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Self-regulating Behavior of a Pilot-scale Forward Osmosis-Reverse Osmosis Hybridized System

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14. ABSTRACT

Though reverse osmosis (RO) is an industrially mature and widespread desalination technology, its susceptibility to fouling makes it challenging to operate using more difficult feedwaters. Pretreatment is one approach to reducing fouling in RO membranes and such systems often comprise a majority of a desalination plant's total footprint. Hybridization of forward osmosis (FO) with RO has been considered as an alternative configuration to more conventional pretreatment schemes, but the lack of understanding of how these systems might operate and the potential for complex control schemes to balance fluxes between the FO and RO systems create uncertainty. In this work, we demonstrate self-regulating behavior of FO-RO hybrid systems that can lead to drastically reduced complexity of these systems. We show this behavior using a module-scale test bed that can mimic the behavior of larger scale systems. Significantly, the system shows permeate flow rate near-convergence between the FO and RO modules when perturbed by a change in RO module pressure and therefore does not need to have complex controllers in place to ensure even flows between the two processes.

15. SUBJECT TERMS

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Self-regulating Behavior of a Pilot-Scale Forward Osmosis-Reverse Osmosis Hybridized System

Prepared for the Bureau of Reclamation under Agreement No. R17AC00144

by

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Acknowledgments

The Desalination and Water Purification Research and Development Program, Bureau of Reclamation, sponsored this research. Major contributors include:

Jeffrey McCutcheon, principal investigator: Wrote the proposal and managed the project.

Maqsud Chowdhury, graduate researcher: Constructed pilot scale FORO apparatus and wrote original data collection programming

Noah Ferguson, graduate researcher: Identified and effected apparatus improvements/repairs, prepared stock solutions, calibrated sensors, updated data collection program, ran apparatus experiments, analyzed collected data, prepared and presented project poster, wrote progress reports, wrote FORO simulation program, ran simulations, analyzed simulation results, drafted DWPR final report.

Colin Fitzsimonds, undergraduate researcher: Assisted with apparatus improvements/repairs, prepared stock solutions, assisted with sensor calibrations, assisted with apparatus experiments, analyzed collected data.

Acronyms and Abbreviations

DI	Deionized
FO	Forward osmosis
HFM	Hollow fiber membrane
PLC	Programmable logic controller
RO	Reverse osmosis
ROCP	Reverse osmosis concentration polarization
SWM	Spiral wound membrane

Measurements

K	Degrees kelvin
Gal.	Gallons
GMH	Grams per square meter per hour
gpm	Gallons per minute
LMH	Liters per square meter per hour
M	Moles per liter
psi	Pounds per square inch

Variables

AFO	Water permeance of the FO membrane (LMH/bar)
ARO	Water permeance of the RO membrane (LMH/bar)
i	van't Hoff constant (~2 for NaCl)
JFO	Area normalized water flux across the FO membrane without salt permeation
JFOSP	Area normalized water flux across the FO membrane with salt permeation
JRO	Area normalized water flux across the RO membrane without salt permeation
JROSP	Area normalized water flus across the RO membrane with salt permeation
M	Solution molarity
MDI	FO draw-in molarity without membrane salt permeation
MDISP	FO draw-in molarity with membrane salt permeation
MDO	FO draw-out/RO feed-in molarity without membrane salt permeation
MDOSP	FO draw-out/RO feed-in molarity with membrane salt permeation
MFI	FO draw-in molarity without membrane salt permeation
MFISP	FO draw-in molarity with membrane salt permeation

MP	RO permeate molarity without membrane salt permeation
MPSP	RO permeate molarity with membrane salt permeation
MRSP	RO retentate molarity with membrane salt permeation
R	Gas constant, = 0.082057 (L*atm)/(mol*K)
SR	RO salt rejection (percent)
T	Temperature (kelvin)
ΔP	Hydraulic pressure gradient across the RO membrane
$\Delta \Pi FO$	Osmotic gradient across the FO membrane without salt permeation
$\Delta \Pi FOSP$	Osmotic gradient across the FO membrane with salt permeation
$\Delta \Pi RO$	Osmotic gradient across the RO membrane without salt permeation
$\Delta \Pi ROSP$	Osmotic gradient across the RO membrane with salt permeation
ϕ	Solution osmotic coefficient (~0.92 for NaCl solution at 298 K and between 0.2 and 0.5 M [Partanen and Partanen 2020])
Π	Solution osmotic pressure (atmospheres)

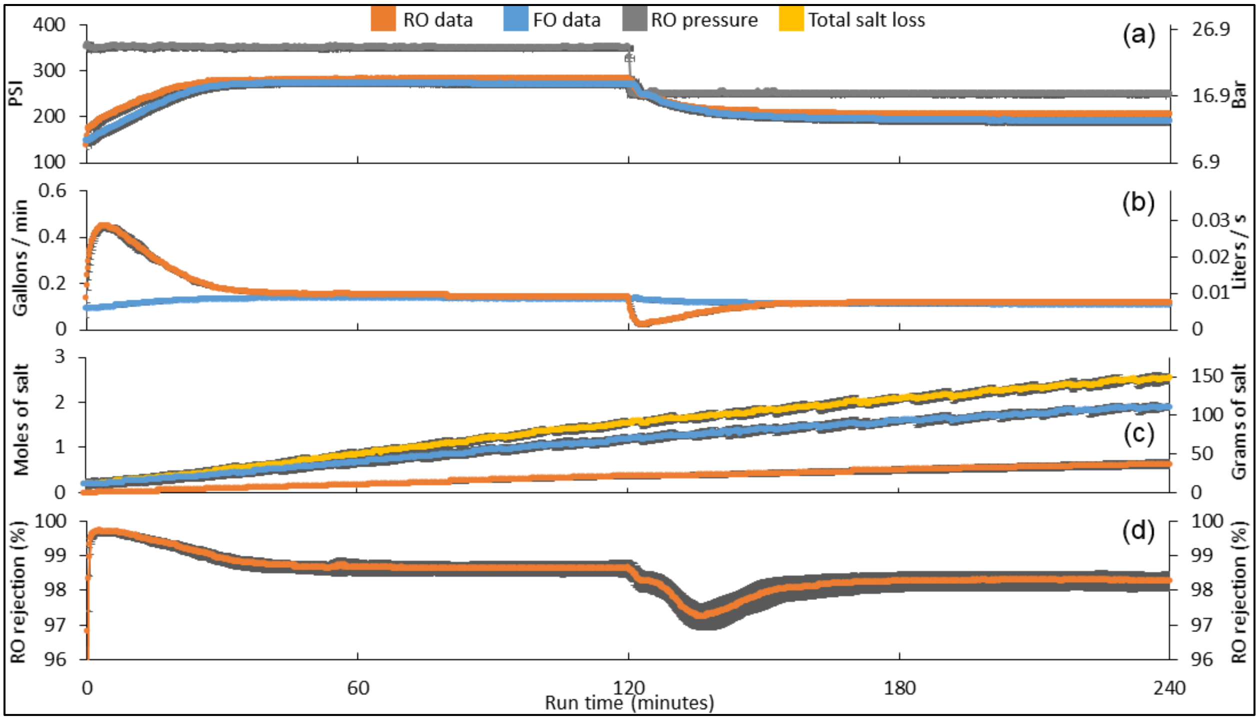
Contents

Executive Summary

Traditional reverse osmosis (RO) desalination requires extensive pretreatment to remove constituents that contribute to membrane-fouling. Such systems can occupy a vast majority of the plant footprint and capital cost associated with plant construction. Recent research has investigated replacing these pretreatment steps with low-pressure membrane foulant removal processes. Ultrafiltration is one option, but it lacks the ability to reject dissolved contaminants that can lead to scaling or fouling in downstream RO membranes. In this work, we evaluate the use of forward osmosis (FO) as a potential upstream process to RO. In this case, RO concentrates a recirculating draw solution that is used to draw water across the FO membrane in the upstream process.

While the fouling phenomenon was originally intended for study, we found that operational aspects of the hybrid system (FORO) required fundamental understanding. In general, it is believed that hybrid membrane processes add a level of complexity to a system, which disincentivizes their use. In particular, using multiple membrane processes in series harbors concerns about balancing flow rates and appropriate sizing for each system. However, we found that the FORO hybrid system exhibited a self-regulatory behavior that greatly simplified operation and design and could address the concern of operators who would consider the use of such a system. During this project, we observed that FO and RO permeate flow rates spontaneously tend toward a stable equivalent value unless perturbed by the operator or by a change in another parameter (such as feed concentration). When perturbed, however, we saw the system self-regulate without the need for operator input. Such a behavior is expected due to the system tending toward a dynamic osmotic equilibrium but had never been demonstrated or reported on. Such a system offers a degree of autonomous operation, with certain constraints, that would reduce the need for frequent manual or rigorous automated control inputs.

This self-regulatory behavior was demonstrated on a custom-built element scale FORO system that was dedicated to this project. The system was mounted with one of two different commercial FO membrane elements (one from FTS and the other from Aquaporin A/S). The RO portion of the system was mounted with a seawater reverse osmosis membrane. Representative data are shown in ESFigure 1. The RO and FO flux data always converge with one another, even if they start apart or are perturbed by a change in RO pressure. In addition, complete convergence does not occur due to non-negligible salt permeation of both membranes. Nonetheless, this project firmly establishes the existence of self-regulating behavior of a hybridized FORO system. We hypothesize that a simple measure, such as salt dosing to replace permeating salt, could produce complete convergence of permeate flow rates.



ESFigure-1. FORO data vs. time for an average of three experiments using spiral-wound FO membrane: a) RO hydraulic pressure and osmotic gradients; b) FO and RO membrane permeate flowrates; c) total salt loss across each membrane; d) RO membrane salt rejection. Self-regulating behavior is shown by permeate flow rates in (b), which spontaneously tend toward each other following RO pressure spike at t=0 minutes and pressure drop at t=120 minutes.

1 Introduction

1.1 Project Background

Reverse osmosis (RO) is widely used to produce freshwater from brackish water or seawater for municipal and industrial use (Baker 2004, Gude et al. 2010). Though it is a mature technology and is generally more economical than thermal desalination processes (Gude 2010), RO operations require extensive pretreatment of feed waters to maintain the performance of fouling-prone RO membranes (Valavala et al. 2011). The physical footprint of the pretreatment step can be considerable, as it must employ steps to remove multiple types of foulants, including particulate matter, scaling minerals, and organics (Baker 2004). Reduction in size and simplification of pretreatment equipment could allow RO plants to serve new locales with constraints on space and technical resources.

Recent research has investigated replacing pretreatment steps, such as settling tanks and chemical flocculation, with low-pressure membrane processes to remove foulants (Valavala et al. 2011). These pretreatment membranes are still subject to fouling; however, their foulant layers are thicker and looser than those on RO membranes, making them cleanable via simple backflushing rather than harsh chemical treatments required to clean RO membranes (Blandin et al. 2016a, Lee et al. 2010). Thus, a relatively compact membrane pretreatment step could replace traditional large-footprint measures without presenting unreasonable membrane cleaning requirements.

System simplification is also preferred for reducing desalination cost and resource requirements. Minimizing the need for sensor and controller equipment could expedite the development of future small-volume, distributed desalination plants that serve areas that are inaccessible to current large plant operations. Complex pretreatment trains, with their associated supply chain challenges, have limited value to distributed desalination systems.

Forward osmosis (FO) membranes have been conceived of as a pretreatment option for RO systems. FO membranes have demonstrated fouling resistance and thus, when paired with RO, can operate using RO as the draw solution regeneration process. In these hybridized configurations, the FO unit takes full brunt of the raw feedwater while passing none of the organics. Meanwhile, the RO system is exposed only to a pristine, salty draw solution.

