilized at concentration slightly higher than its concentration in the feed. This likely indicates that under the tested conditions, zero net transport of ammonia through the forward osmosis membrane was reached when the ammonia concentration in the draw solution was approximately 8 mg/L and the feed concentration approximately 6 mg/L. Nonetheless, in an open draw solution loop, such as in a proposed full-scale process, ammonia would not be accumulated but discharged with the concentrated brine after RO. The RO permeate contained very low concentrations of ammonia and this illustrates the ability of the hybrid system to consistently produce very high quality water.

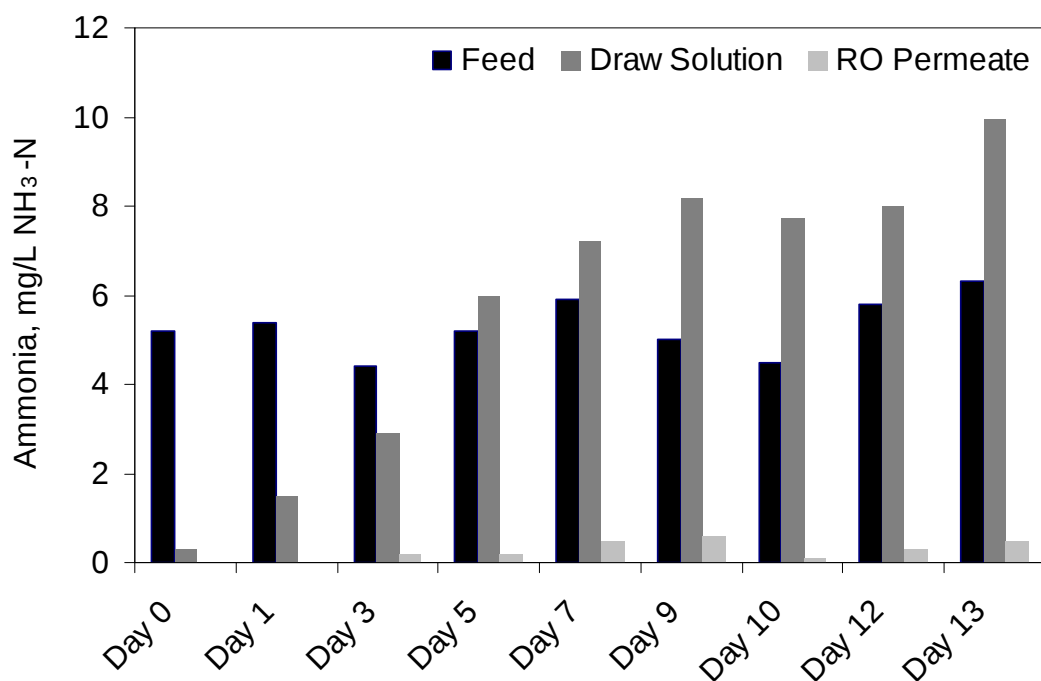


Figure 3.11 Ammonia concentrations as a function of time in the feed, draw solution, and RO permeate during pilot-scale forward osmosis experiment with 35 g/L sea salt draw solution and secondary effluent feed. The temperature of the feed and draw solutions was 22 ± 0.5 °C and the feed and draw solution flow rates were 2.4 L/min.

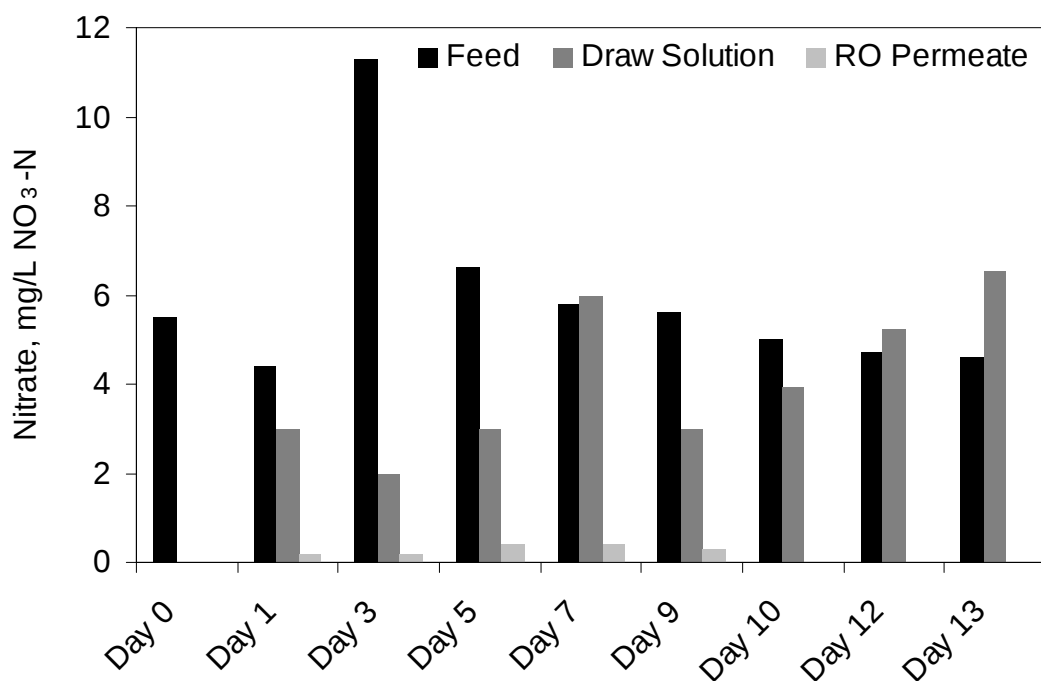


Figure 3.12 Nitrate concentrations as a function of time in the feed, draw solution and RO permeate streams during pilot-scale forward osmosis experiment with 35 g/L sea salt draw solution concentration and secondary effluent feed solution.

