NWRI GRADUATE FELLOW SEMI-ANNUAL PROGRESS REPORT

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Project Title:	Bioinspired hypochlorite-resistant reverse osmosis membranes
Graduate Fellow:	Michael Geitner
Advisor:	Manish Kumar & Enrique D. Gomez
Institution:	The Pennsylvania State University

Background and Introduction

The objective of the work described herein is to develop bioinspired reverse osmosis (RO) membranes that can withstand cleaning with hypochlorite (bleach). Biofouling, the attachment of microbes to the membrane surface and subsequent biofilm formation, is especially detrimental to the performance of RO membranes. Biofilms reduce permeability, negatively impact hydrodynamics, and trap excess salt near the membrane surface (Herzberg & Elimelech, 2007). The resulting increased salt concentration near the membrane results in "biofilm-enhanced osmotic pressure," an increase in the osmotic pressure opposing flux (Herzberg & Elimelech, 2007). To overcome these effects, greater pressure must be applied and energy costs increase (Matin, et al., 2011). Furthermore, increased solute passage is caused by the excess salt in the biofilm (Herzberg & Elimelech, 2007).

A Biomimetic Solution

Hypochlorite is an effective disinfectant, but cannot currently be applied to commercial RO membranes because it reacts with the polyamide active layer. Damage from hypochlorite occurs in two stages: N-chlorinated products initially form before undergoing an irreversible Orton rearrangement that leads to ring-chlorinated products (**Figure 1**). The addition of an electron-withdrawing group to the ring significantly weakens the amide bond. Ultimately, scission occurs, degrading the polyamide backbone and resulting in increased flux and solute passage (Kang, et al., 2007). Once ring-chlorination occurs, the damage is irreversible and the membrane must be replaced.
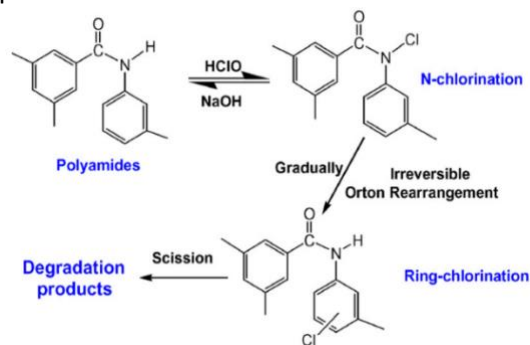
Figure 1. Hypochlorite damage of RO membranes (Kang, et al., 2007).

Recently, genetic systems have been discovered in several microorganisms, including *E. coli*, that produce methionine-rich proteins that are capable of scavenging reactive chlorine species (RCS), including hypochlorite, to prevent oxidative damage (Melnyk, et al., 2015). The sulfur atom in methionine is capable of scavenging RCS by undergoing oxidation to form methionine sulfoxide. In biological systems, these proteins are then returned to their initial state for reuse by an enzyme, methionine sulfoxide reductase. The proposed hypochlorite-resistant membrane will work by mimicking this natural process with a protective,

methionine-rich coating. Introduction of a chemical reducing agent such as dithiobutylamine (DTBA) will allow regeneration of the coating for continued use.

Hypotheses

It is hypothesized that anchoring a methionine-rich polymer to the surface of an RO membrane will prevent damage to the polyamide active layer by scavenging excess hypochlorite, thereby allowing the addition of residual hypochlorite to the feed to prevent biofilm formation. Furthermore, it is hypothesized that periodic addition of a reducing agent will regenerate this polymer to allow its continued efficacy.

