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Application of Used Reverse Osmosis Membrane to Reclamation of Industrial Wastewater in Emerging Countries

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Introduction

Due to a shortage of freshwater sources, reverse osmosis (RO) membranes have been gaining global attention (Lawler et al., 2012). Currently, RO membranes are replaced every three to five years as the polyamide layer ages, resulting in the loss of an enormous number of modules every year. Because RO membranes are composed of various kinds of plastics, including polyamide, polysulfone and polyethylene terephthalate, the recycling and recovery of these systems are quite difficult. In addition, the membrane itself is rigidly packed in a fiber-reinforced plastic case, so it is hard to modify or renovate. As a result, most spent modules are landfilled or incinerated, risking the occurrence of environmental problems such as pollution of public waters with plastics or creating landfill site shortages (Lawler et al., 2012). Recently, it has been proposed that used RO modules could be recycled at the final polishing stage of a wastewater reuse system in place of nanofiltration membranes, because used membranes generally express a high salt rejection of more than 95%. Because these used membranes exhibit serious biofouling and have less economic value, however, recycling schemes for used modules yet to be established (Bartels et al., 2005).

On this basis, we propose a new solution, “upcycling,” in which the value of the product is increased and its lifetime is prolonged by circulating the membrane from downstream to upstream. In this study, used RO membranes are upgraded by the incorporation of additional functions such as antibiotic or antifouling systems. To date, several studies have investigated the functionalization of RO membranes via coating of their surfaces with functional nanoparticles (Landaburu-Aguirre et al., 2016). However, most of these studies faced difficulties maintaining these added functions under high crossflow velocities across the membrane surface, with most of the attached particles being washed out during operation.

Therefore, in this study we first applied a cation binder to ensure better adherence of the functionalized nanoparticles. Polyethyleneimine (PEI) was applied as a cation binder between the copper nanoparticles and an aged membrane. The volume of nanoparticles maintained under a high crossflow velocity and the added antibiotic functions were then evaluated, as were fundamental properties such as salt rejection and water permeability.

Materials and Methods

All membranes used in this study were initially compacted by via water pressure until their water permeability was stabilized. The aged membranes were prepared via contact with sodium hypochloric solution on the surfaces of virgin RO membranes (DOW Chemical, SW: 150 × 100 mm, 150 cm^2) until salt rejection was brought to arbitrary levels (i.e., 95, 85, 75, 65, or 45%). The aged membranes were then

immersed in a 1% (w/v) PEI/isopropanol solution for 60 minutes at a temperature of 70°C. The PEI-coated membranes were then further immersed in a 0.01% (w/v) copper nanoparticle (CuNP; Sigma-Aldrich, 25 nm) suspension for 30 minutes to ensure that the particles adhered to the membrane.

After coating with CuNPs, the membranes were characterized in terms of their salt rejection, water permeability, and ability to maintain the CuNPs. The salt rejection and water permeability values were determined under a constant pressure of 1.5 MPa and a crossflow velocity of 0.1 m/s. After performing the salt rejection measurement, the membrane sheets were cut into small pieces and stirred in distilled water for 50 hours. The amount of detached CuNPs was quantified by Cu concentration of the stirred solution. The antibiotic function of the membranes was then evaluated using a flowing *E. coli* cultured solution through both surfaces of the aged, CuNP-coated membranes. After 48 hours of contact, the membranes were stained with SYTO9 green-fluorescent nucleic acid stains and observed under a fluorescence microscope.

Results and Conclusions

Figure 1 shows the amount of CuNPs attached to the membranes. Interestingly, the attachment of CuNPs (μg/cm^2) was much greater on the aged membranes than on the virgin membrane. In addition, it was observed that a lower salt rejection was correlated with a larger amount of attached CuNPs. This indicates that the used membranes were better modified when both PEI and CuNPs were used. The maximum coating capacity was about 0.8 μg/cm^2; this was achieved on membranes expressing 65% rejection of salt (Fig. 1).

The remaining amount of CuNPs on the membranes after the crossflow experiment was found to be greater than 90% of the original quantity for all used membranes, and this amount increased for the membranes expressing lower rejection. The 65% and 45% rejection membranes were able to maintain more than 95% of their original CuNP content (Fig. 2). It should also be mentioned that water permeability was improved by 10% with the CuNP coating. This is probably because the PEI coating increased the affinity of the membrane toward water molecules, which contributes to the passing of water molecules, possibly leading to a higher flux despite similar salt rejection levels.

The results of the antibiotic evaluation revealed that every CuNP-coated membrane demonstrated antibiotic properties. The level of biofilm reduction was higher for the lower-rejection membranes than for the virgin or higher-rejection membranes. The 65% and 45% rejection membranes enabled an 80% reduction of microbial accumulation. Figure 3 shows the stained *E. coli* that accumulated on the membrane surfaces. Compared with the aged (left, 65% rejection membrane) membrane, the CuNP-coated membrane (right, 65% rejection membrane) was less green, indicating that the coating could prevent the accumulation of *E. coli*.

On the basis of the results obtained in this study, it may be concluded that the application of PEI to aged membranes can increase their ability to maintain CuNP adherence. Because of the specific binding between the aged membranes and the PEI functional groups, the CuNPs were strongly attached to the membrane surface and were maintained even under high crossflow conditions. As a result of this increased ability to maintain CuNP attachment, an antibiotic function was successfully added to the aged RO membranes. It is expected that coating with CuNPs has the potential to contribute to upcycling of used RO modules and reduction of their disposal.

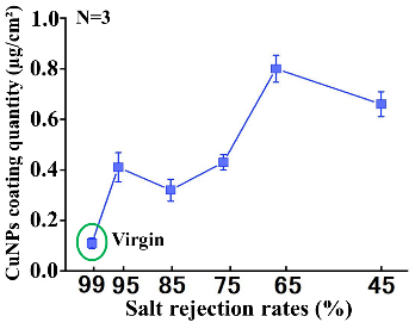

Fig. 1 Relationship between salt rejec-tion rates and maintained CuNP coating quantity.

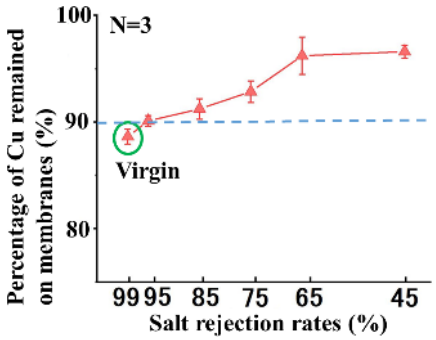

Fig. 2 Relationship between salt rejection rate and percentage of retained Cu.

Fig. 3 Images observed using a fluorescence microscope after exposure to crossflow. (A) Degraded 65%-rejection membrane and (B) CuNP-coated membrane.

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