Nitrate was also found at relatively constant levels in the secondary effluent feed solution, with the exception of one spike on the third day. The high level on this day is most likely due to a short-term change in the blending of the water received by the DWRP, however, it is unknown how long this spike might have lasted. Nitrate was also accumulated in the draw solution loop and unlike ammonia, it reached a similar average concentration in the draw solution as in the feed solution.

The concentration of nitrate and ammonia in the forward osmosis and RO permeates were determined by calculating the mass flow rate and dividing by the water flow rate through the forward osmosis. Using this information, the rejection of nitrate and ammonia by the forward osmosis and reverse osmosis membranes was calculated and is summarized in [Table 3.3](#). Results indicate that both the forward osmosis and RO membranes provided moderate rejection of ammonia and nitrate, but the total system rejection (i.e., combined forward osmosis and RO) was relatively high. Thus, even with a high concentration of nitrate and ammonia in the draw solution closed loop, there was still good rejection of ammonia and nitrate by the FO/RO system as a whole. Overall, the multiple barrier approach for both ammonia and nitrate was demonstrated to be effective. Rejection of nitrogen was good (exceeding 94%) and the RO membranes were protected from fouling. At full-scale, the process would likely perform even better because of the lack of accumulation of contaminants in an open draw solution loop.

Table 3.3
Ammonia and nitrate rejection by the forward osmosis and RO membranes and combined system rejection for the pilot-scale FO/RO experiment with 35 g/L draw solution concentration and secondary effluent feed solution. The temperature of the feed and draw solutions were 22±0.5 °C and feed and draw solution flow rates were 2.4 L/min.

	FO Membrane	RO Membrane	Total System
Ammonia Rejection	74%	77%	94%
Nitrate Rejection	78%	82%	97%

Organic Solute Transport in the FO/RO System

High rejection of organic solutes is necessary for process sustainability. UV absorbance was measured during several experiments and used as a surrogate for DOC. UV data was used to determine the overall rejection of organic solutes in the FO/RO process. Concentrations of specific organic solutes were also measured during selected experiments to determine what factors may govern organic solute transport, as well as to determine the ability of the hybrid FO/RO system to reject emerging contaminants.

UV absorbance at 254 nm was used as a proxy for aromatic DOC and results are illustrated in [Figure 3.13](#). Similar to ammonia and nitrate, UV absorbing compounds were moderately rejected by the forward osmosis membrane and more highly rejected by the reverse osmosis membrane, causing these compounds to accumulate in the closed draw solution loop. However, UV absorbance was almost not quantifiable in the permeate of the FO/RO system. The UV absorbance of the forward osmosis and RO permeates were determined and suggest very high rejection of organic matter containing aromatic moieties through both the forward osmosis and RO membrane. UV absorbing compound rejection is summarized in [Table 3.4](#).

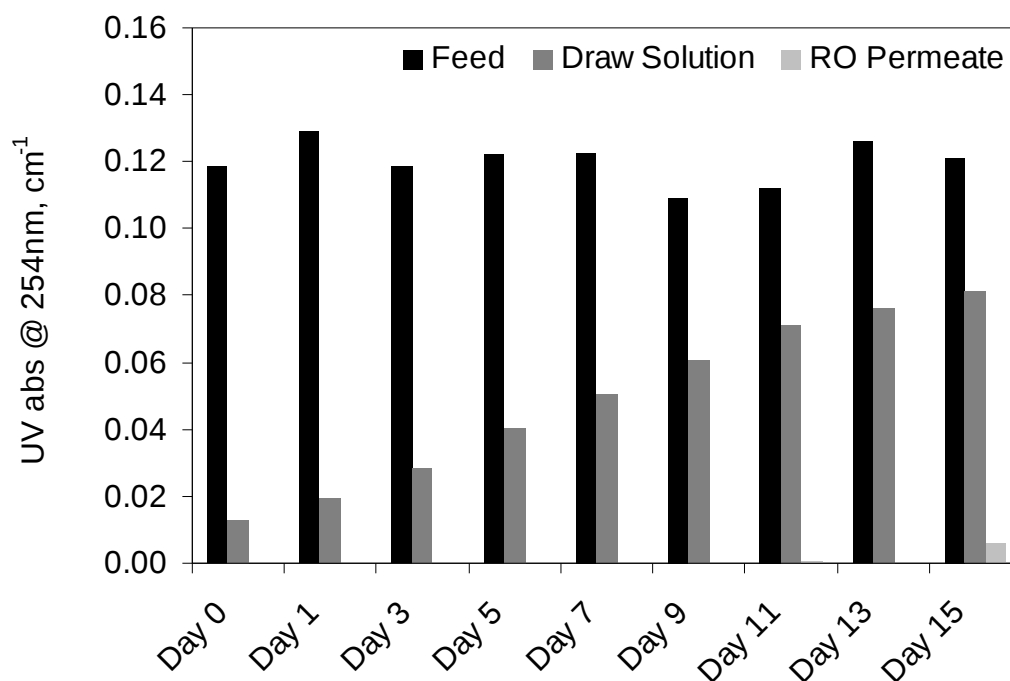


Figure 3.13 UV absorbance at 254 nm as a function of time in the feed, draw solution, and permeate streams for pilot-scale forward osmosis experiment with 35 g/L draw solution concentration and secondary effluent feed water.

