NWRI-SCSC GRADUATE FELLOW SEMI-ANNUAL PROGRESS REPORT

DATE:	December 30,2017
Project Title:	Impacts of Long-Term Exposure to Flow with Elevated Salinity and Temperature on Hydrophobicity of Membranes used for Membrane Distillation
Graduate Fellow:	Ryan Gustafson
Advisor:	Amy Childress
Institution:	University of Southern California

Background and Introduction

Drinking water sources throughout the world are becoming increasingly saline over time. This increase in water resource salinity has several 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 maintained. If the hydrophobicity is not

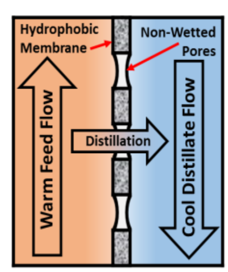

Figure 1: Membrane distillation diagram.

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 to Date

Previous progress reports have described the data required to determine that long-term exposure of MD membranes to viscous flow does cause a reduction in surface roughness and contact angle (hydrophobicity) over time. This conclusion was determined based on measurements and scanning electron microscopy (SEM) images taken on the distillate side of the membrane. The feed side of the membrane could not be characterized after experiments due to the presence of a fouling layer, which was suspected to have developed because of dust and other foulants entering the system through a heated auxiliary feed tank that was partly open to the surroundings throughout the previous experiments. The heater was removed from the auxiliary feed tank and the tank remained fully covered throughout all following experiments, except when the auxiliary tank was refilled twice per day.

A series of 30-day experiments are currently underway to evaluate the relative impacts of solution viscosity, temperature, and salinity on long-term MD membrane hydrophobicity. Two of these three 30-day experiments have been completed thus far – one with a high-viscosity feed solution and one with a low-viscosity feed solution. These two experiments were performed to determine whether higher-viscosity solutions result in larger changes in membrane surface characteristics than lower-viscosity solutions, during long-term MD experiments. The high-viscosity experiment was performed with a 200-g/L NaCl feed solution at 45 °C, and the low-viscosity experiment was performed with a 5-g/L NaCl feed solution at 65 °C, corresponding to viscosities of 9.95×10^{-4} and 4.39×10^{-4} N-s/m^2, respectively. The feed and distillate solution flow rates were 1.5 L/min and the distillate solution temperature was 38 °C in each experiment. Both SEM imaging and energy dispersive x-ray spectroscopy (EDS) analyses were performed before and after each experiment. The SEM images were used for qualitative 2-dimensional surface morphology assessment, and EDS spectra were used to analyze the elemental make-up of membrane samples before and after experiments.

