SCSC-NWRI GRADUATE FELLOW FINAL PROGRESS REPORT

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Project Title:	Impacts of Long-Term Exposure to Flow with Elevated Salinity and Temperature on Hydrophobicity of Membranes used for Membrane Distillation
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Background and Introduction

Drinking water sources throughout the world are becoming increasingly saline over time. This increase in water resource salinity has a number of different causes, including: urban runoff, residential water treatment systems (e.g., water softeners), industrial uses (e.g., cooling towers), agricultural practices (e.g., fertilizers and animal wastes), and water and wastewater treatment systems (e.g., brines and chemicals used in treatment). The increased salinity of drinking water sources has spurred interest in desalination technologies. Additionally, historic droughts like the one recently experienced in California reduce the reliability of traditional water systems that import water from water-rich regions to water-scarce regions. For these reasons, water managers in areas with scarce water resources are turning to water reuse and desalination to meet their water supply needs.

Although water reuse and desalination technologies are a viable option to enhance local water supplies, these processes can consume larger amounts of electrical energy than conventional water treatment technologies [1]. Consequently, these technologies may contribute more greenhouse gases to the atmosphere than conventional water treatment processes do, thereby exacerbating concerns regarding climate change. These concerns create the need for water treatment technologies that require low levels of electrical energy. To achieve this end, my research project focuses on an option for a low-energy desalination process.

Membrane distillation (MD) is an innovative water treatment technology that can be driven by alternative energy sources like solar energy or low-grade (waste) heat [2].
In direct contact MD, the feed solution (e.g., wastewater, seawater, or brine) is heated and passed along one side of a membrane, while a cooler pure water solution (the distillate) is passed along the other side of the membrane (Figure 1). The membranes used in MD are microporous–meaning that they have pore sizes less than one micrometer–and hydrophobic–meaning that they repel water. In MD, water evaporates at the feed membrane surface, passes through the membrane pores, and condenses upon contact with the cool distillate stream. Because the vapor pressure driving force is unaffected by salinity, MD can be used to treat high-salinity process streams that are challenging or impossible for conventional technologies to treat. The vapor phase separation results in a characteristically high rejection of non-volatile contaminants, but the high rejection of non-volatile contaminants can only be maintained as long as the hydrophobicity of the membrane is

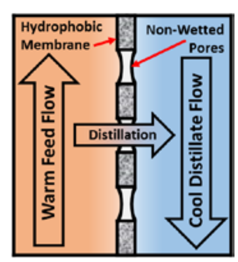

Figure 1: Membrane distillation diagram.

maintained. If the hydrophobicity is not maintained, the pores will become flooded with feed water, allowing passage of feed solution and its contaminants into the distillate solution.

Similar to how the flow of water in a river smooths the rocky surface of a riverbed, **it is my hypothesis that long-term exposure of MD membranes to viscous flow (e.g. wastewater, seawater, or brine) reduces surface roughness over time.** Because surfaces with a higher roughness are more hydrophobic [3], a reduction in MD membrane surface roughness would result in a reduction in membrane hydrophobicity and therefore a lower rejection of contaminants in the feed solution. Additionally, feed solution salinity and temperature impact membrane hydrophobicity. A smaller pore size and a higher liquid surface tension result in a higher liquid entry pressure and therefore a higher hydrophobicity, as described by the modified Young Laplace equation [4]. Because a higher salinity solution has a higher surface tension, membrane hydrophobicity would be expected to be higher for a higher salinity solution. However, higher temperatures have been demonstrated to result in pore size expansion [5], which would result in a lower membrane hydrophobicity. This indicates that the net effect on MD membranes of temperature, salinity, and potential changes in membrane surface roughness over time is unknown. The interplay between temperature, salinity, and surface roughness in affecting long-term MD membrane hydrophobicity is not well-described in the scientific literature, and my research addresses this concern.

The objective of the research described in this report is to determine (a) whether long-term exposure to viscous flow results in a reduction in MD membrane surface roughness over time, (b) the net effect of long-term exposure of MD membranes to viscous flow, elevated temperature, and salinity on membrane hydrophobicity, and (c) the relative contributions of each of these three variables to changes in membrane surface properties over time.

Progress Since the Beginning of the Project

Experimental System Development

The first stage of research involved the design and construction of a bench-scale MD system that was capable of continuous operation for long time periods while maintaining constant operating conditions and withstanding high temperatures. A photo and schematic of the long-term MD system are shown in Figure 2. A key feature of the design was to use non-metallic or titanium parts, in order to avoid accumulation of corrosion byproducts on the membrane surface during long-term experiments. The feed solution's concentration was kept constant through the use of an automated valve switching system that periodically replenished the feed tank with pre-heated distilled water over time. The thermal driving force was provided by a plastic-coated inline heater and a recirculating chiller connected to a titanium heat exchanger.