Table 3.4

Rejection of UV absorbing compounds during pilot-scale forward osmosis experiment with 35 g/L draw solution concentration and secondary effluent feed by forward osmosis membrane, RO membrane, and total system. The temperature of the feed and draw solutions was 22±0.5 °C and the feed and draw solution flow rates were 2.4 L/min.

	UVA Rejection
FO Membrane	85%
RO Membrane	99%
Total System	>99.9%

Transport of select organic micropollutants was studied at both bench- and pilot-scale. Bench-scale experiments were conducted with deionized feed water and a 35 g/L draw solution to determine micropollutant rejection by a virgin membrane not compromised by fouling. Results in [Table 3.6](#) indicated that the compounds studied were all well rejected by a virgin forward osmosis membrane.

To determine the effect of fouled forward osmosis membrane on rejection of organic micropollutants, secondary effluent feed solution and 35 g/L sea salt draw solution were used during a longer-term pilot-scale experiment. During this experiment, streams were analyzed for target organic micropollutants using GC/MS. Only six of the 14 micropollutants analyzed for were detected in the secondary effluent feed water. The concentrations of the six micropollutants

in the feed, seawater draw solution, and RO permeate of the pilot-scale FO/RO system measured on the eighth day are summarized in Table 3.5. The micropollutants that were present in the feed varied in concentrations between 100 and 1,000 ng/L. Over the course of the eight-day experiment, micropollutants were slowly accumulated in the draw solution loop. However, unlike ammonia and nitrate, gemfibrozil was accumulated and exceeded the concentration observed in the feed. Additionally, only ibuprofen and TCEP were detected in the RO permeate, and at very low levels.

The concentration of each of the micropollutants in the forward osmosis and reverse osmosis permeates was calculated and used to determine the rejection through each of the membranes. Rejection values were averaged and are summarized in Table 3.6 and illustrated in Figure 3.14. Note that the concentrations reported in Table 3.5 were measured on day eight, at the end of the experiment. While four of the compounds were not detected in the permeate, the rejection summarized in Table 3.6 is less than 100 percent due to low concentrations that were detected earlier in the experiment and included in the average. All the results from the micropollutant analysis are included in Appendix B.

Table 3.5
Concentration of organic solutes after eight days of operation for pilot-scale forward osmosis experiment with 35 g/L draw solution concentration and secondary effluent feed. The temperature of the feed and draw solutions was 22±0.5 °C and the feed and draw solution flow rates were 2.4 L/min (n.d. – not detected)

	Diclofenac	Gemfibrozil	Ibuprofen	Naproxen	Salicylic Acid	TCEP
	(ng/L)					
Feed	155	960	385	435	360	800
Draw	65	1650	255	360	85	625
RO Permeate	n.d.	n.d.	33	n.d.	n.d.	70

Table 3.6
Rejection of organic solutes during; bench-scale 35 g/L draw solution with deionized water feed by forward osmosis membrane, and pilot-scale forward osmosis experiment with 35 g/L draw solution concentration and secondary effluent feed by forward osmosis membrane, RO membrane, and total system. The temperature of the feed and draw solutions was 22±0.5 °C and the feed and draw solution flow rates were 2.4 L/min.

	Diclofenac	Gemfibrozil	Ibuprofen	Naproxen	Salicylic Acid	TCEP
Bench-scale FO Membrane	>99%	80%	n/a	90%	72%	n/a
Pilot-scale FO Membrane	89%	78%	87%	85%	>99%	31%
Pilot-scale RO Membrane	>99%	78%	64%	94%	>99%	94%
Pilot-scale Total System	>99%	97%	93%	98%	>99%	95%

Results in Table 3.6 and Figure 3.14 confirm that the forward osmosis membrane provided relatively high rejection of most of the targeted organic micropollutants, and the remainder were well removed by the RO membrane; four of the six micropollutants could not be detected in the RO permeate at the end of the experiment. Micropollutant rejection through the RO membrane for gemfibrozil, ibuprofen, and naproxen was lower than seen in other studies (Xu et al. 2005). This is likely due to the low cross-flow velocity at which the RO was operated (Table 2.4). The only micropollutants that were detected in the RO permeate after eight days of operation were ibuprofen (analgesic) and TCEP (chlorinated flame retardant). TCEP is a common flame retardant in many plastic products (including PVC pipe and fittings) and is prevalent in many wastewaters. Because TCEP is a compound used in PVC, it is possible that it was leached into the draw solution and RO permeate streams from the plastic parts that are used in the RO sub-system. An experiment was conducted to determine if TCEP was being leached in the RO sub-system. Deionized water with 1 g/L sea salt was used as a feed solution to the RO sub-system and water was continuously treated and recycled for 48-hours. Samples were collected for TCEP analysis before and after operation. Results were inconclusive, but suggest that minimal leaching of TCEP from the plastic indeed occurred.