However, if we are to hybridize these systems, we must understand how they interplay with one another. To that end, we used idealized operating conditions (i.e., conditions without fouling) to investigate the self-regulating permeate flow rate behavior of a desalination system, which uses an FO membrane as pretreatment for RO (referred to as FORO). Hybrid processes often require complex control systems to ensure steady-state operation between the multiple membrane systems. However, we hypothesized that such control was unnecessary with FORO systems because the driving force for both systems would be thermodynamically limited by osmotic pressure. More specifically, if there were a difference in flow between the FO and RO systems, the system should spontaneously stabilize to have equal flow of both systems as a dynamic osmotic equilibrium is established. In this equilibrium, there would still be osmotic flow in the FO system and reverse osmotic flow in the RO system, but they would be balanced and equal through osmotic selfregulation. Such a finding would suggest that such systems would be relatively easy to control and not require complex pumps and controls to ensure steady-state operation.

1.1.1 Objectives and Goals

This project was intended to demonstrate the self-regulating behavior of a hybridized system of FO and RO units. The desired self-regulating behavior entails spontaneous convergence between the FO and RO permeate flow rates, which are initially different upon system startup. Convergence of the flow rates means that water is flowing into the FORO system via the FO membrane at the same rate that it is flowing out via the RO membrane. Ideally, the FORO system can maintain this steady state for an arbitrarily long period, allowing for simple operation with few control inputs.

1.2 Project Overview

1.2.1 Overall Technical Approach and Concepts

This project employed a pilot-scale FORO apparatus that used commercial elements, rather than small flat-sheet membranes, to demonstrate hybrid operation. We used commercial elements to obtain volumetric fluxes that were large enough to establish convergence of flux within reasonable timeframes.

The pilot-scale apparatus consisted of separately constructed FO and RO units, each capable of independent operation. Testing for self-regulating behavior entailed establishing reciprocal flows between the FO Draw and RO Feed tanks (see Figure 1) and observing whether the initially different membrane permeate flow rates spontaneously tended toward a stable mutual value without operator action. Permeate flow rates were measured by inline flow meters.

1.2.2 Overall Accomplishments

This project succeeded in demonstrating the existence of self-regulating behavior in a hybridized FORO system, and that this behavior can reestablish stable steady state following a pressure-induced system perturbation. In doing so, the project achieved its objective and showed that such a desalination system, with simple controls and a reduced physical footprint, has the potential to treat water in areas not served by traditional operations. We also developed a computational model to help predict the flux behavior of FORO systems, enabling us to explore which membrane and processing parameters have the most impact on overall system performance.

2 Technical Approach and Methods

2.1 Technical Approach

2.1.1 Research Idea

The test apparatus built for this project was intended to demonstrate and characterize the self-stabilizing behavior of a hybridized FORO osmotic system. A low-salinity feed water (deionized water for demonstration purposes) is fed to the FO module. A high-salinity draw solution passes on the downstream side of the membrane. This diluted draw solution is used as a feed to the RO system, where freshwater permeates the membrane and the concentrate is routed back to the FO module.

Key to this concept is the buffering of the volume of water that recirculates between the FO and RO systems. This volume serves as a buffer and can increase and decrease in volume with subsequent decrease and increase in salinity, respectively, as the system equilibrates. By demonstrating this self-regulatory behavior, we can show that FO hybrid systems might be relatively easy to control. We also aim to use data captured on such a system to experimentally validate a model that can predict system performance and enable us to explore other key parameters of the membranes that might improve overall system performance.

2.1.2 Equations

Osmotic Pressure:

$$\Pi = i\phi MRT \quad (1)$$

Salt rejection:

$$SR = 100(1-(M\_PSP/M\_RSP)) \quad (2)$$

FO Flux:

$$JFO = AFO\Delta\Pi FO = AFO(i\phi RT(MDI-MFI)) \quad (3)$$

RO Flux:

$$JRO = ARO(\Delta P-\Delta\Pi RO) = ARO(\Delta P-(i\phi RT(MDO-MP)) \quad (4)$$

Observed osmotic gradient across the FO membrane:

$$\Delta\Pi FOSP = (i\phi RT(MDISP-MFISP)) < \Delta\Pi FO \quad (5)$$

Flux across the FO membrane:

$$JFOSP = AFO\Delta\Pi FOSP < JFO \quad (6)$$

Osmotic gradient across the RO membrane:

$$\Delta\Pi ROSP = (i\phi RT(MDOSP-MPSP)) < \Delta\Pi RO \quad (7)$$

Flux across the RO membrane:

$$JROSP = ARO(\Delta P-\Delta\Pi ROSP) > JRO \quad (8)$$

Where:

AFO is water permeance of the FO membrane (LMH/bar)

ARO is water permeance of the RO membrane (LMH/bar)

i is the van't Hoff constant (~2 for NaCl)

JFO is area-normalized water flux across the FO membrane without salt permeation

JFOSP is area-normalized water flux across the FO membrane with salt permeation

JRO is area-normalized water flux across the RO membrane without salt permeation

JROSP is area-normalized water flux across the RO membrane with salt permeation

M is solution molarity

MDI is FO draw-in molarity without membrane salt permeation

MDISP is FO draw-in molarity with membrane salt permeation

MDO is FO draw-out/RO feed-in molarity without membrane salt permeation

MDOSP is FO draw-out/RO feed-in molarity with membrane salt permeation

MFI is FO draw-in molarity without membrane salt permeation

MFISP is FO draw-in molarity with membrane salt permeation

MP is RO permeate molarity without membrane salt permeation

MPSP is RO permeate molarity with membrane salt permeation

MRSP is RO retentate molarity with membrane salt permeation

R is the gas constant, = 0.082057 (L*atm)/(mol*K)

SR is RO salt rejection percent

T is temperature (kelvin)

ΔP is the hydraulic pressure gradient across the RO membrane

ΔΠFO is the osmotic gradient across the FO membrane without salt permeation

ΔΠFOSP is the osmotic gradient across the FO membrane with salt permeation

ΔΠRO is the osmotic gradient across the RO membrane without salt permeation

ΔΠROSP is the osmotic gradient across the RO membrane with salt permeation

ϕ is the solution osmotic coefficient (~0.92 for NaCl solution at 25° C and between 0.2 and 0.5 M [Partanen])

Π is solution osmotic pressure (atmospheres)

2.2 Project Facility/Physical Apparatus

2.2.1 Design Criteria

The pilot-scale FORO system was designed to demonstrate that hybridized FO and RO units can achieve self-stabilizing flux behavior, allowing sustained desalination operation with minimal operator input. The system was built for single FO and RO elements and incorporated appropriately sized pumps for the RO system (a diaphragm pump that can operate at over 800 psi) and gear pumps for the FO system (that are meant to operate at ambient pressures). Onboard flow, temperature, and conductivity provided needed system monitoring during tests.

2.2.2 Source Water

DI water (0.87 MΩ·cm) was used directly as FO feed water. FO draw solution was made by dissolving NaCl (EMD Millipore, Taunton, MA) in DI water at a concentration of 0.25 M.

2.2.3 Set Up

The system layout is shown in Figure 1 and Figure 2. FO feed, FO draw, and RO feed solutions were contained in 16-gallon tanks. The FO membrane was fed by the FO feed and draw tanks. The draw solution was diluted by osmotically driven permeate from the feed side. Feed water retentate returned to the FO feed tank. The diluted draw solution was routed to the RO feed tank, then to the RO membrane. Desalinated RO permeate left the system, while RO retentate was routed to the FO draw tank as reconcentrated draw solution. The FO feed-in and FO draw-in streams were driven by centrifugal pumps (Goulds Water Technology, Auburn, NY), while the RO feed-in stream was driven by a diaphragm pump (Wanner Engineering, Inc., Minneapolis, MN). Water flow rate data were collected via in-line flow meters (Omega Engineering, Inc., Norwalk, CT and IFM Efector, Inc., Malvern, PA). Temperatures and membrane entrance/exit pressures were collected with electrical sensors (AutomationDirect, Cumming, GA). Data regarding flow rates, temperatures, and pressures were collected by a programmable logic controller (PLC) (AutomationDirect). Salinity data were collected by in-line probes in the FO feed-in, FO feed out, FO draw-out, and RO permeate streams. Salinity instrumentation and data collection software were obtained from Vernier (Beaverton, OR). Water temperature was maintained at 25° C by tube-and-shell heat exchangers served by two chillers (Thermo Fisher, Waltham, MA).

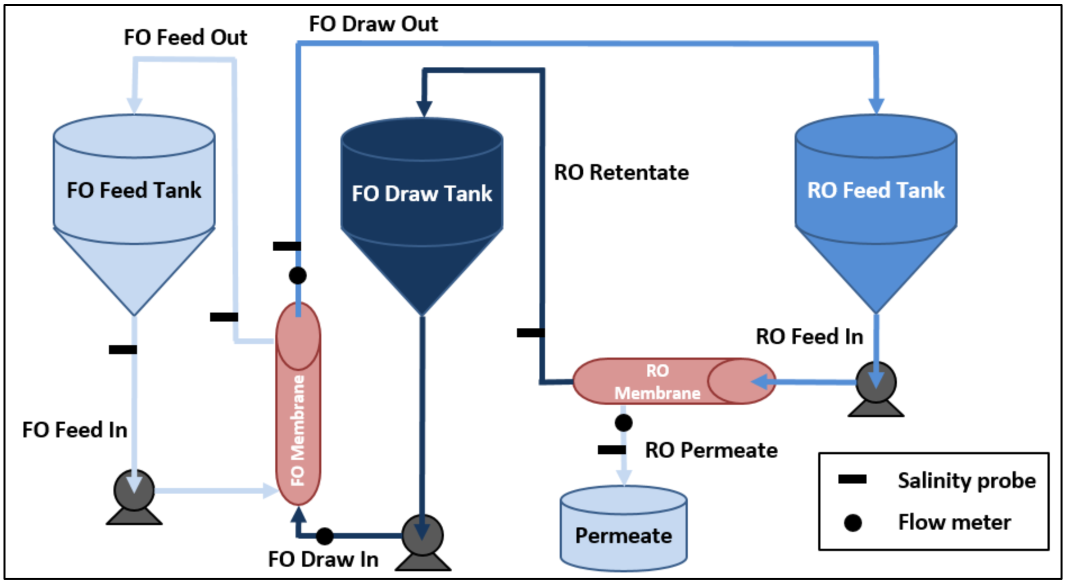


Figure 1. Schematic of the hybridized FORO system showing layout and sensor locations. Shades of blue show relative salinities, with darker blue indicating greater salinity.

Figure 2. Left: Photograph of the FO unit. The FO membrane module is the white vertical tube. Right: Photograph of the RO unit. The RO membrane module is the white horizontal tube. FO and RO units may be operated independently or hybridized.