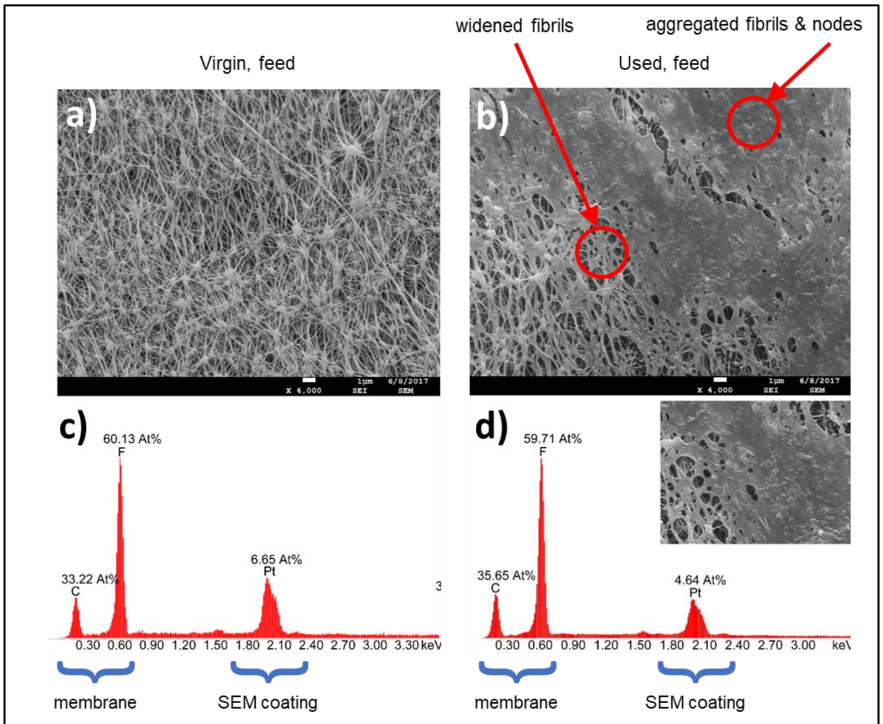

Figure 2: SEM images for (a) virgin membrane and (b) used membrane, and EDS spectra for (c) virgin membrane and (d) used membrane. The experiment was performed with a 200-g/L NaCl feed solution at 45 °C (high-viscosity), a 38 °C distillate solution, and 1.5 L/min flow rates in the feed and

The SEM and EDS results for the feed side of the membrane in the low-viscosity experiment are shown in **Figure 2.** The feed side of the virgin membrane sample for this experiment shows the network of fibrils (polymer strands) that meet at nodes throughout the membrane material, which are characteristic of expanded PTFE membranes. The feed side of the used membrane demonstrates a significant change in the surface characteristics after the 30-day experiment, including areas of widened fibrils and areas of aggregated fibrils and nodes. The EDS spectra demonstrate the lack of any foulants on the membrane surface because the carbon and fluorine peaks represent the elemental makeup of the membrane and the platinum peak is indicative of the platinum coating used in the SEM procedure. The lack of any oxygen or nitrogen in the EDS spectra for the virgin and used membrane samples indicates that no organic foulants were present, indicating that the changes in the membrane surface shown in the SEM images were due to morphological changes in the membrane surface rather than fouling.

The SEM and EDS results for the high-viscosity experiment are shown in **Figure 3.** While changes in the membrane surface characteristics are apparent after the 30-day experiment, these changes are much less significant than observed in the low-viscosity experiment. Similar to that observed for the low-viscosity experiment, the EDS spectra for the high-viscosity experiment demonstrate that no organic foulants were present on the membrane surface, indicating that changes in surface characteristics were not due to organic fouling. A comparison of the SEM images for the low- and high-viscosity experiments clearly indicates that the low-viscosity feed solution resulted in much more significant changes in membrane surface characteristics than the high-viscosity solution. However, because viscosity is affected by solution temperature and salinity, an additional experiment must be performed for comparison to the high- and low-viscosity experiments in order to determine the relative impacts of temperature and salinity on changes in membrane surface characteristics during long-term experiments. This additional experiment will be performed during the next reporting period.