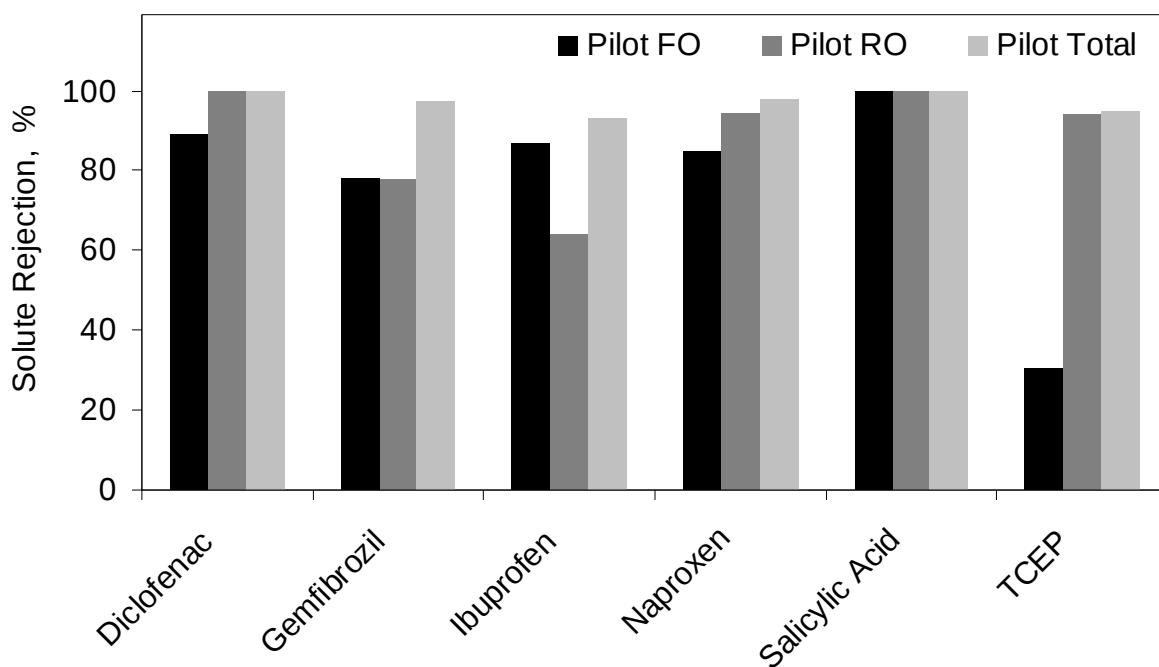


Figure 3.14 Rejection of micropollutants during pilot-scale forward osmosis experiment with 35 g/L draw solution concentration and secondary effluent feed by forward osmosis membrane, RO membrane, and total system. The temperature of the feed and draw solutions was 22 ± 0.5 °C and the feed and draw solution flow rates were 2.4 L/min.

Overall, rejection of both organic and inorganic solutes proved to be very good, with total system rejection of greater than 97 percent for most solutes. Additionally, while accumulation of micropollutants and loss of salt from the draw solution are important when operating the draw solution in a closed loop, operating in an open loop would not allow micropollutants to

accumulate and would continuously refresh salts lost from the draw solution. Therefore, process performance during full-scale would likely be superior to the pilot-scale.

The rejection of organic compounds by the forward osmosis membrane also allowed the RO sub-system to be operated continuously with no fouling and no cleaning needed. Thus, the RO membranes were effectively protected from the wastewater effluent feed solution.

ECONOMIC FEASIBILITY

With any semi-permeable membrane process, feasibility strongly depends on economics. In a pressure-driven membrane processes such as RO or NF, economic feasibility maximized by the optimal recovery of pure water from saline water. Higher recoveries increase the reject concentration and increase energy requirements. Conversely, lower recovery desalination, while using less energy for RO, inefficiently uses and spends more energy on pretreatment of feed water.

In an osmotically driven membrane process such as forward osmosis, the draw solution is diluted when recovery increases. This dilution decreases the driving force, and subsequently the water flux through the membrane. This increases the required membrane surface area to achieve the additional water production. The maximum economically feasible recovery depends on the osmotic pressure and flow rates of the streams.

To determine the maximum economically feasible recovery, a combined forward osmosis/reverse osmosis model was developed which simulates increasing recoveries as a function of TDS concentrations and flow rates of the streams, characteristics of the forward osmosis membrane, capital cost of forward osmosis per unit area, and cost of energy. The model can be configured to either increase water flux through the RO system (constant energy) or decrease the energy demand of the RO system (constant flux). Impaired water recovery can be increased incrementally and feasibility is determined at each unit increase in impaired water recovery. Water flux and performance data from this study were used to configure the model, and a schematic of the model flow streams is illustrated in [Figure 3.15](#).

In the constant flux model, the RO influent stream flow rate is held constant and the flow rate of water across the forward osmosis membrane is increased in steps of 1 percent of the RO influent flow rate. At each step the incremental capital cost of the forward osmosis system is calculated, along with the incremental energy savings due to dilution of the RO influent. The return on investment ratio is calculated at each 1 percent step, and when the ratio becomes less than the acceptable ratio for an investor (assumed to be 2 for this study), additional forward osmosis dilution is no longer economically feasible.

As an example, a simulation of a small desalination plant was generated and energy reduction by forward osmosis dilution was modeled. Operational characteristics are summarized in [Table 3.7](#). The results in [Figure 3.16](#) illustrate that dilution of seawater with impaired water was economically feasible up to approximately 57 percent recovery of impaired water. Beyond 57 percent recovery, the area of forward osmosis membrane needed increases asymptotically and to a maximum impaired water recovery of approximately 90 percent. Additionally, at 57 percent impaired water recovery, the energy cost of desalination is reduced to approximately 55 percent of the initial, non-diluted cost. Assuming an interest rate of 10 percent and 15-year amortization, the yearly capital cost of the forward osmosis membranes is approximately \$7,100, and resulted in an energy savings of approximately \$23,000 per year. Thus, with these assumptions, the

forward osmosis process could save a utility approximately \$15,600 per year when operating a very small, 100 m³/day desalination facility.

