Effects of Membrane Surface Modification on Calcium Carbonate Fouling and Membrane Efficiency for Desalination

Whitney Wong

Biomedical Engineering, University of Texas at Austin

NNIN REU Site: Nano Research Facility, Washington University in St. Louis, St. Louis, MO

NNIN REU Principal Investigator: Dr. Young-Shin Jun, Department of Energy, Environmental and Chemical Engineering (EECE), Washington University in St. Louis

NNIN REU Mentor: Jessica Ray, EECE, Washington University in St. Louis

Contact: whitney.wong@utexas.edu, ysjun@seas.wustl.edu, jessica.ray@go.wustl.edu

Introduction:

Desalination can be used as a means to replenish freshwater supplies of communities with growing population needs. Reverse osmosis (RO) is a pressure-driven process that requires a semi-permeable membrane to selectively remove salts and other particulate matter from brackish water or seawater. Common RO membranes are thin-film composites (TFCs), which are composed of a thin polyamide layer supported by a porous polysulfone layer. Although membrane desalination is an efficient method, a persistent problem is that the membrane is highly susceptible to fouling—accumulation of particles onto the membrane surface over time that can clog or otherwise compromise the efficiency or performance of the membrane [1]. The main cause of fouling appears to be a hydrophobic interaction between the membrane surface and the solutes in the water [2]. In our approach, we grafted polyethylene glycol (PEG), a hydrophilic monomer, to help disrupt hydrophobic interactions with calcium carbonate ($CaCO_3$), a common hydrophobic fouling agent (Figure 1). After membrane characterization, we analyzed the interaction between $CaCO_3$ and the membrane surface.

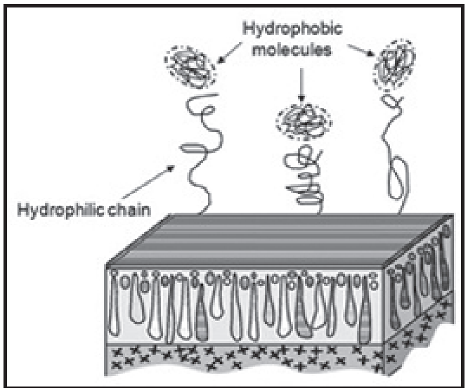

Figure 1: Experimental approach. Graft PEG to membrane surface to help reduce fouling of hydrophobic solutes [3].

Experimental Procedures:

Monomer Grafting. Commercially available BW30 TFC membranes were purchased from Dow-Filmtec in flat sheet form. Grafting materials purchased from Sigma-Aldrich included potassium disulfite (PD) and potassium persulfate (PP) to initiate the reaction, polyethylene glycol (PEG) as the hydrophilic monomer, and ethyleneglycol dimethacrylate (EGDMA) as the crosslinker. Various concentrations and grafting times were tested. The final conditions chosen were a graft time of one hour with a solution that consisted of 0.1 M PEG, 0.01 M EGDMA, and a 0.025 M equimolar PP and PD solution.

Contact Angle. To determine the wettability of the membrane, we measured contact angles of samples with and without surface modification. Twenty microliters of de-ionized (DI) water was pipetted onto the membrane surface, where images were then captured using a Motic digital microscope and the Motic Image Plus 2.0 software.

$CaCO_3$ Nucleation and Salinity Testing. Various concentrations of sodium bicarbonate ($NaHCO_3$) and calcium chloride dihydrite ($CaCl_2$) were used to form $CaCO_3$, which could be deposited onto the membrane surface. To mimic brackish water conditions, we replaced double-filtered water in the original solution with a background solution of sodium chloride (NaCl). Concentrations of 0.1, 0.5, and 1 M NaCl were added to observe the effect of increasing NaCl on $CaCO_3$ formation.

Because the $CaCO_3$ saturation index (SI) changes with ionic strength, the Geochemist's Workbench software was used to calculate the adjusted $CaCl_2$ and $NaHCO_3$ concentrations to maintain an SI of 2.16 for calcite formation for all experiments.

Thus, a final solution with concentrations of 0.025 M $NaHCO_3$ and 0.025 M $CaCl_2$ was used.

Results and Discussion:

Characterization of the membrane before and after grafting included scanning electron microscopy (SEM) and measuring contact angles. In order to see whether grafting was successful, contact angle measurements were determined to observe whether grafting made the membrane more hydrophilic. The best concentration, 0.1 M PEG for one hour, was chosen because it had a smaller contact angle than the unmodified membrane.