2.2.4 Runs and Experiments Completed

Timeline

Before January 2018: The system was assembled and shakedown was completed with Porifera membrane. The Porifera module failed due to leakage. Ph.D. student Maqsud Chowdhury graduated and the system was passed on to new student Noah Ferguson

Jan.-Mar. 2018: Operator familiarization with test apparatus; installation of heat exchangers; development of SOP manual

Apr.-Jun. 2018: Collection of early data and detection of flow meter deficiencies

Jul.-Sep. 2018: Upgrade and standardization of flow meters; update of data collection software to accommodate changes; replacement of RO pressure regulator; repair of apparatus cooling unit; rerouting of electrical wires to improve safety

Oct.-Dec. 2018: Collection of first data confirming FORO self-regulating behavior; decision to make all sensors electronic; upgrade of PLC to accept more digital input connections

Jan. 2019: Onboarding of a new undergraduate research assistant

Feb.-Mar. 2019: Upgrade of temperature and pressure sensors; update of data collection software to accommodate changes

Apr.-Jun. 2019: Collection of improved data; discovery of incomplete FO and RO permeate flow rate convergence; poster presentation of project and early data at NAMS in Pittsburgh, PA

Jul.-Aug. 2019: Apparatus moved to a new laboratory; replacement of damaged FO draw pump

Sep. 2019: Apparatus moved to a new laboratory; safety barrier installed; discovery of poor RO rejection; replacement of RO membrane and RO pressure vessel gaskets

Oct. 2019-Feb. 2020: Restart of data collection with new RO membrane; repair of damaged FO feed pump

Mar.-Jul. 2020: Project idled due to coronavirus pandemic

Aug. 2020: Development of FORO modeling program; repair of apparatus cooling unit; replacement of damaged salinity sensor

Sep.-Dec. 2020: Detection and replacement of failing flow meters; detection of new RO salt rejection problems

Jan.-Mar. 2021: Replacement of the RO pressure vessel to solve poor salt rejection; further replacement of failing flow meters; repair of damaged FO feed pump; replacement of damaged salinity sensor; improvement of FORO modeling program

Apr.-May 2021: Collection of definitive high-quality data using both spiral-wound and hollow-fiber FO membrane modules

Jun. 2021: Final collation and analysis of collected data

Experimental Approach

Prior to an experiment, the FO feed tank was filled with 16 gallons of DI water, and the FO draw tank was filled with 8 gallons of draw solution. The RO feed tank was initially empty. The feed and draw solutions were pumped through the FO membrane. FO draw-in flowrate was maintained at 1.25 ± 0.03 gallons per minute (gpm) for all experiments. When the RO feed tank volume reached 4 gallons, the RO feed motor was started. RO feed-in flowrate was set to keep the FO draw and RO feed tanks filled approximately equally. The FO feed tank was kept full (approximately 16 gallons) by periodic manual addition of DI water throughout the experiment. No hydraulic pressure was applied to the RO membrane during experiment startup, allowing all water to exit the membrane as retentate and return to the FO draw tank. Once stable desired flow rates were achieved, RO feed pressure was increased to 350 psi at less than 10 psi/second. The low operating pressure and slow rates of pressure change were employed in this project to protect the RO membrane against possible damage from pressure-cycling over many experiments. Run time and data recording were started at the moment when the RO feed pressure reached 350 psi. The system was then allowed to run itself, with the operator making only small adjustments to flow rates, topping off the FO feed tank, and ensuring that membrane pressures did not wander from their set values. At t = 7,200 seconds (2 hours), the system was perturbed by dropping RO pressure from 350 psi to 250 psi, again at less than 10 psi/second. From the time of perturbation to the end of the experiment (t = 14,400 seconds = 4 hours), the system was allowed to run with the same limited operator inputs. Data were collated and analyzed using Microsoft Excel. Bulk osmotic pressures were calculated by equation (1). RO salt rejection was calculated with equation (2).

Modeling Work

A program for modeling the behavior of the physical FORO system was written using MATLAB software (see Section 7 Supplementary Material). The program was given initial values reflecting the physical system's startup conditions, such as tank volumes, tank salinities, and water flow rates, as well as system constants, such as membrane areas, permeance values, and pressures. Simulated concentration polarization was calculated for the RO membrane using an equation from the membrane manufacturer. Concentration polarization was not calculated for the FO membranes because no manufacturer equations were available, and because obtaining experimental data to formulate in-house equations would have demanded unreasonable extra time.

To simulate a run, the program iteratively calculated FO and RO permeate flow rates versus time, according to the conditions within the simulated FORO apparatus. Plots of simulated behavior were created for comparison with recorded experimental behavior. Once the modeling program was found to reasonably reflect the performance of the physical apparatus, the program was altered to simulate permeate flow rate performance resulting from variations in system parameters, including membrane permeance, tank volumes, and salt rejection. A brief exploration of permeate flow rate behavior under fouling conditions was also performed. Severe FO fouling was modeled as a 25 percent reduction in FO permeance, applied linearly and progressively over a simulated 4-hour run.

3 Results and Discussion

3.1 Results

3.1.1 Experimental Results

As shown in Figure 3b and Figure 4b, the hybridized FORO system displayed spontaneous membrane flow rate convergence following RO pressure perturbations. Tests were run with two different FO modules. The first is a spiral-wound module (SWM) from Fluid Technology Solutions (FTS). The other test uses hollow-fiber modules (HFM) from Aquaporin A/S. For the SWM and HFM experiments, membrane flowrates immediately diverged upon the change of RO pressure, and then converged within 1 hour at or near a new mutual value. The RO permeate flow rate response to pressure changes is more dramatic than the FO response in both experimental sets because of the RO membrane's direct dependence on applied hydraulic pressure for permeation. Permeation of the FO membrane is instead driven by osmotic pressure, which begins to change only after RO hydraulic pressure is perturbed. Thus, FO permeate flow rate responses to pressure perturbations are slower and gentler than RO responses.

Of note are the different mutual permeate flow rates achieved at steady state during the SWM and HFM experiments. Steady-state flow rates in the HFM experiments are more than twice those seen in the SWM experiments. This difference is created by the higher permeation rate, which is more attainable across the HFM than the SWM, due to the HFM's significantly higher area (13.8 m2 vs. 3.2 m2). This faster transfer of water across the HFM yields RO feed solution that is more dilute than in the SWM experiments. The resulting lower RO osmotic gradient (shown in Figure 3a, vs. Figure 4a) allows faster RO permeation, and thus the higher mutual flow rates seen with the HFM. This suggests that the factor limiting overall system flux in our system is the FO module.

The small but statistically significant disparity between the RO and FO steady-state flow rates was unexpected. It was observed in both SWM and HFM tests. For both membrane types, the RO flowrate was observed to stabilize at a slightly higher value than the FO flow rate, regardless of whether the RO flow rate was converging from above or from below the FO flow rate. This phenomenon is created by salt permeation across both the FO and RO membranes, which lowers the osmotic gradients across each. In the FO membrane, the diminished osmotic gradient reduces water permeation below its theoretical (no salt permeation) rate, while in the RO membrane, the lowered gradient allows higher permeation than would occur without salt loss. The flow rate disparity is larger for the SWM than for the HFM because of the higher rate of salt loss across the SWM (compare Figure 3c to Figure 4c). Regardless of the chosen FO membrane, this small gap between FO and RO steady-state flow rates implies that the salt in the recirculating draw solution will become depleted at long run times, necessitating the replacement of lost salt to the tanks. Otherwise, the flux will continue to trend toward zero.

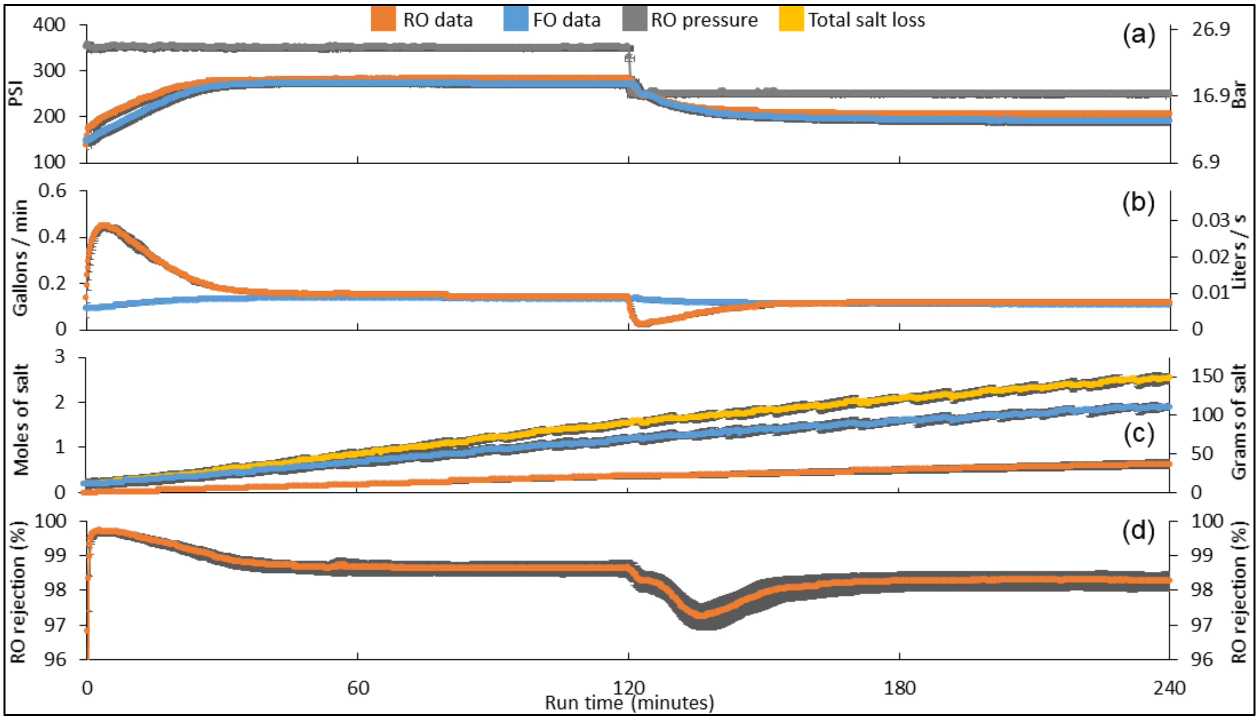


Figure 3. FORO data vs. time for average of three experiments using spiral-wound FO membrane. Top to bottom: (a) RO hydraulic pressure and osmotic gradients; (b) FO and RO membrane permeate flowrates; (c) total salt loss across each membrane; (d) RO membrane salt rejection.

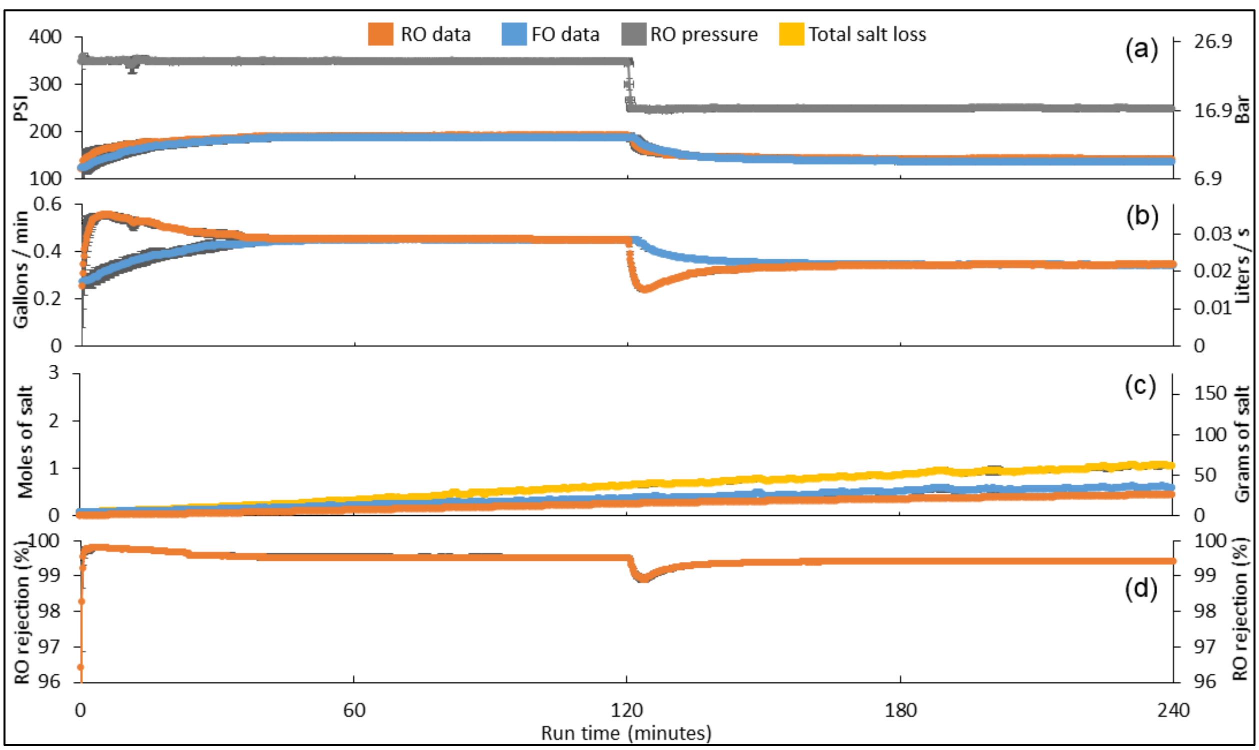


Figure 4. FORO data vs. time for average of three experiments using hollow-fiber FO membrane. Top to bottom: (a) RO hydraulic pressure and osmotic gradients; (b) FO and RO membrane permeate flowrates; (c) total salt loss across each membrane; (d) RO membrane salt rejection.