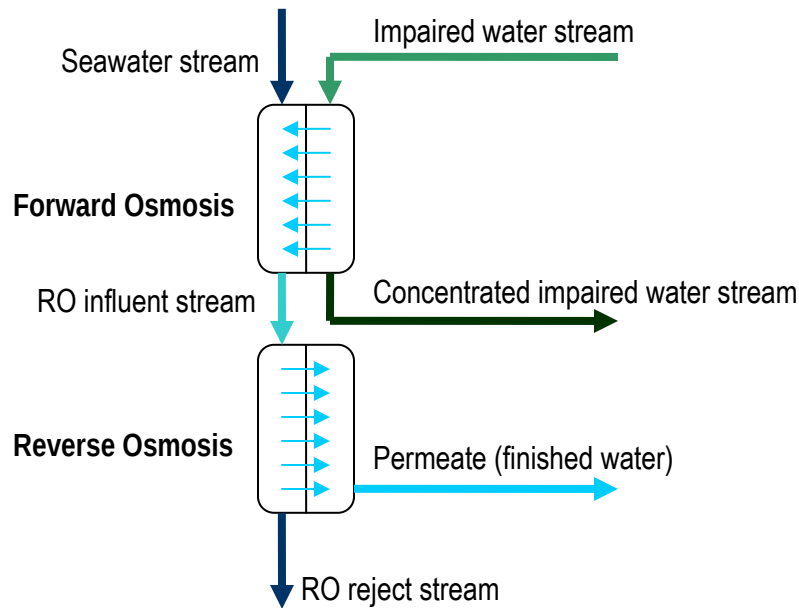


Figure 3.15 Economic feasibility model schematic

Table 3.7
Operational characteristics for modeling of FO/RO hybrid membrane system for reduction of energy demand during desalination

Parameter	Unit	Value
Finished water flow rate	m ³ /day	100
Impaired water flow rate	m ³ /day	200
Seawater TDS concentration	g/L	35
Impaired water TDS concentration	g/L	0.5
RO recovery	%	50
Energy cost	\$/kWh	0.31
Forward osmosis system cost	\$/m ²	45.00
Minimum return on investment ratio		2

As illustrated in [Figure 3.16](#), the process becomes more and more economically feasible as energy prices are increased, from not feasible at \$0.10/kWh, to 60 percent fraction of impaired water at \$0.30/kWh. However, while the flow rate of the impaired water stream has an effect on feasibility, it is much less and generally does not affect the economics as long as the flow rate is close to, or higher, than the influent flow rate to the RO desalination plant.

In another case, forward osmosis could be used to increase the production of an existing desalination facility. Diluting the RO influent while maintaining a constant pressure on the RO membranes will increase the flux through the membranes, and thus increase permeate flow rate.

For the new example, the same RO desalination facility that was modeled in the previous example is used. However, here it is assumed that the seawater stream flow rate is constantly 200 m³/day and forward osmosis permeate is added to it. The impaired water stream flow rate is assumed to be 200 m³/day as well. At each step the flow rate through the forward osmosis membrane is increased by 1 percent (i.e., 2 m³/day). As the seawater becomes diluted by increasing volumes of water diffusing through the forward osmosis membrane, the RO influent stream flow rate increases, and 50 percent recovery is maintained in the RO process.

The economic viability in this case is determined by comparing the cost of increasing the permeate flow rate with forward osmosis versus the cost of increasing the size of the RO system. As illustrated in [Figure 3.17](#), it is possible to nearly double the permeate production of the RO desalination plant to 196 m³/day. Utilizing forward osmosis instead of increasing the size of the RO system could save a utility over \$38,000 per year.

Yet, there are several caveats to this analysis. It assumes that the RO system is only limited by the feed solution concentration and can operate at increased flux and permeate flow rate. Additionally, it assumes that 50 percent recovery in the RO system is maintained; however, because the RO influent stream is diluted, higher recoveries are possible.

Thus, the hybrid forward osmosis process studied is economically feasible over a wide range of scales, from very little to very high dilution. Additionally, economic feasibility was unaffected by the capacity the water treatment operation, however savings were proportional to plant size. It is anticipated that in very large installations, savings could be even greater.