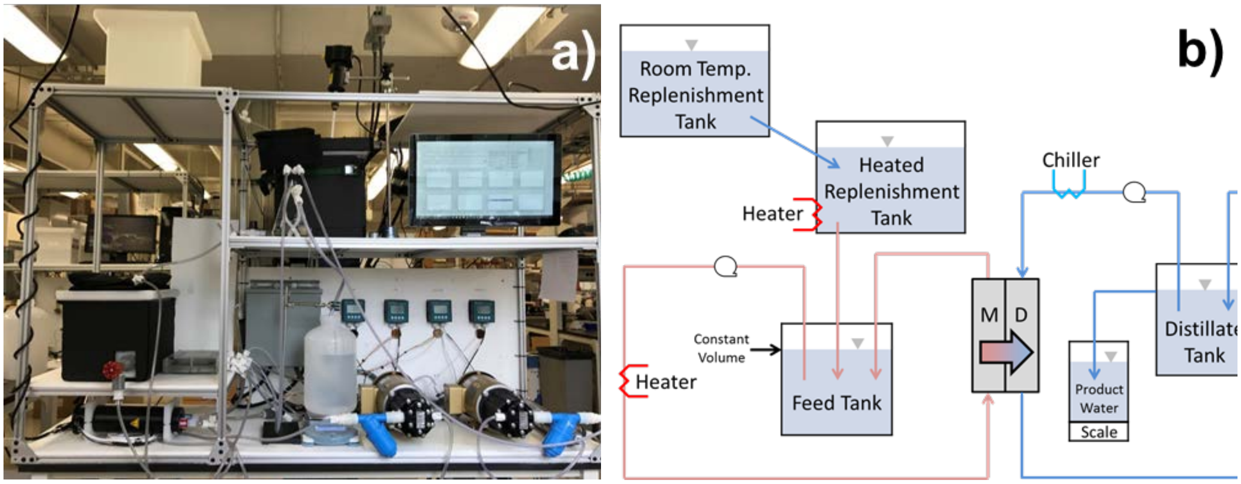

Figure 2: (a) Photo and (b) schematic of long-term bench-scale membrane distillation testing system.

Experiments and Methods

Numerous experiments were performed with a flat-sheet, expanded polytetrafluoroethylene (ePTFE) membrane, and these experiments were performed in two phases. Phase 1 involved operation of a long-term 100-day experiment and operation of a shorter-term 20-day experiment with scaling. The first experiment was used to determine if membrane hydrophobicity decreases during long-term exposure to viscous flow with elevated temperature and high salinity. The second experiment provided opportunity for comparison of changes to the membrane surface with and without scaling, and provided the opportunity to evaluate changes in membrane surface properties during shorter exposure periods. Phase 2 involved a series of three 30-day experiments that were used to separate the effects of temperature and salinity on changes in the membrane surface over time. The experimental conditions are summarized in Table 1.

Table 1: Experimental matrix.

Experiment Number	Feed Inlet Temperature (°C)	Distillate Inlet Temperature (°C)	Feed Salinity (g/L NaCl)	Flow Rate (L/min)	Time (days)
1	65	38	200	1.5	100
2	65	38	200	1.5	20
3	45	38	200	1.5	30
4	65	38	5	1.5	30
5	65	38	200	1.5	30

MD system performance was evaluated through monitoring of water flux over time, and membrane surface characterization was carried out through surface roughness measurements with atomic force microscopy (AFM), surface imaging with scanning electron microscopy (SEM), and surface elemental composition analysis with energy-dispersive x-ray spectroscopy (EDS). Membrane hydrophobicity was quantified with the contact angle – the angle between the membrane surface and a drop of water placed on that surface.

Results and Discussion

The results of the 100-day experiment clearly demonstrated a significant change in membrane surface properties and a decrease in performance (i.e., water flux) that correlated with a decrease in membrane hydrophobicity. A significant decrease in membrane surface roughness was observed on the feed (hot) and distillate (cool) sides of the membrane, and these decreases in surface roughness correlated with decreased contact angles (i.e., hydrophobicity) on both sides of the membrane. SEM images appeared to show a fouling layer on the feed side; elemental analysis with EDS confirmed the presence of a fouling layer. Results from the 20-day experiment, which included short-term scaling of the membrane with NaCl crystals approximately halfway through the experiment, also demonstrated the presence of a fouling layer confirmed with SEM and EDS analyses. The results of this 20-day experiment also demonstrated significant decreases in water flux over time, and membrane surface roughness and contact angle on the feed and distillate sides.