3.1.2 Modeling Results

We developed a model to predict FO and RO water and salt flux behavior in our hybrid system. Such a model was designed around the SWM equipped system and could be experimentally verified. Such a model can then be used to predict system performance with different kinds of membranes being used in the RO and FO configurations.

Figure 5 shows the simulated behavior of the SWM-equipped apparatus and demonstrates the complete permeate flow rate convergences that would be realized without salt loss across the membranes. Simulations accounting for salt loss were also performed. In these, the simulated apparatus demonstrated similar behavior to that of the physical apparatus, in that FO and RO flow rates approach each other following a pressure change but ultimately stabilize at slightly different flow rate values. As seen in the experimental data, the simulated RO permeate flow rate stabilizes at a slightly higher value than the FO permeate flow rate. Modeling results accounting for salt loss are compared with experimental data in Figure 6 and Figure 7. The agreement between simulated and experimental permeate flow rates was closer when modeling the SWM than when modeling the HFM. The reason for this is unclear but may be related to the simplicity of the simulation, which may make it inappropriate for modeling HFM modules.

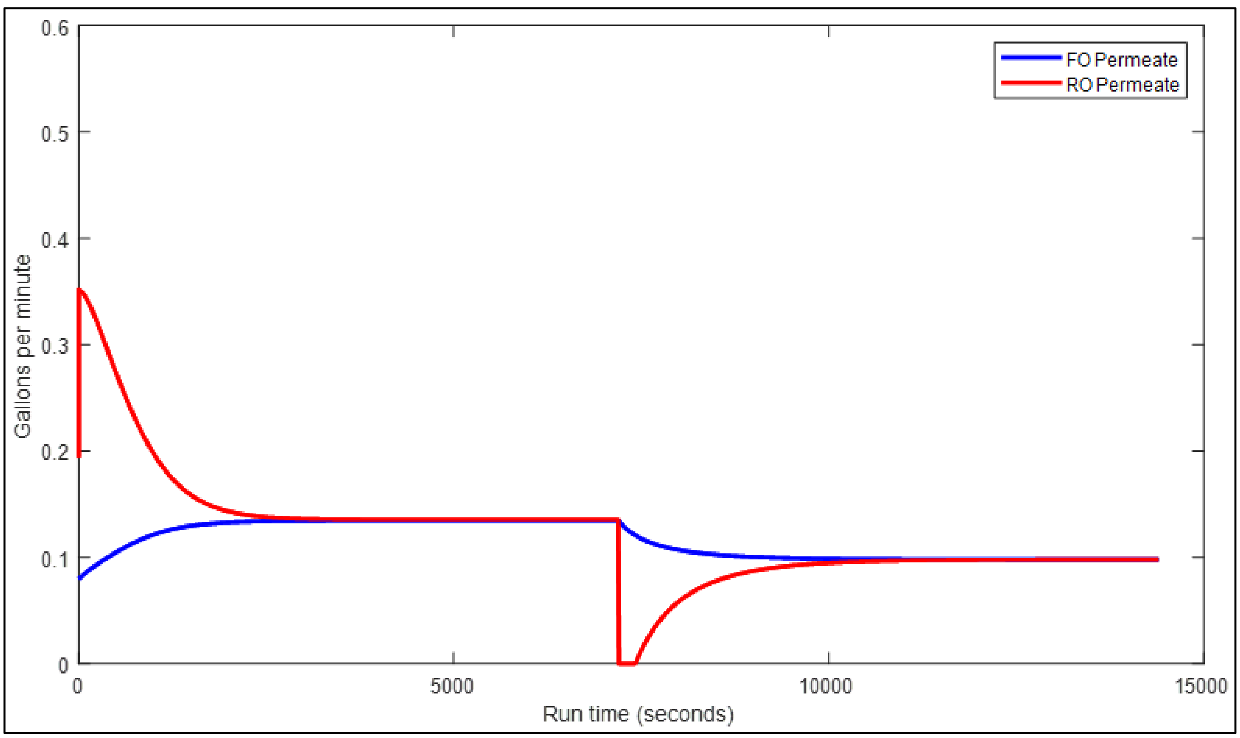


Figure 5. Simulated complete convergence of FO and RO permeate flow rates without salt loss across the membranes (SWM-equipped apparatus modeled).

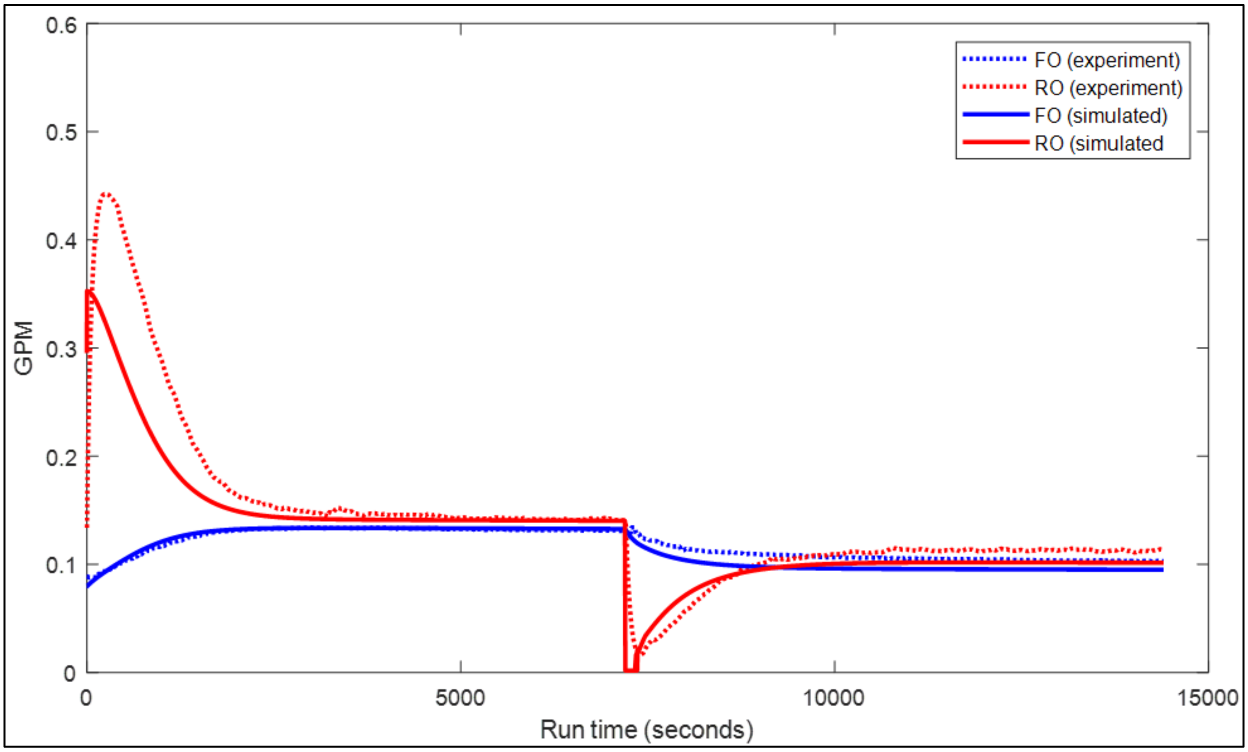


Figure 6. Comparison between simulated and experimental permeate flowrate behavior of SWM-equipped FORO apparatus.

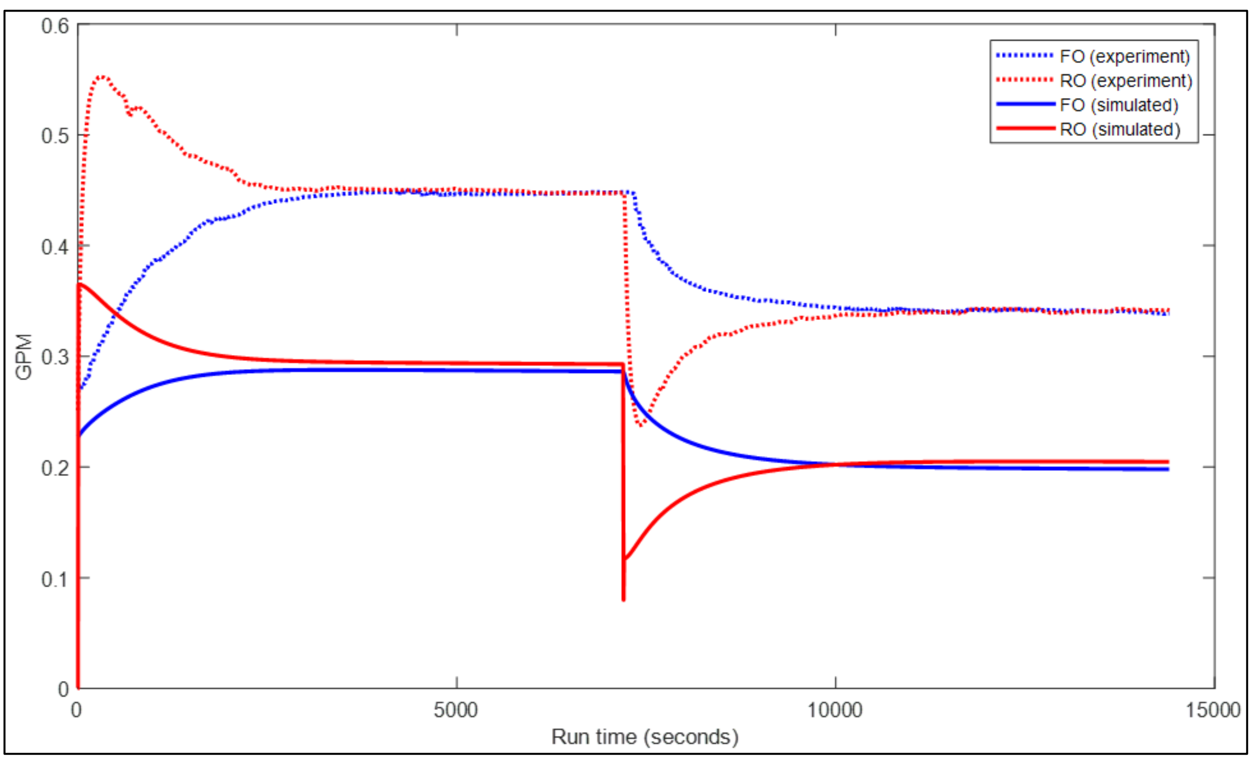


Figure 7. Comparison between simulated and experimental permeate flowrate behavior of HFM-equipped FORO apparatus.

