

■受領No.1398

## 逆浸透膜のナノスケールレベルの欠陥を簡易に修復する 『ナノスケールバンドエイド』の開発

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### Enhancement of solute removal efficiency of polyamide reverse osmosis membrane without water permeability loss

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本研究では逆浸透膜 (RO 膜) を用いて下水処理水を処理した際の溶質除去率の向上を検討した。RO 膜の透過性が異なる 3 つの溶質 (亜ヒ酸、電解質、ローダミン-WT) を用いてろ過実験を行った結果、バイオポリマーの代表物質として用いたアルギン酸が共存する条件下では水透過性と犠牲にすることなくローダミン-WT の透過量が 45% 減少 (2.0 MPa にて) した。また、亜ヒ酸と電解質の透過量は減少しなかったことから、アルギン酸が RO 膜に存在するナノスケールレベルの欠陥を塞いでいることが示された。

This study investigates the enhancement of the solute removal efficiency of reverse osmosis (RO) membranes without water permeability loss during the treatment of secondary wastewater effluent (SWE). Filtration experiments were performed using a synthetic SWE containing three types of solutes with different membrane transport properties, namely arsenious acid ( $H_3AsO_3$ ), electrolyte, and rhodamine-WT (R-WT), and alginate as a representative biopolymer foulant. The flux of R-WT at 2.0 MPa decreased by up to 45% in the presence of alginate without decreasing water permeability; this trend was not observed for  $H_3AsO_3$  and the electrolyte, indicating that nanoscale imperfections that allow unselective solute transport were plugged by alginate. These results demonstrated that nanoscale imperfections in the RO membrane could be plugged by the biopolymer contained in SWE and that the removal of large solutes was enhanced without forfeiting water permeability.

#### 1. Research objective

RO membranes are often utilized for the reclamation of municipal wastewater to produce drinking water. However, it is widely recognized that advanced thin-film composite polyamide RO membranes have nanoscale imperfections in the active layer that allow for the advective transport of solutes [1-2]. Consequently, although RO membranes provide an effective barrier to viruses

(removal percentage > 99.9999%), the virus removal efficiency of most RO membranes is not 100%. Because of the imperfect integrity of active layers and the incomplete rejection of contaminants, integrated membrane systems for recovering municipal wastewater to produce drinking water are typically followed by ultraviolet (UV) treatment for reliable virus removal performance [3].

Our previous study [4] demonstrated that nanoscale

imperfections present in the active layers of pristine polyamide RO membranes can be effectively plugged by filtering an aqueous solution of polyvinyl alcohol (PVA) and subsequent cross-linking with glutaraldehyde forming a stable plug. The key idea that makes this strategy promising is that we filtered only a small volume of PVA aqueous solution to selectively plug nanoscale imperfections without forming a PVA deposition layer on top of the RO membrane. This successful demonstration of a “nanoscale adhesive patch” makes it reasonable to assume that dissolved organic matter with a relatively high molecular weight like PVA (e.g., biopolymers such as polysaccharide and protein) in secondary wastewater effluent (SWE) might work as “nanoscale adhesive patches” and improve solute removal efficiencies during the treatment of SWE. Biopolymers have been widely recognized as common foulants of RO membranes in the wastewater reclamation process and could have a negative influence on water permeability by forming a foulant layer on top of the RO membrane. However, if we can demonstrate that these foulants also work as “nanoscale adhesive patches,” we could utilize this natural phenomenon as a strategy to improve RO membrane performance by optimizing operational and cleaning conditions.

Based on the abovementioned considerations, this study investigates the potential enhancement in the removal of solutes by RO membranes during the treatment of SWE. A solution containing three types of solutes with different membrane transport properties and mechanisms, namely arsenious acid ( $\text{H}_3\text{AsO}_3$ ), electrolyte, and rhodamine-WT (R-WT), and alginate as a representative biopolymer foulant was used as feed water to investigate the influence of alginate on RO membrane performance.

## 2. Research content

### 2.1 Reagent and RO membrane

Sodium alginate with a viscosity of 80–120 cPa·s at a concentration of 10 g/L was obtained from

FUJIFILM Wako Pure Chemical Corp. (Osaka, Japan). R-WT has a molecular weight of 480, and its removal by RO membranes is well correlated with the removal of the bacteriophage MS2; it was purchased from Turner Designs, Inc. (San Jose, CA, USA). All other chemicals used in this study were guaranteed to be of reagent-grade quality and were obtained from Nacalai Tesque, Inc. (Kyoto, Japan) or FUJIFILM Wako Pure Chemical Corp.; they were used without further purification. The commercial RO membrane used in this study was a thin-film composite fully aromatic polyamide membrane, and the active layer was formed by interfacial polymerization between trimesoyl chloride and *m*-phenylenediamine. According to the manufacturer, the surface of the active layer was covered with PVA to improve the fouling propensity.