Progress to Date

Experimental Design

Our biomimetic hypochlorite scavenger is a methionine-rich polymer formed by reacting polyallylamine hydrochloride (PAH) chains with L-methionine, here referred to as PAH-Met. The amine group from the former undergoes a condensation reaction with the carboxylate group on the latter in the presence of 1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC) and N-Hydroxysuccinimide (NHS), forming an amide bond. EDC activates the carboxylate group, allowing NHS to form an intermediate that shifts the reaction toward the desired product (ThermoFisher Scientific, 2018). Anchoring PAH-Met to polyamide is achieved through a similar reaction. EDC is used to activate carboxylate groups on the membrane surface, and an amine group of PAH-Met then reacts at these sites to form an amide bond between the methionine-rich polymer and the polyamide backbone.

Data Analysis

Two primary analytical methods have been used in this work and refined for our purposes. Neutron activation analysis (NAA) provides a highly sensitive measurement of hypochlorite damage to RO membranes. An elemental technique, it is capable of detecting N-chlorination that occurs before any performance changes are observed, revealing early and low-level damage that cannot be observed with other methods.

X-ray photoelectron spectroscopy (XPS) can be used to quantify the amount of sulfur added to the membrane surface, as well as its nearest-neighbor chemical environment. The latter capability reveals whether sulfur is in its oxidized or reduced state, allowing us to probe the efficacy of regeneration after hypochlorite exposure.

Finally, atomic force microscopy (AFM) will be used to characterize the surface of the commercial membranes used before and after application of our coating. AFM is widely employed to determine membrane surface properties, such as area and roughness. This analysis will allow us to determine if our coating significantly impacts the membrane surface, which could alter performance and fouling behavior and may warrant further investigation.

Results and Discussion

XPS results have shown that successful anchoring of our PAH-Met polymer to the surface of commercial RO membranes can provide an additional 1.2 percent sulfur at the surface, compared to uncoated membranes. Furthermore, NAA has been used to quantify low-levels of chlorine incorporation after hypochlorite exposure in both uncoated and coated membranes. Recent efforts to refine these analytical techniques will ensure greater accuracy moving forward.

Our polymer synthesis methods have shown no increase in sulfur content (via XPS) at methionine to PAH monomer unit ratios beyond 1:1, indicating that the maximum sulfur content (1.3 percent in bulk polymer) has been achieved. The synthesis has been scaled up to allow multiple experiments to be performed from a single batch, in order to eliminate the effect of variability between small batches on results.

AFM parameters for analysis of commercial membranes have been optimized for resolution of their surface characteristics, and will be applied to our coated membranes.

Initial experiments exploring the effects of hypochlorite exposure were inconclusive, as high hypochlorite concentrations resulted in extensive damage, even for short periods. Our previous approach was to target periodic exposure for biofilm removal, and therefore high concentrations were initially of interest. However, based on ease of implementation in real systems, we are now designing for operation with a low-concentration hypochlorite residual in the feed.

Conclusions

The proposed hypochlorite-scavenging polymer has been successfully synthesized and applied to commercial RO membranes, and its synthesis optimized and scaled up. All analytical methods required for characterization of our system and its efficacy have been refined for our purposes.

Extensive damage caused by high concentrations of hypochlorite in initial tests and the operating needs of real-world systems have led us to explore the use of our coating to withstand a low-level hypochlorite residual, with periodic regeneration of the PAH-Met coating. Instead of attempting to remove biofilm, we will now seek to prevent its formation using the same coating design.

Next Steps

, We will characterize samples prepared from a single batch of PAH-Met using established analytical methods and appropriate experimental conditions. XPS of bulk polymer, uncoated, and coated membranes will be used to ensure that optimal sulfur content has been reached. NAA of uncoated and coated membranes before and after low-concentration hypochlorite exposure for increasing time intervals will determine the capacity of the protective coating. Various reducing agents will be tested to find viable candidates for regeneration, with changes in the oxidation state of sulfur after exposure observed via XPS.

AFM will be used to characterize changes in the membrane surface properties after coating. If significant changes are observed, further testing to determine the effects of these changes on performance and fouling will also be conducted.

Finally, once the system has been optimized, filtration tests will be carried out in dead-end and crossflow configurations.

References

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