Study on the Surface Modification of Membrane for Water Filtration and its Performance of Chlorine Resistance

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Fouling and subsequent chemical cleaning are two important issues for sustainable operation of Reverse osmosis (RO) and nanofiltration (NF) membranes in water treatment and reuse applications. Therefore, this dissertation research has direct implications for improving the membrane performance of chlorine resistance and by delaying their fouling time with high flux recovery.

In this study, membrane fouling and chemical cleaning under condition typically to that in water recycling applications were investigated. Consequently, appropriate selection of the chemical cleaning solutions can be seen as a critical factor for effective fouling control. The effectiveness of hypochlorite cleaning for fouling mitigation of a chlorine-resistant nanofiltration (NF) membrane – namely CR10 – was evaluated using a secondary treated effluent. The fundamental properties of this chlorine-resistant NF membrane (e.g. chlorine resistance and separation performance) were also evaluated and compared to commercial NF and reverse osmosis (RO) membranes. The CR10 NF membrane did not show any changes in permeability and conductivity rejection after exposing a NaClO solution for up to $5 \times 10^4$ ppm-h. By contrast, considerable rejection deterioration was observed for the other two commercial membranes that are not chlorine resistant. Salt and micropollutant ($N$-nitrosamines) rejection by the CR10 NF membrane was comparable to that by the commercial NF membrane. These results suggest that the chlorine-resistant CR10 NF membrane has a potential to replace conventional NF membranes for water treatment applications. Direct filtration of a secondary treated effluent resulted in a progressive reduction in the permeability by up to 25% after 10 h of filtration. The membrane permeability was fully restored by chemical cleaning with a 2,000 ppm NaClO solution (pH 11.1) for 1 h. Effective flux recovery by hypochlorite cleaning was also demonstrated with multiple chemical cleaning cycles. Membrane fouling and hypochlorite cleaning were also simulated using three model foulants (e.g., sodium alginate, humic acids, and bovine serum albumin). Among these potential foulants in secondary treated effluent, a complete flux recovery was not achieved after humic acids fouling. Further research is recommended to develop new chemical cleaning techniques to control membrane fouling caused by humic substances.
To further examine in which protective coatings on commercial reverse osmosis membrane ESPA2, an industrial grade epoxy resin was used to modify the membranes to enhance the chlorine resistance via the reaction between the amide nitrogen and epoxy bond. Coatings solution were prepared from epoxy with silane coupling agent at concentration (0.001 wt% and 0.0014%). Moreover, the chlorine resistance of the membranes was evaluated by comparing the permeation and separation properties of the uncoated and coated membranes after chlorine exposure. And the experimental results indicated that the chlorine tolerance of ESPA2 membrane was improved significantly.

For fouling prevention, we designed a new membrane system using a coating technique to modify membrane surface properties to avoid adsorption of foulants like Bovine Serum Albumin. In organic fouling test, the modified membranes significantly decrease the potential of fouling to the membrane. Thus compared to the uncoated membrane, epoxy resin coated membranes prepared from that solution suffered flux declines of 10% and 5%, respectively. Lab scale filtration studies with Bovine Serum Albumin (BSA) prove that the coated membranes have lower tendency to form organic fouling layers showing a relatively slower flux decline due to fouling than the virgin membrane. The successful modification of the membrane surface was confirmed by using various analytical tools. ATR-FTIR and contact angle measurements indicated that the epoxy resin with silane coupling agent was adsorbed onto the membrane. It is believed that the surface coating layer works as a protective and sacrificial layer, preventing the attack of chlorine on the underlying polyamide film. Furthermore the performance of an epoxy coated RO membrane was investigated and its surface structure analysis using field emission – scanning electron microscopy (FE-SEM), X-ray photo electron spectroscopy (XPS). In the uncoated membrane, degradation of the polyamide network of the membrane surface by free chlorine resulted in significantly decreased salt rejection (5%) and increase water flux for twice after 50,000 ppm-hr treated chlorine intensity. However, the epoxy coated membrane maintained a salt rejection of above 92% even after 50,000 ppm hr. For that reason, the coated membrane offers potential use as a novel RO membrane with improved antifouling performance and chlorine resistance.