SEM proved to be a powerful tool for analyzing both the unmodified and grafted membranes after $CaCO_3$ was deposited onto the surface. As the NaCl concentration increased, there was a definite increase in $CaCO_3$ nucleation for both the unmodified and grafted membranes. An increase in nucleation as ionic strength increases has been reported in literature [4]. There was also a distinct decrease in the amount of nucleation between the unmodified and grafted membranes at each respective concentration of NaCl. For example, this can be seen in Figures 2 and 3.

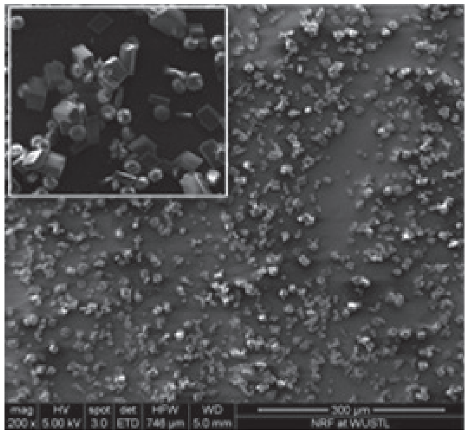

Figure 2: Unmodified membrane with $CaCO_3$ nucleation and a background solution of 0.5 M NaCl. Inset in the upper left corner is magnified with a scale of 40 µm.

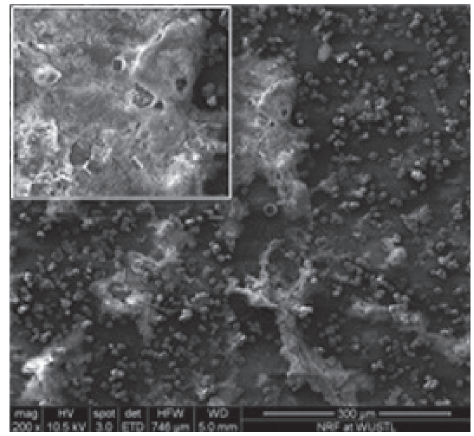

Figure 3: PEG-grafted membrane with $CaCO_3$ nucleation and a background solution of 0.5 M NaCl. There is less nucleation around and on dense areas of PEG. Inset in upper left corner is magnified with a scale of 50 µm.

A final observed trend was a difference in $CaCO_3$ morphologies. In the unmodified membrane, amorphous $CaCO_3$ (spherical), calcite (rhombohedral), and aragonite (fibrous-shaped) were identified. While in the grafted membrane, mostly calcite was observed. This could be due to the differences in binding sites after grafting with PEG.

Conclusions and Future Work:

In this project, PEG was successfully grafted onto the TFC membrane surface. From the SEM images of both the unmodified and grafted membranes, there was clearly a decrease in the degree of $CaCO_3$ nucleation as the surface became more hydrophilic. This was what was expected when a hydrophilic component was added to the membrane. After analyzing the interaction between the membranes and the $CaCO_3$ particles, it was determined that hydrophilic/hydrophobic interactions govern nucleation.

In the future, a working laboratory-scale RO system is desired to test grafted membrane efficiency in salt rejection. There are implications for this grafting procedure to be a viable modification that could help to reduce water pretreatment costs, extend the lifetime of TFC membranes, and improve the overall membrane desalination process. Thus, it is extremely important to test and compare the efficiency of the unmodified and grafted membranes.

Acknowledgements:

Thank you to Dr. Young-Shin Jun, Jessica Ray, and everyone at the Environmental Nanochemistry Lab for their guidance and support. I would also like to give thanks to the Nano Research Facility, the National Nanotechnology Infrastructure Network Research Experience for Undergraduates (NNIN REU) Program, and the National Science Foundation for giving me this opportunity and an unforgettable experience.

References:

[1] Freger, et al.; Membrane Science, 209, 283-292 (2002).

[2] Koo, et al.; "Fouling resistant reverse osmosis membranes"; 1-10 (2003).

[3] Kang, et al.; Polymer, 48, 1165-1170 (2007).

[4] Boerlage, S.; "Scaling and particulate fouling in membrane filtration systems"; Dissertation, Swets and Zeitlinger Publishers, 208 (2001).