Results of simulations using manipulated system parameters are shown in Figure 8. The variation of FO draw and RO feed tank initial volumes (Figure 8a) does not influence final permeate flow rate values but does determine how much time is required to attain stable steady state. This is because the tanks must remove a different amount of water from the circulating draw solution in order to arrive at the same tank salinities at which stable steady state is achieved under baseline conditions. A positive correlation is seen between applied RO pressure and stable permeate flow rates (Figure 8b). This is due to higher RO pressure increasing RO permeation and yielding more concentrated retentate/FO draw solution, which generates a higher FO osmotic gradient. Positive correlations are seen between rates of salt loss across membranes and the stable discrepancies between FO and RO permeate flow rates (Figure 8c and Figure 8d). This result owes to the fact that salt permeation across membranes lowers the membranes' osmotic gradients, which is discussed in further detail in Section 3.2. Finally, membrane permeances are found to influence stable permeate flow rates (Figure 8e and Figure 8f). Increasing RO permeance raises RO permeate flow rate and produces more concentrated retentate, which also raises FO permeate flux. Increasing FO permeance raises FO permeate flow rate, resulting in a more dilute draw solution being sent to the RO membrane and increasing RO permeate flow rate. The simulation of increased FO permeance to 50 LMH/bar in Figure 8e indicates that too wide a disparity in FO and RO membrane permeances (for constant membrane area) can yield behavior in which the RO permeate flow rate never matches the FO permeate flow rate, and the FO draw/RO feed tank pair will gain water for an arbitrarily long period; this behavior is shown more clearly in supplementary figure SFigure 1. While the general influence of RO permeance on stable permeate flow rates shown in Figure 8f is realistic, the damped harmonic behavior of the RO permeate seen for an RO permeance of 50 LMH implausible and is likely an artifact of the simulation program.

The FO fouling simulation is shown in Figure 9. It indicates that a progressive decrease in FO permeance leads to declining permeate flow rates for both membranes. As with non-fouling simulations that account for salt loss, this simulation demonstrates a continual disparity between FO and RO permeate flow rates that will eventually empty the FO draw and RO feed tanks.

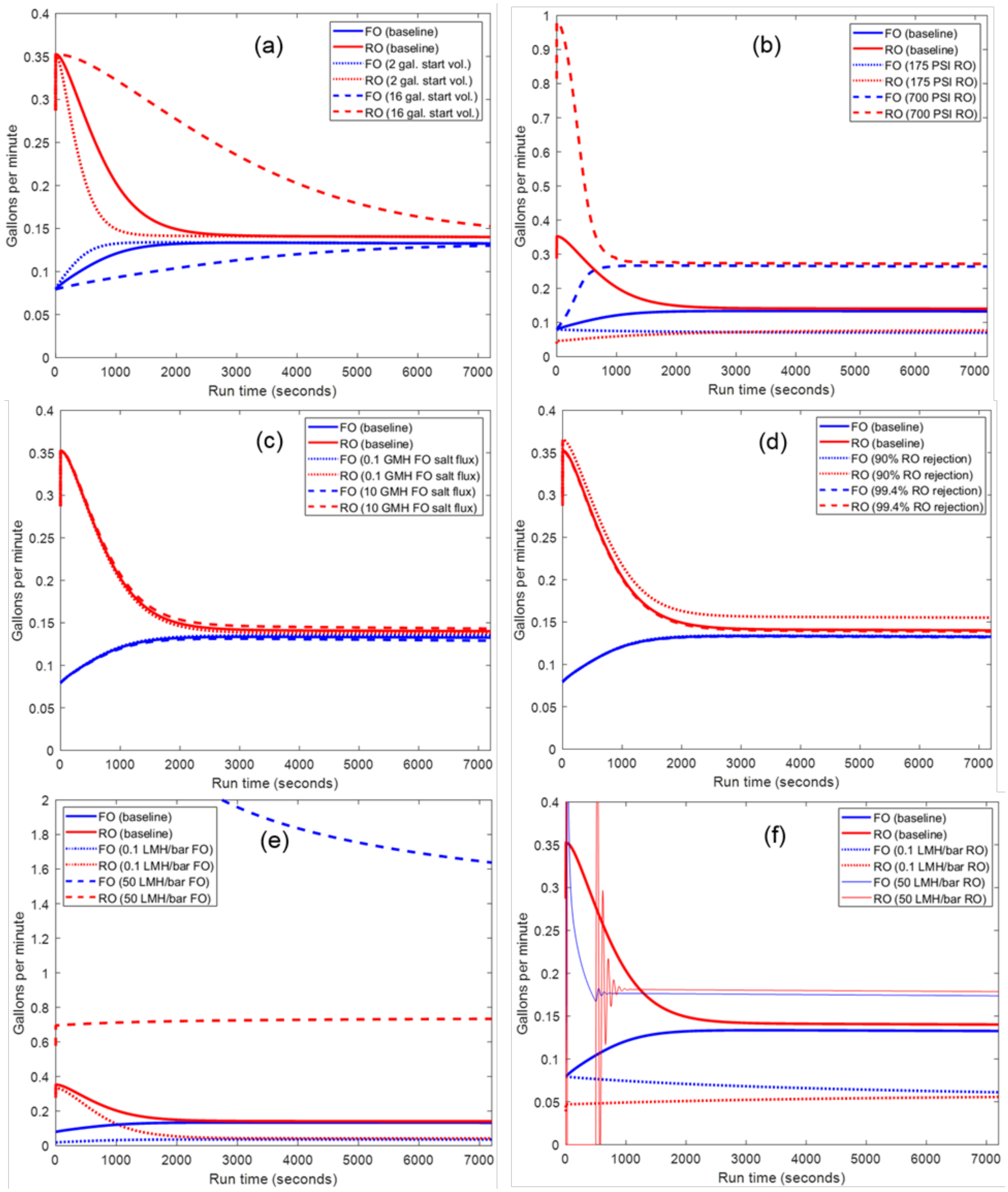


Figure 8. Results of simulated FORO permeate flow rate behavior under manipulated system parameters. Changed parameters are a) FO draw and RO feed tank initial volumes; b) applied RO membrane pressure; c) FO membrane salt permeability; d) RO membrane salt rejection; e) FO water permeance values; and f) RO water permeance values. The damped harmonic behavior displayed in (f) is a simulation artifact and likely unrepresentative of realistic behavior.

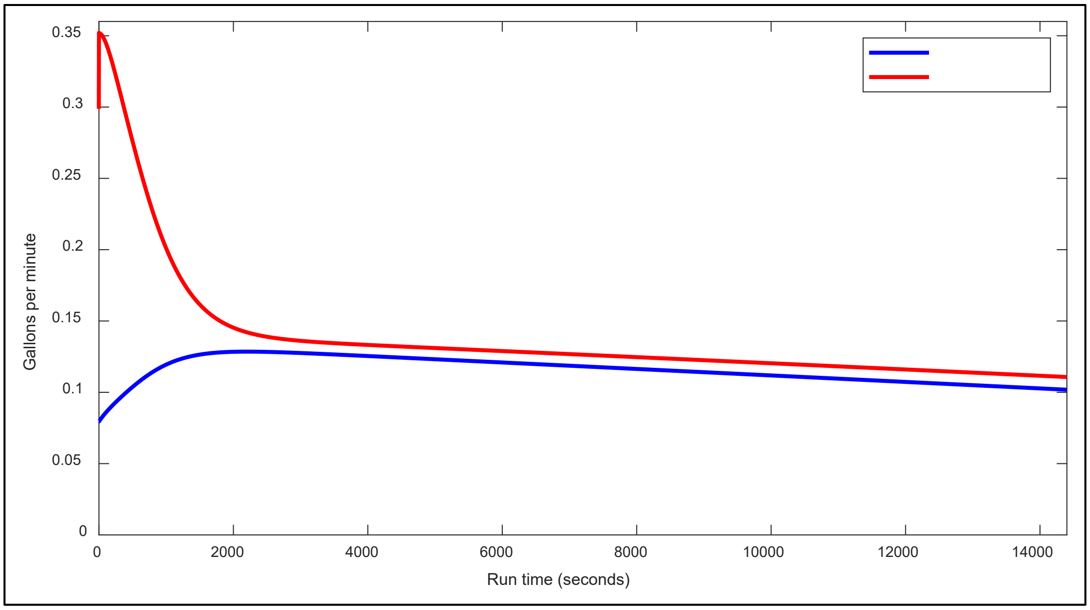


Figure 9. Simulated permeate flow rate behavior of SWM-equipped FORO apparatus under fouling conditions. FO permeance declines by 25 percent over a 4-hour run.

3.2 Analysis

Algebraic rationale for the relationship between membrane salt permeation and the disparity between steady-state FO and RO permeate flow rates is given in Figure 10. In the ideal case of zero membrane salt permeation, the FO feed and RO permeate streams are free of salt, and water fluxes across the FO and RO membranes are found with equation 3 and equation 4, respectively. Under conditions of membrane salt permeation, however, nonzero salt concentrations exist on both sides of each membrane, reducing their osmotic gradients. As the osmotic gradient provides the driving force for FO permeation, permeate flow rate under salt loss conditions will be lower than in the ideal case of no salt permeation, as shown in equation 5 and equation 6. Conversely, in the RO membrane, the osmotic gradient is opposed by hydraulic pressure; thus, permeate flow under salt loss conditions will be higher than in the case of no salt permeation, as shown in equation 7 and equation 8. For both FO and RO membranes, increased salt permeation causes greater deviation from ideal transmembrane osmotic gradients and a wider disparity between steady-state permeate flow rates. Minimization of salt loss across membranes is desirable for this reason, and because lost salt is lost draw solution solute, replacement of which increases operational expenditures. Salt permeability varies across membrane formats and materials (Kim et al. 2017); thus, proper FO membrane selection will be an important factor in building a commercial FORO system with a minimized salt loss.

Simulation and experimental results demonstrate that a positive correlation exists between applied RO pressure and steady-state permeate flow rates, suggesting that a specific permeate flow rate (and thus the rate of desalinated water production) can be selected by manipulating the RO pressure. Nonetheless, the range of practical operational flow rates for a commercial FORO system may be heavily constrained by the need to minimize FO fouling, which occurs more quickly and severely both at higher permeate flow rates (Blandin et al. 2016b) and when treating more foulant-rich feed water, such as primary wastewater (Volpin et al. 2018). An FO membrane used as the sole pretreatment step in FORO desalination would likely need to operate below its critical flux, which is the flux value at which foulant convective transport toward the membrane surface is balanced by foulant diffusive transport away from the membrane feed surface (Baker 2004). FORO operation below the FO critical flux would prevent or minimize foulant cake formation and ease eventual cleaning (Field et al. 1995). This might also help prevent the problem of cake-enhanced osmotic pressure, wherein salt permeate is trapped at the membrane surface by the foulant layer and greatly exacerbates concentration polarization issues (Lee et al. 2010; Blandin et al. 2016b). Selection of membrane chemistry appropriate to local feed water is important as well, as different membrane materials possess differing resistances to organic and inorganic foulants (Tow et al. 2018).

