論文の要旨

題　目: Evaluation of Biofouling and Its Control by Hypochlorite on Polyamide Reverse Osmosis Membranes
(ポリアミド RO 膜でのバイオファウリングの評価と次亜塩素酸塩によるバイオファウリングの制御)

氏　名　　　Manalo Cervinia Velasco

Biofouling is a prevailing problem associated with the performance of reverse osmosis (RO) membrane technology, which has emerged as a promising technology directed towards solving the world's problem in water scarcity and increasing global water demand, through its application in seawater and brackish water desalination and wastewater reuse and reclamation. Since biofouling potential is a key ingredient in biofouling studies, a part of this research aims to develop a biofouling potential test that is novel, simple, fast, and suitable for determination of biofouling on RO membranes. In this research, the method developed evaluated biofouling potential by direct analysis of RO membrane through fluorescence intensity analysis of biofilm formed on the membrane surface, thereby incorporating fouling tendencies of both feedwater and membrane. Evaluation of the biofouling potential on the RO membrane was done by accelerated biofilm formation through soaking of membranes in high biofouling potential waters obtained by adding microorganisms and glucose in test waters. The biofilm formed on the soaked membrane was quantified by fluorescence intensity microplate analysis. The soaking method's capability in detecting biofilm formation was confirmed when percentage coverage obtained through fluorescence microscopy and intensity values exhibited a linear correlation ($R^2 = 0.96$). Continuous cross-flow experiments confirmed the ability and reliability of the soaking method in giving biofouling potential on RO membranes when a good correlation ($R^2 = 0.87$) between intensity values of biofilms formed on the membrane during soaking and filtration conditions was obtained. Applicability of the test developed was shown when 3 commercially available polyamide RO membranes are assessed for biofouling potential. This new method can also be applied for the determination of biofouling potential in water with at least 3.6 mg L^{-1} easily degradable organic carbon, thus is more applicable for high fouling waters. The applicability of this method would be most prominent in current times since water sustainability technologies are geared towards the re-use of polluted waters so as not to further deplete traditional water sources.

Particles and colloids in feedwater for RO processes are typically removed by pretreatment to silt density index (SDI) allowable levels to prevent accumulation on membranes. However, the accumulation is mostly caused due to combined biofouling-particulate accumulation and it is important to quantitatively understand particle accumulation as affected by biofilm. Since biofilm formation cannot be avoided on membrane surfaces, its influence on the accumulation of inorganic suspended solids (SS) on RO membranes needs further understanding. Thus, a part of this research aims to examine qualitative and quantitative information regarding the influence of biofilm on SS accumulation. Continuous flow (without filtration) experiments of 1 μm filtered secondary effluent water and pure water (as control) with kaolin as representative SS particles were conducted and results indicate that organic matter (mainly coming from biofilm) deposited does not correlate with the amount of initial kaolin in the feedwater. However, inorganic matter amount deposited showed a correlated increase with initial kaolin amount in the feedwater. The rate of inorganic matter deposition is twice as fast when secondary effluent water was used as feedwater and showed a higher linear correlation ($R^2 = 0.997$) in contrast to pure water. With the same kaolin concentration contained on the feedwater, the amount of inorganic material deposited is greater by 0.16 mg/cm^2 when secondary effluent water was used in contrast to pure water, signifying quantitative enhancement of accumulated SS on the membrane. Amount of glucose in feedwater did not result in a related increase in inorganic material since deposition seemed to be influenced by biofilm coverage on a preformed biofilm, as indicated by similar biofilm percentage coverage with and without glucose in feedwater. Micrographs indicated the preferential deposition of SS on the spacer filaments and membrane areas that were covered with biofilm. The initial site for biofilm formation seemed to be a result of the continuous flow under no filtration conditions, thereby an almost negligible concentration polarization, which makes the biofilm in greater contact with the spacer rather than on the membrane surface. The SS preferentially deposited on the biofilm formed on the membrane surface again due to the greater contact of the biofilm to the SS flowing in the liquid. This effect of biofilm on inorganic SS accumulation will be highly useful in designing pretreatment strategies by addressing biofilm control to prevent both biofilm formation and SS accumulation.