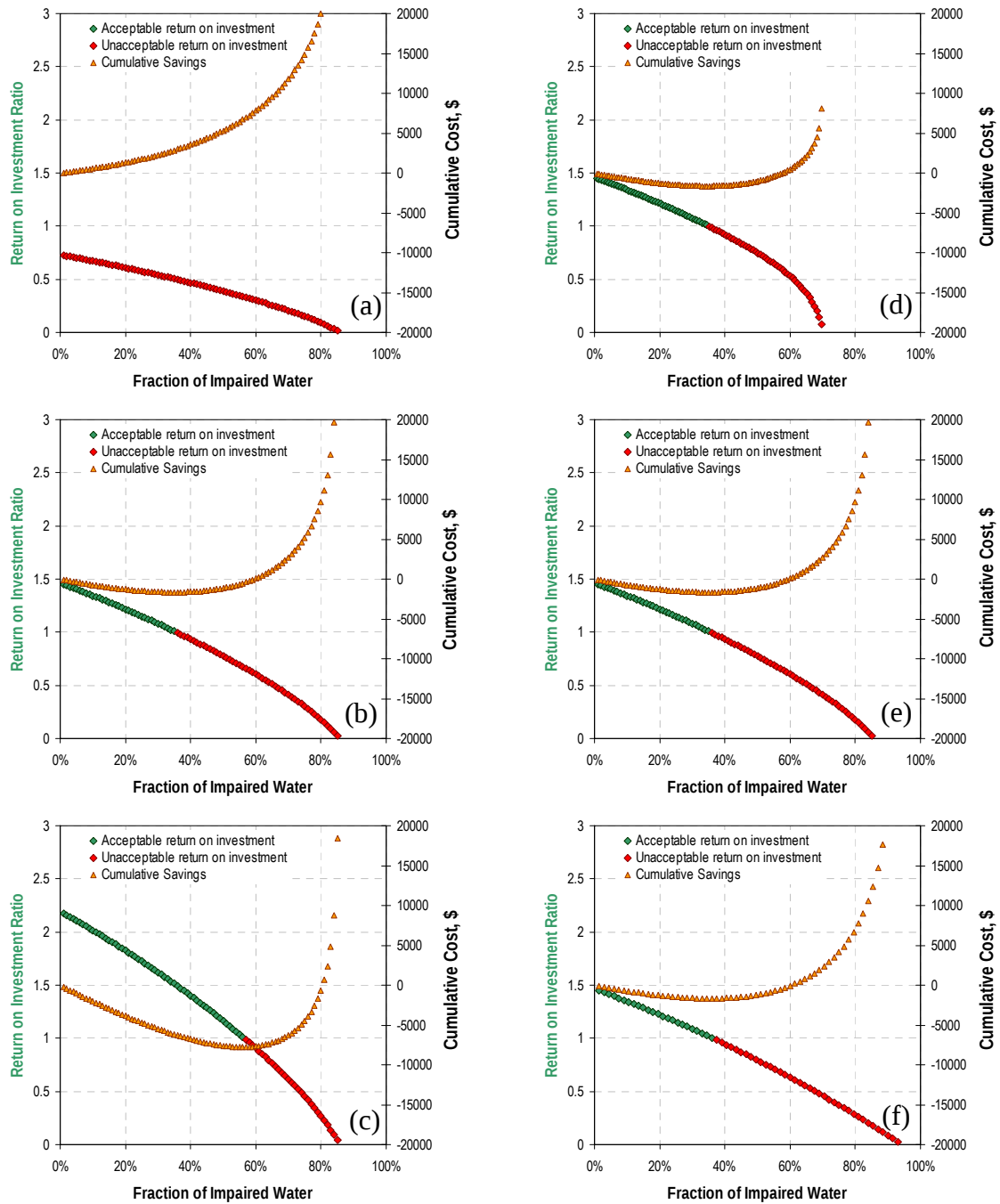


Figure 3.16 Return on investment ratio and cumulative cost as a function of impaired water stream recovery. Energy cost and impaired water flow rate are (a) \$0.10/kWh – 200 m³/day (b) \$0.20/kWh – 200 m³/day (c) \$0.30/kWh – 200 m³/day (d) \$0.20/kWh – 150 m³/day (e) \$0.20/kWh – 200 m³/day (f) \$0.20/kWh – 300 m³/day.

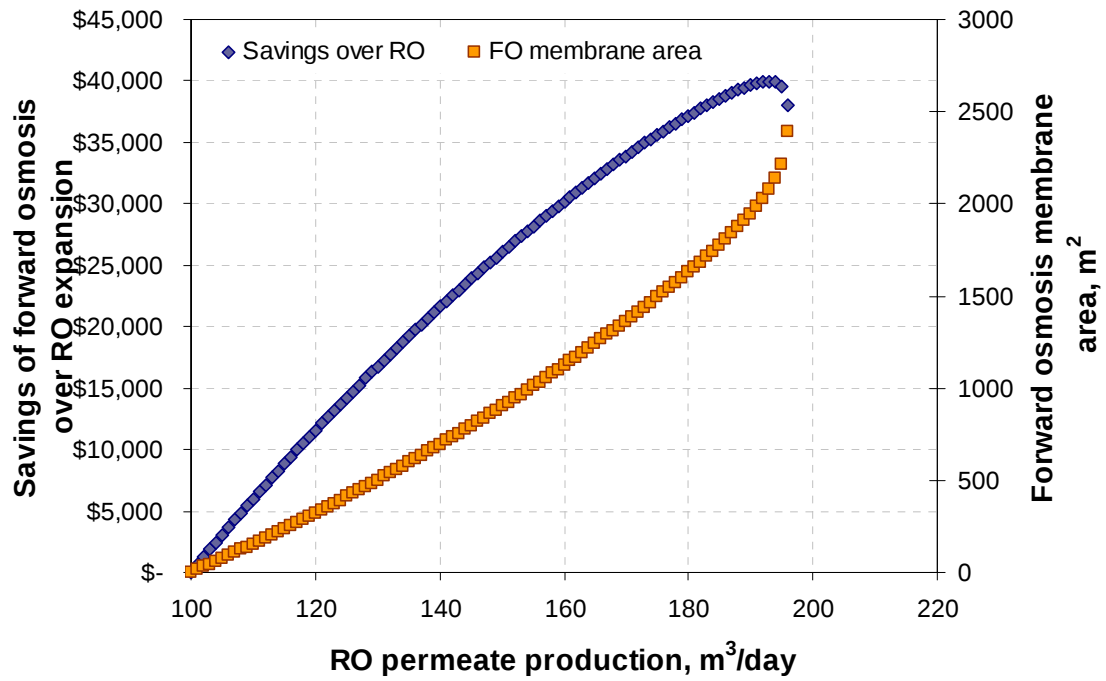


Figure 3.17 Savings of forward osmosis over RO expansion to increase the capacity of an existing RO desalination plant and needed forward osmosis membrane area as a function of RO permeate production (above 100 m³/day).

