Optimization of Thin Film Composite Polyimide Reverse Osmosis Membrane by Polyethylene Glycol for Enhanced Fouling Resistance

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Introduction:

Water scarcity is a serious concern for the world and it is projected to get worse. Water desalination is an important source of fresh water to alleviate water scarcity, especially in water stressed regions, and it will continue to grow in importance. Many desalination plants use reverse osmosis (RO) to generate fresh water [1]. RO is a high pressure process that uses thin film composite polyamide (TFC-PA) membranes to remove contaminants from the water. Unfortunately, these membranes commonly experience fouling, which can decrease water flux and salt rejection [1]. Polyethylene glycol (PEG) is a hydrophilic material that, when attached to the membrane surface, can enhance fouling resistance and increase membrane flux by making the surface both more neutrally charged and hydrophilic [2]. However, multi-component foulant resistance of modified membrane has not been tested. Thus, in this study, we investigated the efficacy of the PEG-modified TFC-PA RO membranes in fouling resistance to calcium carbonate ($CaCO_3$), calcium sulfate ($CaSO_4$), and humic acid.

Experimental Procedure:

One commercially available TFC-PA membrane (BW30) was used to investigate the effect of PEG modification on mineral fouling ($CaSO_4$ and $CaCO_3$) and organic fouling (humic acid). The membrane was soaked in deionized (DI) water for 24 hours before testing or modifying. The membrane was modified in a solution of PEG monomer, PEG crosslinker (ethyleneglycol dimethacrylate), and initiators (potassium persulfate and potassium disulfite). The membrane was then pretreated for membrane compaction and conditioning with DI water for seven hours at 260 psi. Then the membrane was tested with fouling influent for four hours.

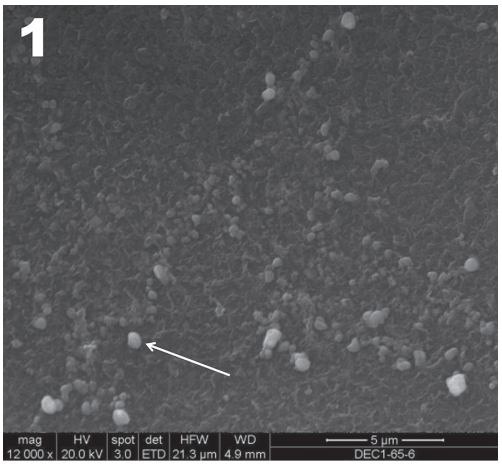
There were three fouling influents of interest, all dissolved into DI water. First, $CaCO_3$-forming solution was made by mixing 10 mM NaCl with 3.3 mM $CaCl_2$ and 3.3 mM Na_2CO_3. Second, $CaSO_4$-forming solution was made by mixing 19.5 mM $CaCl_2$, and 19.5 mM Na_2SO_4. Third, humic acid solution was prepared to contain 10 ppm humic acid. Continuous samples of effluent were taken every five minutes. Water flux and salt rejection were tested every five minutes for the first hour, then every 30 minutes. The extent of membrane fouling was examined by contact angle measurement and scanning electron microscopy (SEM).

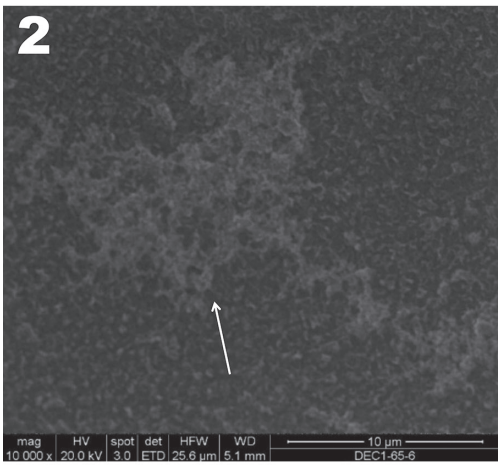
Results and Discussion:

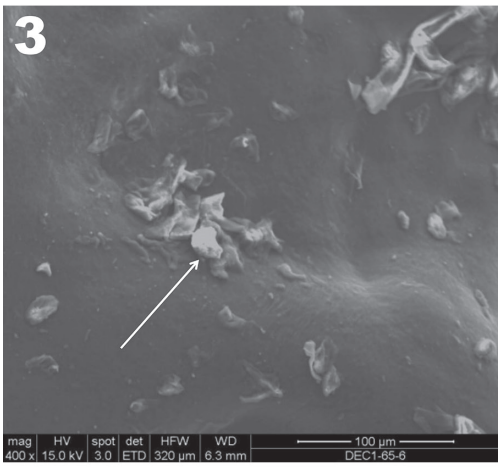
Before fouling experiments, SEM images showed PEG attached to the modified membrane. Also, contact angle analysis done before fouling showed that PA-PEG had a much lower contact angle at 13.2° than PA at 42.2°.