One of the critical issues in membrane processes is the low tolerance of the RO membranes to oxidants like chlorine. But with the current trend of developing chlorine-resistant membranes direct chlorine washing will be a viable option to avoid biofouling on these chlorine-resistant membranes. Since it has been shown that particle accumulation is

exacerbated by the presence of biofilm, particle accumulation has the potential of being prevented by biofilm control, specifically chlorine washing. Thus, expensive pretreatment for particle removal can either be removed or simplified, which could lessen associated cost in pretreatment operations. A part of this research, aims to determine the effective hypochlorite washing condition required for controlling biofilm formation as well as inorganic particle accumulation on a RO membrane in a continuous flow channel with RO membranes and spacer. Results showed that comparable biofilm formation control can be achieved with continuous and intermittent washing (10 mg/L chlorine), but with lesser exposure to chlorine during intermittent washing. For 48 h of soaking tests, the fluorescence intensity, a measure of biofilm on the membrane surface, was 470 and decreased to 0 by hypochlorite washing with 10 mg/L chlorine concentration, 2 times/day washing interval, and 30 min washing time. Results showed that the chlorine concentration required to control biofilm formation decreased as the chlorine concentration (0.5–10 mg/L), the washing interval (1–4 times/day), or the washing time (1–30 min) increased. For the sample solutions used in the study, 10 mg/L chlorine concentration with 2 times/day interval, and 5 min washing time was required for biofilm control. The optimum hypochlorite washing condition obtained from soaking experiments proved to be applicable also in controlling biofilm formation in continuous flow experiments. In addition, based on calculation of CT (Concentration of free chlorine-time of exposure) values, the intermittent chlorine washing conditions are within the limits of allowed exposure conditions for commercial RO membranes within expected membrane lifetimes.

Particle accumulation control by chlorine washing experiments were done and results showed that for the sample water with kaolin and hypochlorite, the accumulation amounts were 0.03 mg/cm^2 for organic and 0.14 mg/cm^2 for inorganic, respectively, which were lower than that for sample water without hypochlorite (0.14 mg/cm^2 and 0.33 mg/cm^2, respectively). The amount of biofilm formed was 79% controlled by continuous washing with 10 mg/L of free chlorine concentration, and the inorganic accumulation amount was decreased by 58% to levels similar to that of pure water with kaolin (0.17 mg/cm^2). These results confirmed the acceleration of particle accumulation due to biofilm formation, and that the inhibition of biofilm growth can almost completely reduce further particle accumulation. In this research, it was shown that effective hypochlorite washing condition which can control both biofilm formation and particle accumulation could be achieved.

In the current state of membrane development, RO membranes cannot have the perfect resistance to free chlorine as long as polyamide (PA) is used as a membrane material due to its sensitivity to chlorine. Therefore, studies that deal on PA membrane degradation by chlorine

is very important. Water sources and their quality are vital in the RO membrane processes, and determining the effects of the quality of the source on the PA membrane degradation will be helpful in designing and developing chlorine-resistant membranes. Since source waters have a wide array of metal ions and of variable concentrations, and because metal ions have been reported to accelerate membrane degradation, part of this research aims to determine the enhancing effect of the coexistence of metal ions on PA membrane degradation by hypochlorite using a commercial PA membrane. The mechanism of the PA membrane degradation by hypochlorite was also examined. Results showed that the acceleration of membrane degradation by hypochlorite was caused by all monovalent (Na^+, K^+) and divalent metal ions (Ca^{2+}, Mg^{2+}, and Ba^{2+}) used in this study, as shown by the decrease in salt rejection and an increase in flux. The acceleration of PA membrane degradation was caused by divalent ions in much lower concentrations than the monovalent metal ions, indicating the potency of divalent ions in membrane degradation. In addition, the Na^+ did not accelerate the degradation of the PA membrane in less than 100 mM concentration, whereas Mg^{2+} and Ca^{2+} did not have a threshold limit. In the presence of both monovalent and divalent metal ions, membrane degradation seemed to be influenced by the threshold limit of the monovalent ion within the range of concentration of each of the ions used in this study. Below that threshold limit, the divalent ion gives greater effect in the membrane degradation while higher than the threshold limit, the monovalent ion has a greater effect. The effect of chlorination was shown for both size exclusion and electric charge repulsion performance of the RO membrane. For the membrane degradation mechanism, as indicated by FTIR results and zeta potential analysis of the membranes, the degradation process of PA membranes does not change even if metal ions are present in the reaction. However, acceleration of amide hydrolysis was possibly catalyzed by the divalent ion leading to PA membrane degradation.