Even below critical flux, however, complete foulant removal may prove challenging for FO membranes in the role of single step pretreatment. FO membranes have recently been found to exhibit poor rejection of some small, neutral organic solutes (Blandin 2016a, Salamanca et al. 2021). A previous study of a FORO system has shown that organic micropollutants can become greatly concentrated in FO draw solution after passing through the FO membrane (D'Haese et al. 2021), meaning that RO fouling may potentially occur even in the absence of FO fouling. The draw solution can be purged (either continuously or replaced occasionally), but this creates a disposal problem and adds to operational cost, as the solutes must be replaced.

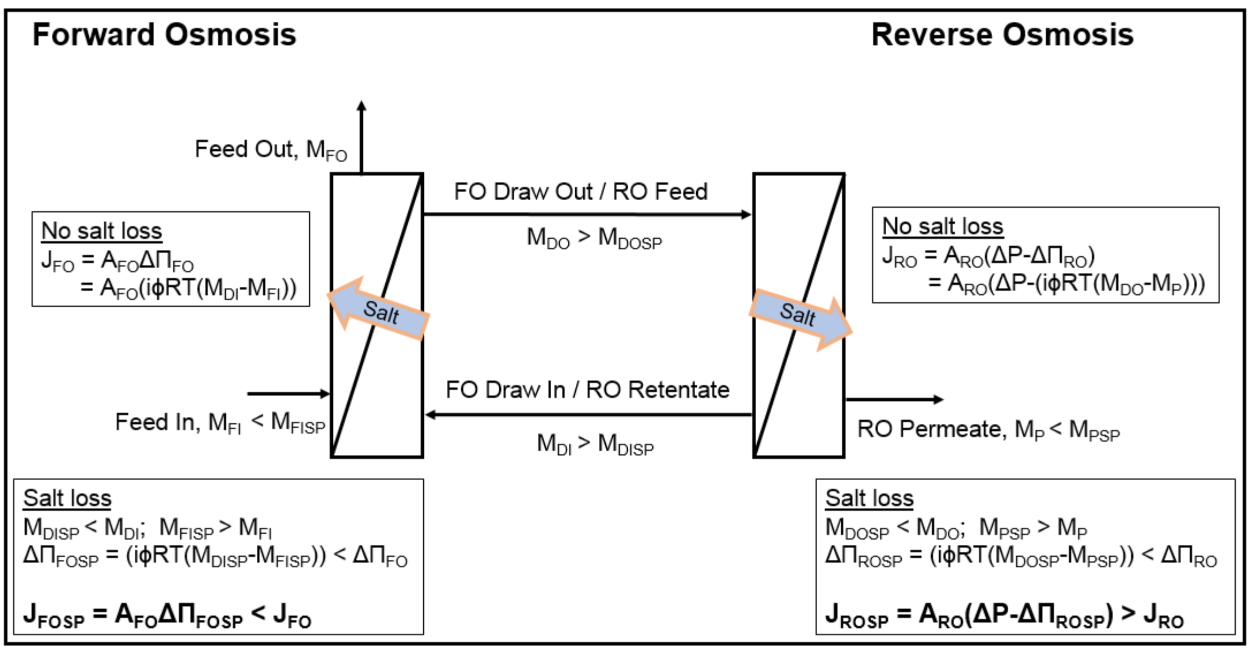


Figure 10. Consideration of osmotic gradient and membrane water flux differences under conditions of salt loss and no salt loss. Salt diffusion across each membrane lowers the osmotic gradients from their values in the ideal case of no salt loss. For FO membranes the lower osmotic gradient reduces flux, while in RO membranes, it increases flux.

3.3 Conclusions

The results of the experimental and computational portions of this project demonstrate clearly that systems of hybridized FO and RO units exhibit self-regulating behavior, wherein the permeate flow rates of each membrane spontaneously tend toward a mutual stable value. This behavior is demonstrated upon apparatus startup, and again following a perturbation of steady state by changing RO pressure. Similar behavior is predicted by simulations of a FORO system using a range of membrane permeances, operating pressures, and tank sizes. These results suggest that an improved, commercialized FORO system could operate stably with minimal operator input and a simple set of controls. Nonetheless, slight but continual salt permeation across the membranes reduces the membrane osmotic gradients, causing a lower FO permeate flow rate and a higher RO permeate flow rate than would exist without salt loss. Salt permeation thus prevents the two permeate flow rates from stabilizing at an exactly mutual value, meaning that the FO draw/RO feed tank system is always gradually decreasing in volume and will eventually run dry without resupply of salt and/or water to the tanks. Salt replacement via dosing to the FO draw and RO feed tanks might solve this problem. Additionally, experimental study of the fouling behavior of FORO systems is necessary to determine whether they can sustain self-regulating behavior during progressive fouling, and whether any foulants are able to pass the FO membrane and then foul the RO membrane.

3.4 Challenges

3.4.1 Challenges for Future Development

Salt Loss

As discussed in Section 3, salt loss across the membranes prevented complete convergence between the FO and RO permeate flow rates. Without remedy, the FO draw and RO feed tanks will eventually run dry, prohibiting long-term FORO operation. This problem might be countered in a commercial system by adding replacement salt to the FO draw and RO feed tanks, in order to maintain membrane osmotic gradients conducive to complete permeate flow-rate convergence. Higher-selectivity membranes are also an option to mitigate some of this problem, but that may be more challenging to realize than a simple dosing pump, especially for a low-cost draw solute like sodium chloride.

Membrane Fouling

The computer model developed during this project indicated that progressive fouling of the FO membrane during FORO operation would prevent the maintenance of steady-state permeate flow rates (shown in Figure 9). A commercialized FORO system might avoid or minimize fouling-induced permeance decline by operating the FO membranes below their critical flux, and by increasing the frequency of membrane cleaning.

3.4.2 Challenges during the Project

Equipment Failures

Despite considerable labor by the original graduate student researcher, graduate students only have so much capability in system construction. They had used low-cost components whenever possible, and that led to time-consuming repairs and component replacements. Saltwater-intolerant pumps and a badly worn RO pressure regulator were inexplicably included on the original system, along with narrow conduit that limited practical water flow rates to less than 2 gpm. Additionally, all of the system's original temperature and pressure sensors were analog and did not allow for automatic data collection. Flow meters, though electronic, were old, of three different types, and possessed different degrees of precision. Equipment repairs, sensor standardization, and remedial system upgrades consumed most of the time and labor applied to this project.

Poor Continuity between Researchers

The graduate student who built the test apparatus left the university before the next graduate student arrived to inherit the system. The original student did not create a manual of standard operating procedures, and the inheriting student was given only limited training by an undergraduate researcher who did not fully understand the system's workings. This resulted in very poor communication of the system's capabilities and limitations, which greatly slowed the project's progress.

Instrumentation Accuracy

Even following flow meter standardization, the meters needed frequent recalibration due to calibration drift. Maintenance of perfect agreement between all flow meters was crucial, as flow meter readings were used to assess FO and RO permeate convergence. Calibrations were required every 4 to 5 testing days.

Membrane and Module Changes

The RO membrane experienced numerous pressure swings as part of this project's testing regime. The original RO membrane was subjected to particularly sharp pressure changes (before a method of gentler changes was adopted) and began to indicate damage through declining salt rejection. The RO membrane and all gaskets within the pressure vessel were replaced; however, the poor salt rejection issue was not resolved. Finally, the new membrane was placed in a new pressure vessel, and normal performance was restored.

Test Apparatus Transport

The FORO test apparatus was moved twice during the project due to PI laboratory moves. Each move required significant system disassembly/reassembly/recalibration and the apparatus incurred light accidental damage.

Coronavirus Pandemic

The FORO project was idled between March and July 2020 because of laboratory closures. When the project resumed, it resumed at lower-than-normal productivity due to social distancing guidelines.

3.4.3 Addressing the Challenges

A commercialized version of the FORO system could circumvent most of the pilot-scale project's challenges through use of basic best practices. These include:

- Competent system design and construction
- Attentive project oversight
- The use of high-quality, standardized sensors

- Timely completion of, and universal familiarity with, a set of standard operating procedures
- Confinement of operation to well within the system's safe performance envelope.

Such needs would have cost more than this project budget would have allowed.

3.5 Recommended Next Steps

The future of hybridized FORO systems and determination of their viability for commercial application will depend on their ability to run continuously, and on demonstration that the FO component can reliably replace current pretreatment measures. To these ends, experiments in four areas are indicated.

First, salt dosing to the FO draw and/or RO feed tanks should be investigated, to assess whether full permeate flow rate convergence can be realized by replacing salt that is lost across the membranes. As seen in this project's experimental and simulation results, salt loss prevents complete permeate flow rate convergence, eventually emptying apparatus tanks and making sustained operation impossible. Closing the disparity between RO and FO flow rates by maintaining tank salinities is key to achieving FORO operation of arbitrary duration. Future investigations should assess the efficacy of dosing in maintaining membrane osmotic gradients, and whether salt can be dosed at a constant rate, or one that must be continuously scaled according to system conditions.

Second, we would recommend a reconfigured system that drew the FO draw and RO feed off of the same tank. This would disable the system's ability to be split and run as independent RO and FO systems, but it would reduce system complexity and allow for more accurate salinity measurements in the buffer tank, which is critical to long-term operation of such FO hybrid systems.

Third, we would recommend using higher-grade parts. Using all stainless-steel parts with high-quality pipe fittings, sensors, flow meters, and modules would greatly reduce the likelihood of system failures. Using trained engineers or fabricators, rather than untrained graduate students, to build the system would also yield better results. Such an approach would exceed the budget of this program.

Lastly, the self-regulating steady-state behavior of FORO systems, which was observed using pure feed water, must be demonstrated again using feed water that contains foulants. The capability to operate stably and continuously when treating real feed water is paramount, for without this ability, the technology does not present a useful alternative for recovered water treatment. Additionally, however, FO membranes must also be verified as a suitable pretreatment step, which can remove all foulants and threatens the performance of the RO membrane. Experimentation using realistic feed water should assess whether permeate flow rate convergence can be attained/sustained during progressive FO membrane fouling, and whether low-molecular-weight foulants (either organic or inorganic) are able to pass the FO membrane and then foul the RO membrane. Finally, the relationship between feed water permeation rate and fouling rate at the FO membrane should be established so that the FO fouling rate can be minimized, and the time between membrane cleanings can be maximized.

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5 Glossary

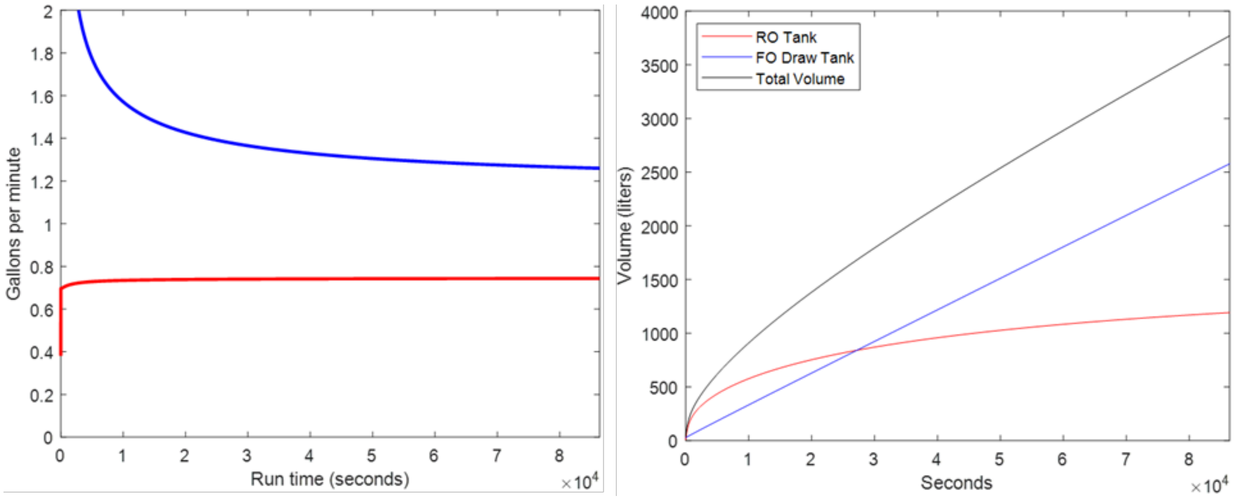
Osmotic gradient: The difference between the osmotic pressures on each side of a membrane.

