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Effects of chloraminated seawater on the SW30HR reverse osmosis membrane

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Reverse Osmosis (RO) membrane filtration is a promising technology to produce safe drinking water because it provides a physical barrier for a broad range of contaminants. However, membrane operational problems and sometimes failure tend to occur due to fouling, or the accumulation of unwanted materials on the membrane surface in contact with the feed water. Biofouling, or the formation of a biological film, is often controlled with the application of disinfectants to the feed water. However, oxidizing agents commonly used as water disinfectants and some of their associated byproducts could lead to membrane degradation. Most commercial RO membranes have a similar composition consisting of a thin polyamide active layer on top of a thicker polysulfone support and are, therefore, susceptible to similar damage. Understanding the extent and mechanisms of degradation will provide valuable information necessary to prevent compromised membrane performance.

Preliminary experiments conducted with varying concentrations of monochloramine (NH₂Cl) in standard seawater containing bromide and iodide revealed that structural changes could possibly correspond to degradation of reverse osmosis membrane polymers. Changes observed included the halogenation of the polyamide active layer and the apparent uptake of calcium and magnesium cations by the polysulfone support of the DOW FilmTec SW30HR RO membrane [1]. The data suggest that contact time, as opposed to monochloramine concentration, was the key parameter affecting the phenomena.

In an effort to confirm that the phenomena observed with standard seawater also occurred with real seawater, the objectives of this study were 1) to assess changes in the membrane active and support layers due to exposure to chloraminated seawater, 2) to compare these results to previous data pertaining to experiments with standard seawater disinfected with monochloramine, 3) investigate any differences in results between the standard and real seawater experiments, and 4) attempt to make generalizations about these phenomena based on specific water composition/conditions.

Experiments were conducted in batch reactors containing real seawater (pH=7.8-7.9). SW30HR (Dow FilmTec Co., USA) thin-film composite RO membrane coupons were placed in amber-colored jars containing monochloramine (NH₂Cl). Additionally, polysulfone membrane coupons (Sepro, USA) were used in the batch experiments to emulate the polysulfone support layer part of the SW30HR membrane. Because previous experimental results revealed that contact time was the key parameter rather than monochloramine concentration, the relatively low concentration of 2 ppm of monochloramine as Cl₂ was used in the batch reactors. Fresh solutions of seawater containing monochloramine were prepared daily.

Samples from the batch reactors were taken after contact times of 21, 43, 51, 61, and 68 days (up to ~1632 hours) and characterized by Rutherford Backscattering Spectrometry (RBS). RBS is an experimental technique used to determine the elemental composition and depth

distribution within the top 2 micrometers of the surface being analyzed [2]. The profiling ability of RBS was useful for this project because it enabled determination of the composition of both the active and support layers without compromising the integrity of the membrane [3].

Similar to the standard seawater experiments [1], halogenation of the active layer of the polyamide membranes was observed. Results showed that bromine and iodine concentrations increased throughout the 68 days of the experiment. The levels of bromine were generally consistent with those observed in the experiments with standard seawater while the iodine levels were somewhat lower. This was possibly the result of chloramines reacting faster with bromide at the lower pH of the real seawater and, thus, outcompeting the reaction with iodide. Using the polymer repeating unit for the fully aromatic polyamide, $C_{36}H_{24}N_6O_6$, the bromination levels observed would correspond to approximately 60-80 percent of the polyamide having one bromine addition or $C_{36}H_{23}N_6O_6Br$, ~1 percent being in the form $C_{36}H_{23}N_6O_6I$ and the rest remaining in its original form $C_{36}H_{24}N_6O_6$.

Unlike the previously conducted standard seawater experiments [1], the incorporation of divalent ions was not observed suggesting that this phenomenon depends on water composition and conditions. Results showed that the amount of bromine and iodine present within a thin layer of the polysulfone coupons at the interface with the active layer increased slowly until day 51, after which the levels decreased to approximately the same levels observed earlier at day 43. These results indicated that the reactions between the polysulfone support layer and secondary oxidizing agents occurred relatively slowly and eventually stabilized. Using the polymer repeating unit for polysulfone, $C_{27}H_{26}O_6S$, the bromination and iodination levels observed corresponded to less than ~.01 percent of the polysulfone having one bromine or iodine addition, $C_{27}H_{25}O_6SBr$ or $C_{27}H_{25}O_6SI$, respectively.

RBS analyses revealed structural changes of both the polyamide active layer and polysulfone support. As previously mentioned, different phenomena were observed when the polyamide and polysulfone membrane coupons were exposed to varying concentrations of monochloramine in real and standard seawater. In the standard seawater experiments, halogenation and the uptake of divalent cations were observed in contrast to the real seawater experiments where only halogenation was evident. These differences are currently being explored to attempt to make generalizations about these phenomena based on the water composition/conditions and to further investigate the effects observed in the polysulfone.

References

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