While the membrane surface was fully covered by a fouling and/or scaling layer on the feed side of the membrane in both the 100- and 20-day experiments, significant changes to the actual membrane surface were able to be observed on the distillate side in both experiments. These results indicated that significant changes to the membrane surface could be observed even in twenty days of operation. The results also indicated that the system design needed to be altered to prevent foulants from entering the system, so that changes to feed-side membrane properties could be observed. The most likely pathway that foulants were determined to be entering the system was through the heated replenishment tank (see Figure 2b), which had a partly open top required for insertion of the submerged heater and mixer. Considering this, the heated replenishment tank was removed from the system, and the feed tank was replenished with room-temperature water. Initial testing indicated that this did not negatively impact temperature stability in the MD system, so the series of three 30-day experiments were operated without the heated replenishment tank.

The first 30-day experiment (Experiment 3 in Table 1), with a 45 °C and 200 g/L feed solution, served as the low-temperature feed solution experiment. The second 30-day experiment (Experiment 4 in Table 1), with a 65 °C and 5 g/L feed solution, served as the high-temperature feed solution experiment. The third 30-day experiment (Experiment 5 in Table 1), with a 65 °C and 200 g/L feed solution, served as a comparison experiment for the first and second 30-day experiments to separate the effects of temperature and salinity on changes to the membrane surface. Significant changes in feed-side membrane surface properties were observed qualitatively by comparing SEM images of virgin membranes to those of used membranes for all three experiments; similar changes were observed on the distillate side, but to a lesser extent. EDS results showed that the used membrane samples were composed solely of membrane material, and were not coated with a fouling or scaling layer. These results indicate that long-term exposure to viscous flow with elevated temperature and high salinity can result in permanent changes to the membrane surface structure.

Comparison of SEM images from the three 30-day experiments shows much more significant changes to the membrane surface in the two experiments with a 65 °C feed solution, indicating that higher temperatures result in more significant changes to the membrane surface. Comparison of SEM images from the two 65 °C experiments – one with a 5 g/L and the other with a 200 g/L feed solution – does not show a significant difference in changes to the membrane surface. This indicates that salinity does not play a significant role in the changes to the membrane surface during long-term experiments. These qualitative results (SEM images) were confirmed by measured decreases in membrane surface roughness and contact angle, indicating that changes in membrane surface characteristics caused by long-term exposure to flow with elevated temperature can reduce membrane hydrophobicity over time – even in the absence of fouling or scaling. The observed decreases in membrane hydrophobicity (i.e., contact angle) also correlated with a decrease in water flux over time in all three 30-day experiments, indicating that the decreases in hydrophobicity result in decreases in MD system performance.

Conclusions

The results presented indicate that long-term operation of MD systems can result in significant changes in membrane surface characteristics, on a time-scale as short as twenty days. Changes in membrane surface properties were measured qualitatively with SEM imaging, and elemental analysis results using EDS confirmed that the observed changes were due to changes in the membrane surface structure, rather than fouling or scaling. The qualitative changes to the membrane surface observed through SEM imaging were confirmed quantitatively through decreased surface roughness and contact angle in each experiment. Decreased contact angle is indicative of decreased hydrophobicity. Comparison of SEM images and measurements of membrane surface roughness between experiments indicated that feed solution salinity did not play a significant role in the changes to the membrane surface, but high-temperature was responsible for the majority of the changes to the membrane surface. The observed decreases in contact angle (i.e., hydrophobicity) in each experiment correlated with decreased water flux over time, indicating that long-term exposure to flow with elevated temperature can result in changes in membrane hydrophobicity that negatively affect MD system performance.

MD can provide significant benefits to the water treatment community through its ability to effectively treat high-salinity feed solutions, while using alternative energy sources such as solar thermal or low-grade waste heat. However, the long-term performance of membranes that are commonly used in MD, like ePTFE, must be adequately assessed before they can be implemented in order to realize the benefits that MD can provide to the water treatment community. The results of this study are important because they assess the ability of ePTFE membranes, which are already used for other fully commercialized water treatment processes like microfiltration, to maintain satisfactory performance under the unique operating conditions in long-term MD experiments (high temperature and salinity). Because the ePTFE membranes presented in this research have been shown to have difficulty maintaining adequate performance during long-term experiments, further research should focus on identifying whether similar behavior occurs with other widely available hydrophobic membranes like those made from polyvinylidene fluoride or polypropylene. Further research could also be focused on the development of hydrophobic coatings that are more resilient and less prone to the types of changes in surface properties observed in this research. This research serves the greater good by identifying the major causes of decreased performance of MD membranes during long-term experiments, while providing information that can be used to design better membranes for use in MD systems, allowing the benefits of MD for desalination and water reuse applications to be fully realized.

Journal Articles Associated with this Research

A.L. McGaughey, R.D. Gustafson, A.E. Childress, Effect of long-term operation on membrane surface characteristics and performance in membrane distillation, Journal of Membrane Science, 543 (2017) 143-150.

R.D. Gustafson, A.L. McGaughey, S. McVety, A.E. Childress, Effects of solution temperature and salinity on changes in membrane hydrophobicity in long-term membrane distillation experiments, Journal of Membrane Science – In preparation for submission in May 2018

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