Permeate flow rate: The volumetric rate (e.g., gpm) at which water passes from the feed to permeate sides of a membrane. This unit of measure is preferred over area-normalized flux (e.g., LMH) in the present work because the membranes used had various and unequal areas. Thus, convergence of permeate flow rates, and not fluxes, is the desired behavior of a self-regulating FORO system.

6 Metric Conversions

Unit	Metric equivalent
1 gallon	3.785 liters
1 gallon per minute	3.785 liters per minute
1 gallon per minute	0.0631 liters per second
1 pound per square inch	0.0689 bar
1 square foot	0.093 square meters

7 Supplementary Materials



SFigure 1. Simulation of a 24 hour run of SWM-equipped FORO apparatus with FO membrane permeance of 50 LMH/bar and unlimited tank volumes. The RO permeate flow rate never matches that of the FO membrane, and by the end of the run the aggregate tank volume has grown to approximately 3700 L (978 gal.).

STable 1. MATLAB simulation constants and variables

Variable	Baseline value [ref.]	High value	Low value	Notes
FO membrane (SWM) permeance (L/(atm*s*m^2))	0.000121 [D'Haese]	0.01407 (50 LMH/bar)	0.0000281 (0.1 LMH/bar)	High value: RO Feed set to 0.17 L/s; ROCP initialized to 1.198. Low value: RO Feed set to 0.082 L/s
FO membrane (SWM) salt permeability constant (L/(s*m^2))	0.000046 [D'Haese]	0.00011027 (10 GMH)	0.000001053 (0.1 GMH)	
FO membrane (HFM) permeance (L/(atm*s*m^2))	0.0000847 [Aquaporin]	none	none	Number derived from test conditions described in reference
FO membrane (HFM) salt permeability constant (L/(s*m2))	0.0000107 [Aquaporin]	none	none	Number derived from test conditions described in reference
RO membrane permeance (L/(atm*s*m2))	0.000250 (Hofs et al. 2013)	0.01407 (50 LMH/bar)	0.0000281 (0.1 LMH/bar)	High value: modeled RO memb. as impermeable to salt and set RO Feed to 0.6 L/s for t=0 to t=20 s, then 0.3 L/s for t=20

Variable	Baseline value [ref.]	High value	Low value	Notes
				to t=25 s, then 0.09 L/s for t>25 s. ROCP disregarded (set = 1) throughout. Low value: RO Feed set to 0.0825 L/s
RO membrane salt permeability constant (L/(s*m2))	0.0000139 (Hofs et al. 2013)	0.0001309 (90% rejection)	0.00000625 (99.4% rejection)	90% rej.: RO Feed set to 0.0888 L/s; ROCP initialized to 1.16
Initial FO Draw / RO Feed tank volumes (L)	15.14	60.56	7.57	
FO Feed-in flow rate (L/s)	0.07885	none	none	
FO Draw-in flow rate (L/s)	0.07885	none	none	
RO Feed flow rate (L/s)	0.088	See note	See note	RO Feed was changed only as specifically detailed in above notes

7.1 MATLAB

7.1.1 Comments on MATLAB Simulation

FO feed tank volume was modeled as constant at 60.56 L (16 gal.) as the tank on the physical apparatus was continually topped off. Modeling RO concentration polarization required an initial estimated value to be set by the user; all further ROCP values were then calculated by the program.