CHAPTER 4

CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

The initial objective of this research was to determine the feasibility of a hybrid osmotically driven membrane water treatment system for co-treatment of impaired and saline water. Testing of the processes was completed on both bench and pilot scales and included: level of water flux, fouling propensity, solute transport, and economic feasibility.

Water flux was generally low, approximately 5.6 LMH at 35 g/L sea salt draw solution concentration. Additionally, specific flux, normalized by driving force, decreased at higher draw solution concentrations due to internal dilutive concentration polarization. Interestingly, feed water quality had a minimal effect on water flux through the forward osmosis membrane.

In the short-term bench-scale experiments, minimal fouling of the forward osmosis membrane was observed. However, on the longer-term pilot-scale experiments fouling was more apparent. In the initial experiment, the forward osmosis membrane cell was configured with the feed channel on top of the membrane. Suspended solids were deposited on the membrane, contributing to moderate flux decline. On successive experiments, the forward osmosis membrane cell was inverted, so that the feed channel was oriented beneath the membrane. In this configuration, suspended solids settled away from the membrane, and water flux decline was minimal. Thus, configuration of the membrane cell has a substantial effect on water flux decline due to fouling. Furthermore, physical and chemical cleaning of the forward osmosis membrane reversed water flux decline almost entirely.

To elucidate the effect of alternate feed water qualities, several experiments were conducted with tertiary treated effluent. Experiments with this alternate water showed water flux similar to other feed waters, but minimal water flux decline due to fouling.

Transport of solutes was studied at the pilot-scale, and the forward osmosis / reverse osmosis hybrid system successfully limited the flux of dissolved solids. Reverse diffusion of TDS through the forward osmosis membrane, while greater than through the RO membrane, was within the levels reported by other studies. Ammonia and nitrite were both greater than 97 percent rejected by the system. Additionally, select organic micropollutants studied were all well rejected by the system and most were undetectable in the RO permeate. Thus, the hybrid system represents an effective multiple barrier approach to contaminants removal.

The data collected on the system was used to construct a model of the economic feasibility of the process. The model showed that the process is feasible across a broad range of operating conditions. The forward osmosis process for energy reduction was economically feasible from 0 to almost 80 percent recovery of the impaired water source, significantly decreasing the cost of desalinated water.

Thus, the system was shown to be both economically and technically feasible over a broad range of operating conditions. Moreover, the cost of desalinated water can be substantially reduced with forward osmosis pretreatment, making desalination a more attractive alternative for areas seeking to expand and diversify into unconventional drinking water sources.

RECOMMENDATIONS

Forward osmosis is a simple and spontaneous process that was recently engineered and adapted to various water treatment applications. Specifically in the current project, it was successfully demonstrated that forward osmosis can be coupled with reverse osmosis processes to simultaneously protect the reverse osmosis membranes, recover purified water from a broad range of impaired waters, and to lower the energy required for desalination of seawater.

Due to the limited scope and funding of this study, only the feed (impaired water) side of the forward osmosis process was operated in an open loop, and the reverse osmosis system was operated in a closed loop, continuously reconcentrating the same seawater solution. Future work should be directed at testing the process at a larger scale and preferably at a coastal facility that can provide both seawater and impaired water (e.g., reclaimed water, runoff water, impaired river water, raw wastewater, etc.). In this demonstration-scale project, a large forward osmosis system should be tested that can be operated at high recovery and substantially diluting seawater (at least 50 percent dilution).

The forward osmosis hybrid concept that was tested in this study would be easily implementable in locations where the infrastructure provides a source of seawater and a source of impaired water at the same site/facility. Currently, not many coastal facilities in the U.S. can provide such infrastructure. It is recommended that future design and development of infrastructure in coastal locations will take into consideration hybrid processes like forward osmosis and reverse osmosis or pressure-retarded osmosis for harvesting of renewable chemical potential energy between seawater and any sources of impaired water.

Currently commercially available forward osmosis membranes are limited but already adequate for the tested application; yet, additional improvement can further enhance the efficiency of the hybrid process. Investment in development of forward osmosis membranes with higher solute rejection and higher water flux is strongly recommended. Furthermore, packaging of forward osmosis membrane modules is another area that must be further explored. Results in the current study demonstrated that membrane configuration plays a substantial role in preventing membrane fouling and maintaining process integrity and high performance.