Conclusions

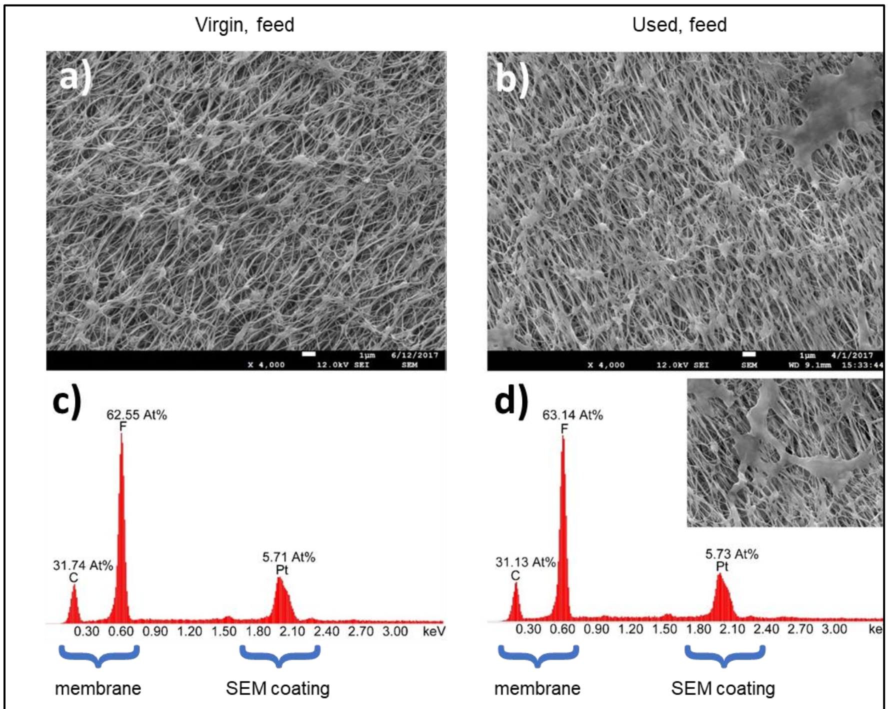

Figure 3: SEM images for (a) virgin membrane and (b) used membrane, and EDS spectra for (c) virgin membrane and (d) used membrane. The experiment was performed with a 5-g/L NaCl feed solution at 65 °C (low-viscosity), a 38 °C distillate solution, and 1.5 L/min flow rates in the feed and distillate channels.

The results presented indicate that long-term operation of MD systems can result in significant changes in membrane surface characteristics, on only a 30-day time scale. The updated system design allowed for assessment of the feed side of the membrane surface after 30-day experiments, preventing fouling from occurring. Changes in membrane surface characteristics were assessed using SEM and EDS analyses, demonstrating that the observed changes in the membrane surface were due to widening of fibrils and aggregation of fibrils and nodes, rather than membrane fouling. The observed changes were assessed qualitatively using SEM analyses and semi-quantitatively using EDS analyses, so future analyses of the high- and low-viscosity experiment membrane samples will be assessed quantitatively using surface roughness and contact angle measurements.

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 PTFE, 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 PTFE 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). If PTFE membranes are shown to have difficulty maintaining adequate performance during long-term experiments, then this research will encourage investment in research on alternative hydrophobic membranes (e.g. polyvinylidene fluoride, polypropylene), which may be able to more adequately maintain performance during long-term experiments. This research will serve 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.

Next Steps

Surface roughness and contact angle measurements will be taken on used membranes from the high- and low-viscosity experiments in order to provide quantitative assessment of the observed changes. The third 30-day experiment, which will be used to isolate the impacts of temperature and salinity from the impacts of viscosity, will be performed during the next reporting period. After the third experiment is performed, changes in membrane surface characteristics will be assessed using SEM, EDS, surface roughness, and contact angle measurements. A literature review will be performed to determine whether such drastic changes in membrane surface characteristics as observed in the high- and low-viscosity experiments have been observed with PTFE membranes in other applications (e.g. microfiltration). A comparison of changes in PTFE membrane surface characteristics during long-term experiments in other applications to those obtained in the current study will help identify whether PTFE membranes will be appropriate for long-term use in MD systems.

References

[1] H. Cooley, M. Heberger, Key issues for seawater desalination in California: Energy and greenhouse gas emissions, Pacific Institute, California, (2013).

[2] R. Schwantes, A. Cipollina, F. Gross, J. Koschikowski, D. Pfeifle, M. Rolletschek, V. Subiela, Membrane distillation: Solar and waste heat driven demonstration plants for desalination, Desalination, 323 (2013) 93-106.

[3] H.J. Busscher, A.W.J. van Pelt, P. de Boer, H.P. de Jong, J. Arends, The effect of surface roughening of polymers on measured contact angles of liquids, Colloids and Surfaces, 9 (1984) 319-331.

[4] E. Guillen-Burrieza, A. Servi, B.S. Lalia, H.A. Arafat, Membrane structure and surface morphology impact on the wetting of MD membranes, Journal of Membrane Science, 483 (2015) 94-103.

[5] R.B. Saffarini, B. Mansoor, R. Thomas, H.A. Arafat, Effect of temperature-dependent microstructure evolution on pore wetting in PTFE membranes under membrane distillation conditions, Journal of Membrane Science, 429 (2013) 282-294.