7.1.2 MATLAB Simulation Code

The code for the SWM simulation is shown below; the HFM code is similar.

```
% This FORO model was created in August 2020 by Noah Ferguson at the
% University of Connecticut.  The code models the behavior of a real, pilot
% scale laboratory system of hybridized forward osmosis (FO) and reverse
% osmosis (RO) units.  The Draw Out stream from the FO membrane is routed to %
the RO membrane; retentate from the RO membrane is routed back to the FO
% Feed tank.  The code models two distinct phases of operation.  In the first
% phase, only the FO unit operates, and the Draw Out stream fills the RO Feed
% tank.  When the RO tank volume reaches 4 gallons (15.14 liters), the second
% phase of operation begins.  In this, the RO Feed stream, which drains the
% RO Feed tank, starts.  Pressure across the RO membrane is applied, causing %
permeation of water across the membrane if the hydraulic pressure exceeds
% the osmotic pressure.  Water and salt which do not permeate leave the RO
% membrane as retentate, flowing to the FO Draw tank.  The modeled process
```

```
% continues until the designated run time is reached.  However, the code may %
stop executing before the end of the run time if the value of a modeled
% system characteristic makes further operation impossible (such as the
% complete drainage of a tank).  The purpose of this model is to demonstrate %
spontaneous convergence (or lack thereof) between the FO and RO membrane
% permeation rates, and to see how parameters such as FO draw salinity, RO
% pressure, and water flow rates affect the system's behavior.
%
% This model treats membranes as homogeneous units which are subject to equal
% conditions (e.g. pressure, salinity, permeance, etc.) at all points on
% the membrane.  Concentration polarization is estimated for the RO membrane %
but not the FO membrane.  Factors such as Reynolds number, fouling, and
% membrane ripening are not considered.
%
% Last modified:  8/25/2021

clear all
clc

TC = 0.1;  % time step, in seconds
runTime = 14400;  % seconds; time that actual experiment is to run, i.e. not %
counting startup time

% FORWARD OSMOSIS constants and initial variable values
FOPermeate = 0;  % liters per second
FOMembPressure = 1.72;  % atmospheres (transmembrane pressure)
FOMembArea = 3.2;  % meters^2; spiral-wound membrane = 3.2 m^2; HFM module = %
13.8 m^2
FOMembPermConst = 0.000121;  % L/(m^2*atm*second); (BASELINE = 0.000121);
% 0.000121 is from "Analyzing organic micropollutant accumulation..."
FOSaltPermConst = 0.000046;  % L/(second*meter^2); (BASELINE = 0.000046);
% 0.000046 is from "Analyzing organic micropollutant accumulation..."
FOSaltPermeate = 0;  % moles/second

FOFeedTankVolume = 60.56;  % liters
FOFeedSaltConc = 0;  % molar
FOFeedSaltMoles = FOFeedSaltConc*FOFeedTankVolume;
FOFeedIn = 0.07885;  % liters/second
FOFeedOut = FOFeedIn - FOPermeate;  % liters per second

FODrawTankVolume = 30.28;  % liters; (BASELINE = 30.28 L); HIGH = 32 gal. =
% 121.12 L; LOW = 4 gal. = 15.14 L
FODrawSaltConc = 0.25;  % molar
FODrawSaltMoles = FODrawSaltConc*FODrawTankVolume;
FODrawIn = 0.07885;  % liters/second
FODrawOut = 0;  % liters per second

% REVERSE OSMOSIS constants and initial variable values
ROPermeate = 0;  % liters per second
ROMembPressure = 23.81;  % atmospheres; (BASELINE = 350 psi = 23.81
% atmospheres)
```

```
ROMembArea = 7.9;  % meters^2
ROMembPermConst = 0.000250;  % L/(m^2*atm*second); (BASELINE = 0.000250, from
% "Characterization and performance of a commercial…")
ROSaltPermConst = 0.0000139;  % liters/(second*meter^2); (BASELINE =
% 0.0000139, from "Characterization and performance of ac commercial...")
ROSaltPermeate = 0;  % moles/second

ROFeedTankVolume = 0;  % liters
ROFeedSaltConc = 0;  % molar
ROPermeateSaltConc = 0.001;  % molar; set nonzero to avoid discontinuity in
% conc. polarization calc. at start of run
ROFeedSaltMoles = 0;  % no salt in initially empty tank
ROFeed = 0;  % liters per second
RORetentate = 0;  % liters per second
ROCP = 1.193;  % RO initial concentration polarization (memb. surface feed
% conc./bulk feed conc.); (BASELINE = 1.193)

totalSaltMoles = FODrawSaltMoles + ROFeedSaltMoles;
totalTankVolume = FODrawTankVolume + ROFeedTankVolume;
permeateDisparity = ROPermeate - FOPermeate;  % difference between RO and FO %
permeates

FOPi = 0;  % FO osmotic pressure
ROPi = 0;  % RO osmotic pressure
i = 2;  % van't Hoff constant for sodium chloride
Phi = 0.92;  % osmotic coefficient for sodium chloride at 25 C between ~0.2
% and ~0.5 M
R = 0.082057;  % liter*atm/mole*K
T = 298;  % kelvin

EVals = [];  % record enrichment factor E for each iteration
FOPiVals = [];  % store FO osmotic gradient values for each iteration
ROPiVals = [];  % store RO osmotic gradient values for each iteration
ROCPVals = [];  % store RO concentration polarization values for each iteration
FOPermVals = [];  % store FO permeate values for each iteration
ROPermVals = [];  % store RO permeate values for each iteration
permeateDisparityVals = [];  % record difference between RO and FO permeates %
at each iteration
FOSaltPermVals = [];  % store FO salt permeate values
ROSaltPermVals = [];  % store RO salt permeate values
ROFeedTankVolVals = [];
FODrawTankVolVals = [];
totalTankVolVals = [];  % record aggregate volume of FO Draw plus RO Feed
% tanks at each iteration
FOFeedSaltVals = [];  % record MOLES of salt in FO feed tank at each
% iteration
FODrawSaltVals = [];  % record MOLES of salt in FO draw tank at each
% iteration
ROFeedSaltVals = [];  % record MOLES of salt in RO draw tank at each
% iteration
totalSaltVals = [];  % record moles of salt remaining in FO draw + RO feed
% tanks at each iteration
```

```
FOFeedSalinityVals = [];
FODrawSalinityVals = [];
ROFeedSalinityVals = [];
ROPermSalinityVals = [];  % record molarity of RO permeate at each iteration
ROSaltRejectionVals = [];  % record RO rejection at each iteration
time = [];  % record time at each iteration
index = 1;  % current bin in vectors

% Initial filling of RO tank to 4 gallons; no water leaves RO feed tank
% during filling period
while ROFeedTankVolume < 15.14  % liters; (BASELINE = 15.14 L); HIGH = 16
% gal. = 60.56; LOW = 2 gal. = 7.57 L
    FOPi = i*Phi*(FODrawSaltConc-FOFeedSaltConc)*R*T;  % accounts for
% difference in FO draw and feed salinities
    ROPi = i*Phi*ROFeedSaltConc*R*T;
    FOPermeate = FOMembArea*FOMembPermConst*(FOMembPressure+FOPi);
    ROPermeate = 0;
    permeateDisparity = ROPermeate - FOPermeate;
    FODrawOut = FODrawIn + FOPermeate;
    FOSaltPermeate      =      FOMembArea*FOSaltPermConst*(FODrawSaltConc      -
      FOFeedSaltConc);
    ROFeedTankVolume = ROFeedTankVolume + FODrawOut*TC;
    FODrawTankVolume = FODrawTankVolume - FODrawIn*TC;
    totalTankVolume = ROFeedTankVolume + FODrawTankVolume;
    FOFeedSaltMoles = FOFeedSaltMoles + FOSaltPermeate*TC;  % salt that
% crosses FO membrane from draw to feed
    FODrawSaltMoles      =      FODrawSaltMoles      -      FOSaltPermeate*TC      -
      FODrawSaltConc*FODrawIn*TC;  % salt carried out of FO draw tank via
% draw in line
    ROFeedSaltMoles = ROFeedSaltMoles + FODrawSaltConc*FODrawIn*TC;  % salt
% carried to RO tank from FO draw tank
    totalSaltMoles = FODrawSaltMoles + ROFeedSaltMoles;  % total salt
% remaining in FO draw and RO feed tanks
    FOFeedSaltConc = FOFeedSaltMoles/FOFeedTankVolume;
    FODrawSaltConc = FODrawSaltMoles/FODrawTankVolume;
    ROFeedSaltConc = ROFeedSaltMoles/ROFeedTankVolume;

    EVals(index) = ROPermeateSaltConc/ROFeedSaltConc;
    FOPiVals(index) = FOPi;  % record current FO osmotic gradient
    ROPiVals(index) = ROPi;
    ROCPVals(index) = ROCP;
    FOPermVals(index) = FOPermeate;
    ROPermVals(index) = 0;
    permeateDisparityVals(index) = permeateDisparity;
    FOSaltPermVals(index) = FOSaltPermeate;
    ROFeedTankVolVals(index) = ROFeedTankVolume;
    FODrawTankVolVals(index) = FODrawTankVolume;
    totalTankVolVals(index) = totalTankVolume;
    FOFeedSaltVals(index) = FOFeedSaltMoles;
    FODrawSaltVals(index) = FODrawSaltMoles;
    ROFeedSaltVals(index) = ROFeedSaltMoles;
    totalSaltVals(index) = totalSaltMoles;
```

```
    FOFeedSalinityVals(index) = FOFeedSaltConc;
    FODrawSalinityVals(index) = FODrawSaltConc;
    ROFeedSalinityVals(index) = ROFeedSaltConc;
    ROPermSalinityVals(index) = ROPermeateSaltConc;
    ROSaltRejectionVals(index) = 100;  % percent; placeholder value because
% there is no RO permeate during filling stage
    time(index) = index*TC;
    index = index + 1;
end

startupTime = (index-1)*TC;  % time (seconds) required for RO Feed tank to
% fill
endTime = index*TC + runTime;  % 'index*TC' was previously 'time' but this
% was a mistake because time is a matrix and the other terms are scalars
ROFeed = 0.088;  % liters per second; (BASELINE = 0.088)

% ACTUAL RUN PERIOD
for j = (index*TC):TC:endTime  % iterate through simulation one time constant
% at a time
    expTime = (index*TC-(endTime-runTime));  % time since actual run period
% started (i.e., after filling period)

%     This section is for changing RO pressure and/or RO Feed flow rate
%     midway through a run. This section can be used as needed or not used
%     at all.
    if expTime > 7200
        ROMembPressure = 17.01;  % atmospheres; 17.01 = 250 PSI
        ROFeed = 0.085;  % liters per second; 0.085 for 350-to-250 PSI drop
    end
%     if expTime > XXX && expTime <= XXX  % seconds
%         ROFeed = XXX;  % liters per second
%     end
%     if expTime > XXX  % seconds
%         ROFeed = XXX;  % liters per second
%     end

    %FOMembPermConst = FOMembPermConst - (2.1e-9*TC);  %Simulates FO
    %membrane fouling with 25% reduction in permeance over 4 hours
    FOPi = i*Phi*(FODrawSaltConc-FOFeedSaltConc)*R*T;  % accounts for
% difference in FO draw and feed salinities
    ROPi = i*Phi*(ROFeedSaltConc*ROCP-ROPermeateSaltConc)*R*T;  % osmotic
% gradient across RO membrane
    %ROMembPermConst = (0.070-0.0001*((ROFeedSaltConc*i*R*T)
% 200))*(3.785*10.764*(1/86400)*14.696);  % from SW30 manual pg. 91
    FOPermeate = FOMembArea*FOMembPermConst*(FOMembPressure+FOPi);
% liters/second
    ROPermeate = ROMembArea*ROMembPermConst*(ROMembPressure-ROPi);
% liters/second
    if ROPermeate <= 0.001  % liters per second
        ROPermeate = (1/ROFeedSaltConc)*ROSaltPermeate;  % liters/second;
% can't actually be zero because this would mess up other calculations in the
% loop
```

```
    end
    ROCP = exp(0.7*(ROPermeate/ROFeed));  % manufacturer equation for
% calculating concentration polarization in spiral wound membranes
    permeateDisparity = ROPermeate - FOPermeate;
    RORetentate = ROFeed - ROPermeate;
    FODrawOut = FODrawIn + FOPermeate;
    FOSaltPermeate = FOMembArea*FOSaltPermConst*(FODrawSaltConc -
      FOFeedSaltConc);  % moles/second
    ROSaltPermeate = ROMembArea*ROSaltPermConst*ROCP*(ROFeedSaltConc -
      ROPermeateSaltConc);  % moles/second
    ROFeedTankVolume = ROFeedTankVolume - ROFeed*TC + FODrawOut*TC;
    FODrawTankVolume = FODrawTankVolume - FODrawIn*TC + RORetentate*TC;
    totalTankVolume = ROFeedTankVolume + FODrawTankVolume;
    FOFeedSaltMoles = FOFeedSaltMoles + FOSaltPermeate*TC;  % salt that
% crosses FO membrane from draw to feed.
    % next line:  salt permeates FO membrane, leaves via FO draw in line,
    % and returns via RO retentate
    FODrawSaltMoles = FODrawSaltMoles - FOSaltPermeate*TC -
      FODrawSaltConc*FODrawIn*TC + ((ROFeedSaltConc*ROFeed)-
      ROSaltPermeate)*TC;
    ROFeedSaltMoles = ROFeedSaltMoles - ROFeedSaltConc*ROFeed*TC +
      ((FODrawSaltConc*FODrawIn)-FOSaltPermeate)*TC;  % salt carried to RO
% tank from FO draw tank
    totalSaltMoles = FODrawSaltMoles + ROFeedSaltMoles;
    FOFeedSaltConc = FOFeedSaltMoles/FOFeedTankVolume;  % molar
    FODrawSaltConc = FODrawSaltMoles/FODrawTankVolume;  % molar
    ROFeedSaltConc = ROFeedSaltMoles/ROFeedTankVolume;  % molar
    ROPermeateSaltConc = ROSaltPermeate/ROPermeate;
    % The next 'if' condition suppresses large values of RO permeate salt
% concentration to avoid a feedback situation wherein very small RO water
% permeate but normal salt permeate create a very large osmotic gradient
% toward the permeate side, causing an instantaneous spike in RO permeate,
% followed by an immediate drop in permeate as the permeate is diluted again.
    if ROPermeateSaltConc > 0.05*ROFeedSaltConc
        ROPermeateSaltConc = 0.05*ROFeedSaltConc;
    end
    ROSaltRejection = 100*(1-(ROPermeateSaltConc/ROFeedSaltConc));
    EVals(index) = ROPermeateSaltConc/ROFeedSaltConc;
    FOPiVals(index) = FOPi;  % record current FO osmotic gradient
    ROPiVals(index) = ROPi;
    ROCPVals(index) = ROCP;
    FOPermVals(index) = FOPermeate;
    ROPermVals(index) = ROPermeate;
    permeateDisparityVals(index) = permeateDisparity;
    FOSaltPermVals(index) = FOSaltPermeate;
    ROFeedTankVolVals(index) = ROFeedTankVolume;
    FODrawTankVolVals(index) = FODrawTankVolume;
    totalTankVolVals(index) = totalTankVolume;
    FOFeedSaltVals(index) = FOFeedSaltMoles;
    FODrawSaltVals(index) = FODrawSaltMoles;
    ROFeedSaltVals(index) = ROFeedSaltMoles;
    totalSaltVals(index) = totalSaltMoles;
    FOFeedSalinityVals(index) = FOFeedSaltConc;
```

```
    FODrawSalinityVals(index) = FODrawSaltConc;
    ROFeedSalinityVals(index) = ROFeedSaltConc;
    ROPermSalinityVals(index) = ROPermeateSaltConc;
    ROSaltRejectionVals(index) = ROSaltRejection;
    time(index) = index*TC;
    index = index + 1;
end

% figure(1)  % plot tank volumes vs. time
% plot((time-startupTime), ROFeedTankVolVals, 'r')
% hold on
% plot((time-startupTime), FODrawTankVolVals, 'b')
% plot((time-startupTime), totalTankVolVals, 'k')
% title('Tank Volumes vs. Time')
% xlabel('Seconds')
% ylabel('Volume (liters)')
% legend('RO Tank', 'FO Draw Tank', 'Total Volume')
% xlim([0 14400])
% ylim([0 35])

% figure(2)  % plot moles of salt in each tank vs. time
% plot((time-startupTime), FODrawSaltVals, 'b')
% hold on
% plot((time-startupTime), ROFeedSaltVals, 'r')
% plot((time-startupTime), FOFeedSaltVals, 'm')
% plot((time-startupTime), totalSaltVals, 'k')
% title('FO and RO Feed Tank Salt Contents vs. Time')
% xlabel('Seconds')
% ylabel('Moles of salt')
% legend('FO Draw Tank', 'RO Tank','FO Feed Tank','Total Salt')
% xlim([0 7200])

% figure(3)  % plot FO and RO permeate flow rates vs. time
% plot((time-startupTime), (60/3.785)*FOPermVals, 'b', 'Linewidth', 2)
% (60/3.785) turns liters per second into gallons per minute
% hold on
% plot((time-startupTime), (60/3.785)*ROPermVals, 'r', 'Linewidth', 2)
% %plot((time-startupTime), (60/3.785)*permeateDisparityVals, 'm',
% 'Linewidth', 2)
% xlim([0 14400])
% ylim([0 0.36])
% %title('FO and RO Permeate Values vs. Time')
% xlabel('Run time (seconds)')
% ylabel('Gallons per minute')
% legend('FO Permeate', 'RO Permeate')

% figure(4)  % plot osmotic pressures vs. time
% plot((time-startupTime), ROPiVals, 'r')
% hold on
% plot((time-startupTime), FOPiVals, 'b')
% title('FO and RO Osmotic Pressures (Atmospheres) vs. Time')
% xlabel('Seconds')
```

```
% ylabel('Pressure (atmospheres)')
% legend('RO', 'FO')

% figure(5)  % plot tank salinity values vs. time
% plot((time-startupTime), FOFeedSalinityVals, 'm')
% hold on
% plot((time-startupTime), FODrawSalinityVals, 'b')
% plot((time-startupTime), ROFeedSalinityVals, 'r')
% plot((time-startupTime), ROPermSalinityVals, 'y')
% title('Tank Molarity Values vs. Time')
% xlabel('Seconds')
% ylabel('Moles per liter')
% legend('FO Feed','FO Draw','RO Feed','RO Permeate')

% figure(6)  % plot RO estimated concentration polarization vs. time
% plot((time-startupTime), ROCPVals)
% title('RO Concentration Polarization vs. Time')
% xlabel('Seconds')
% ylabel('CP coefficient')

% figure(7)  % plot RO salt rejection vs. time
% plot((time-startupTime), ROSaltRejectionVals, 'k')
% xlabel('Run time (seconds)')
% ylabel('RO salt rejection (%)')
% xlim([0 7200])
```