APPENDIX A
WATER FLUX AT VARIOUS DRAW SOLUTION
CONCENTRATIONS AND SEVERAL FEED SOLUTIONS

Table A.1**Water flux at various draw solution concentrations and several feed solutions for bench-scale forward osmosis experiments.**

	Water flux				Specific water flux				TDS flux			
Draw Solution Concentration	DI water feed	Secondary effluent feed	Nitrified effluent feed	South Platte feed	DI water feed	Secondary effluent feed	Nitrified effluent feed	South Platte feed	DI water feed	Secondary effluent feed	Nitrified effluent feed	South Platte feed
g/L	LMH	LMH	LMH	LMH	LMH/bar	LMH/bar	LMH/bar	LMH/bar	mg/L	mg/L	mg/L	mg/L
5	1.13	1.11	1.09	1.20	0.326	0.346	0.339	0.374	619	n/a	517	419
10	2.13	2.24	2.14	2.27	0.304	0.332	0.317	0.337	637	359	464	396
15	2.95	3.02	3.14	3.12	0.283	0.296	0.308	0.306	608	409	371	312
20	3.55	3.73	4.06	3.56	0.255	0.273	0.298	0.261	571	414	386	371
25	4.21	4.42	4.76	4.07	0.242	0.258	0.278	0.238	493	489	371	382
30	4.94	5.27	5.28	4.76	0.236	0.255	0.256	0.231	507	491	362	380
35	5.65	5.37	5.68	5.71	0.231	0.222	0.235	0.236	490	488	382	386
70	8.29	7.95	8.51	7.98	0.169	0.163	0.175	0.164	514	559	430	488

APPENDIX B
MICROPOLLUTANT CONCENTRATION IN FEED, DRAW SOLUTION,
AND PERMEATE STREAMS

Table B.1
Micropollutant concentration in feed, draw solution, and permeate streams during 35 g/L draw solution concentration experiment with secondary effluent feed water over the duration of the experiment.

		Diclofenac	Gemfibrozil	Ibuprofen	Naproxen	Salicylic Acid	TCEP
		(ng/L)	(ng/L)	(ng/L)	(ng/L)	(ng/L)	(ng/L)
Day 1	Feed	210	695	250	400	395	920
Day 5	Feed	145	960	560	465	260	1250
Day 7	Feed	140	1770	560	555	685	n.d.
Day 8	Feed	155	960	385	435	360	800
Day 1	Draw	35	60	36	50	40	333
Day 5	Draw	50	345	80	200	70	1060
Day 7	Draw	65	2055	430	480	175	n.d.
Day 8	Draw	65	1650	255	360	85	625
Day 1	Perm	n.d.	45	25	n.d.	n.d.	n.d.
Day 5	Perm	n.d.	50	50	45	n.d.	80
Day 7	Perm	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Day 8	Perm	n.d.	n.d.	33	n.d.	n.d.	70

Table B.2

Micropollutant concentration in the feed, draw solution, and RO permeate streams during 35 g/L draw solution concentration experiment with secondary effluent feed water. Data is for first and last day of experiment.

		Diclofenac	Gemfibrozil	Mecoprop	Naproxen	Salicylic Acid	TCEP
		(ng/L)	(ng/L)	(ng/L)	(ng/L)	(ng/L)	(ng/L)
Day 0	Feed	155	700	110	250	200	820
Day 1	Feed	130	320	95	83	190	730
Day 6	Feed	175	760	115	265	250	960
Day 0	Draw	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Day 1	Draw	125	250	n.d.	120	130	480
Day 6	Draw	150	320	n.d.	139.6	60.4	1068.4
Day 1	Perm	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Day 6	Perm	n.d.	n.d.	n.d.	n.d.	n.d.	300

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ABBREVIATIONS

A_w	pure water permeability coefficient
AWWA	American Water Works Association
C	Celsius
cm	centimeter
CP	concentration polarization
CSM	Colorado School of Mines
CTA	cellulose triacetate
σ	reflection coefficient
d	day
DI	deionized water
DS	draw solution
DWRP	Denver Water Recycling Plant (Denver, CO)
ECP	external concentration polarization
ESEM	environmental scanning electron microscope
FO	forward osmosis
ft	foot
ft/s	feet per second
GC/MS	gas chromatography/mass spectroscopy
g/L	gram per liter
gpm	gallons per minute
HPLC	high performance liquid chromatography
HTI	Hydration Technologies, Inc. (Albany, OR).
i	dimensionless van't Hoff factor
IC	ion chromatograph
ICP	internal concentration polarization
ICP	inductive coupled plasma
J_w	water flux
k	feed solute's mass transfer coefficient
K	solute's resistivity to diffusion in the porous support layer
L	liters
LMH	liter per square meter per hour
Lpm	liters per minute
m	meter

m/hr	meters per hour
m/s	meters per second
M	Molarity (mol/liter)
MD	membrane distillation
mg	milligram
mg/L	milligrams per liter
min	minute
mL	milliliter
mL/min	milliliters per minute
mm	millimeter
MWRD	Metropolitan Water Reclamation District's (Denver, CO)
µg/L	microgram per liter
NF	nanofiltration
ng/L	nanogram per liter
P	pressure
PRO	pressure retarded osmosis
psi	pound per square inch
PVC	polyvinyl chloride
π	osmotic pressure
π_D	osmotic pressure of the draw solution
π_F	osmotic pressure of the feed solution
R	gas constant ($0.08206 \text{ L}\cdot\text{atm}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$)
RO	reverse osmosis
SCADA	supervisory control and data acquisition
sec	second
SEM	scanning electron microscope
SPE	solid phase extraction
SWRO	seawater reverse osmosis
T	temperature
TCEP	tris(2-chloroethyl) phosphate, chlorinated flame retardant
TDS	total dissolved solids
TOC	total organic carbon
ULPRO	ultra low pressure reverse osmosis
UVA	ultra-violet absorbance