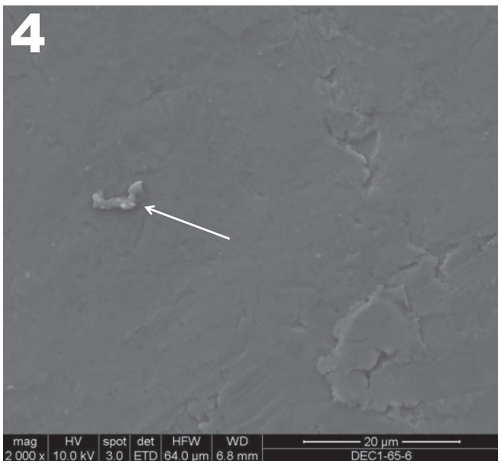
For fouling experiments, overall, there was less fouling for PA-PEG membranes than for PA membranes. For the $CaCO_3$ fouling experiment, we found the PA and PA-PEG membranes had comparable flux and salt rejection. However, the SEM images show that the PA-PEG membrane has fewer foulants than the PA membrane (Figures 2 and 4). For the $CaSO_4$ fouling experiment, we found that PA-PEG had higher initial flux and Ca^{2+} rejection. However the PA membrane had higher SO_4^{2-} rejection, most likely due to the negative membrane surface having more repulsion with the negatively charged ion than the neutral modified membrane surface. Figure 2 showed no $CaSO_4$ fouling on the PA-PEG membrane, but $CaSO_4$ fouling was present on the PA membrane shown in Figure 1. For the humic acid fouling experiment, PA had higher flux, but based on contact angle showing that the PA surface was more hydrophobic and this should result in a lower flux, this can be an error and should be retested.

The PA-PEG membrane had a higher humic acid and Cl- rejection. It also had a lower contact angle after fouling at 38.3° than the PA membrane after fouling at 55.8° and the SEM image in Figure 4 showed less fouling on the PA-PEG membrane than the PA membrane in Figure 3.









PEG modification makes the PA membrane more hydrophilic resulting in higher initial flux than PA in these experiments. PEG modification of the PA membrane increases fouling resistance to humic acid in particular. Based on contact angle analysis, after humic acid fouling, PA-PEG is still more hydrophilic than PA. At very high mineral foulant concentrations, PEG does not obviously enhance salt rejection, but it enhances resistance to inorganic foulants based on smaller foulant sizes in Figure 2 and SEM images of $CaCO_3$ fouled membranes. More tests should be conducted under different concentrations of foulants.

Conclusions and Future Work:

PEG modification of commercially available TFC-PA membrane makes the surface more hydrophilic which increases initial flux and enhances fouling resistance to humic acid in these fouling experiments. However, at very high mineral foulant concentrations, PEG modification does not obviously enhance salt rejection but does decrease mineral precipitation on the surface. To confirm the trend, replicate experiments are needed. Studies of different influent concentrations, pressures, and combinations should be conducted to determine the impact of PEG modification with realistic and complex influents. In addition, the PEG modification should be further studied and optimized to enhance the fouling resistance of PA RO membranes.

Acknowledgments:

Thank you to Dr. Young-Shin Jun, Mr. Zongsen Zou, Dr. Jessica R. Ray, and everyone at the Environmental Nanochemistry Lab for their guidance and support. I would also like to thank the Nano Research Facility and the National Nanotechnology Infrastructure Network Research Experience for Undergraduates (NNIN REU) Program for giving me this opportunity and unforgettable experience. Support from the National Science Foundation under Grant No. ECCS-0335765, Washington University's International Center for Advanced Renewable Energy & Sustainability (I-CARES).

References:

[1] Menachem Elimelech, William A Phillip. The Future of Seawater Desalination: Energy, Technology, and the Environment [J]. Science 333: 712-717 (2011).

[2] Jessica Ray, et al. Hydrophilic, Bactericidal Nanoheater-Enabled Reverse Osmosis Membranes to Improve Fouling Resistance[J]. ACS Appl. Mater. Interfaces 7(21), 11117-11126 (2015).

__Figure 1__: SEM of PA membrane after $CaSO_4$ fouling test. The white structures are foulant deposits. __Figure 2__: SEM of PA-PEG membrane after $CaSO_4$ fouling test. The white cloud like structures are PEG, not fouling, attached to the membrane surface. __Figure 3__: SEM of PA membrane after humic acid fouling test. The debris on the membrane surface is believed to be humic acid fouling. __Figure 4__: SEM of PA-PEG membrane after humic acid fouling test. The membrane is mostly clear, with one possible smaller foulant.