## 2.2 Filtration experiments

### 2.2.1 Experiments using synthetic SWE containing inorganic ions and alginate

5 L of synthetic SWE containing only inorganic ions was prepared by adding 9.2 mmol/L NaCl, 0.94 mmol/L  $\text{NH}_4\text{Cl}$ , 0.45 mmol/L  $\text{KH}_2\text{PO}_4$ , 0.5 mmol/L  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ , 0.5 mmol/L  $\text{NaHCO}_3$ , and 0.6 mmol/L  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ . This chemical composition was selected to represent SWE quality in California [5]. Thereafter,  $\text{H}_3\text{AsO}_3$  (5 mg As/L,  $\text{pK}_a=9.2$ ) and R-WT (5 mg/L) were spiked into synthetic SWE, and the pH was adjusted to  $6.9 \pm 0.1$ , to fully convert  $\text{H}_2\text{AsO}_3^-$  into neutral  $\text{H}_3\text{AsO}_3$ .

The water permeability and solute removal efficiency of the RO membrane were evaluated using a cross-flow closed-loop filtration system with a CF042 flat-leaf cell (Sterlitech Corp., Kent, WA). After installing a membrane coupon and a CF042 high foulant spacer, the membrane was stabilized for 14 days at 2.0 MPa for membrane compaction and conditioning. The feed solution was sent to the cell using a dual pump (KP-22-33, FLOM, Inc., Tokyo, Japan) at 50 mL/min flowrate.

After 14 days of membrane compaction and conditioning, the membrane performance (i.e., water flux and solute rejection) at various applied pressures was evaluated.

### **2.2.2 Experiments using synthetic SWE containing inorganic ions and alginate**

After finishing the experiments described in Section 2.2.1, 500 µgC/L sodium alginate was spiked into the synthetic SWE used in Section 2.2.1 and operated for 14 days at 1 MPa. After 14 days of operation, the membrane performance (i.e., the water flux and solute rejection) at various applied pressures was evaluated.

## **2.3 Results and discussion**

### **2.3.1 Water/solute transport property characterization using synthetic SWE containing only inorganic ions**

The performances of Membrane pieces #1 and #2 in the absence of alginate are shown in Fig. 1 using open symbols. The data showed adequate reproducibility between Membrane pieces #1 and #2 for both water flux and the removal of the three types of solutes, and the solute removal efficiency increased in the order of  $\text{H}_3\text{AsO}_3 < \text{electrolyte} < \text{R-WT}$ . Notably, the removal of  $\text{H}_3\text{AsO}_3$  strongly depended on the water flux, a weaker dependence was observed for the electrolyte, and no dependence was observed for R-WT. This result indicates that the solute permeation mechanism is different depending on the type of solute. This was expected because of three reasons 1) small and neutral molecules, including  $\text{H}_3\text{AsO}_3$ , are not effectively removed by a negatively charged integrated polyamide active layer, 2) the diffusive permeation of small but charged electrolytes is electrically hindered by a negatively charged integrated polyamide active layer; and 3) the diffusive permeation of R-WT via the integrated polyamide active layer is physically hindered owing to its large size.

### **2.3.2 Water/solute transport property characterization after adding alginate to synthetic SWE**

In addition to the membrane performance evaluated in the absence of alginate, the closed symbols in Fig. 1 show the performances of Membrane pieces #1 and #2 after spiking with 500 µgC/L alginate. The average decrease in water permeability between Membrane pieces #1 and #2 was below 5%, indicating that alginate did not form a foulant layer on top of the membranes during 14 days of operation.

Spiking alginate into synthetic SWE differently affected solute removal depending on the type of solute. The addition of alginate did not significantly have either a positive or negative effect on  $\text{H}_3\text{AsO}_3$  and electrolyte removal but had a positive effect on R-WT removal. If we use Membrane piece #1 for analysis, the rejection of R-WT increased from 99.77–99.81% to 99.84–99.89%. This study revealed that the increase in R-WT removal from 99.78% to 99.88% (data obtained at 2.0 MPa) is a slight improvement (0.1%); however, this is a significant decrease (45%) in the R-WT flux across the membrane. These results show that alginate selectively plugged nanoscale imperfections in the polyamide active layer and blocked the pathways for advective solute transport. This plugging significantly decreased the R-WT flux through the membrane and consequently improved the removal because R-WT passes through the membrane only via advection; however, this trend was not observed for  $\text{H}_3\text{AsO}_3$  and electrolyte because diffusion via the integrated polyamide active layer is also an important transport mechanism for these small solutes. In summary, these results showed that the solute rejection capability of the RO membrane could be enhanced by biopolymers in SWE without losing water permeability as long as the following requirements are met: i) advective transport is the dominant transport mechanism (e.g., R-WT), and ii)

nanoscale imperfections are selectively plugged by biopolymers without forming a foulant layer on top of the membranes.

## Reference

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## 3. Publication of research findings

Suzuki, T.; Harada, M.; Wada, Y.; Ichimura, S. Enhancement of solute removal efficiency of polyamide reverse osmosis membrane without water permeability loss. *Journal of Environmental Chemical Engineering*. 2021, 9, 106818

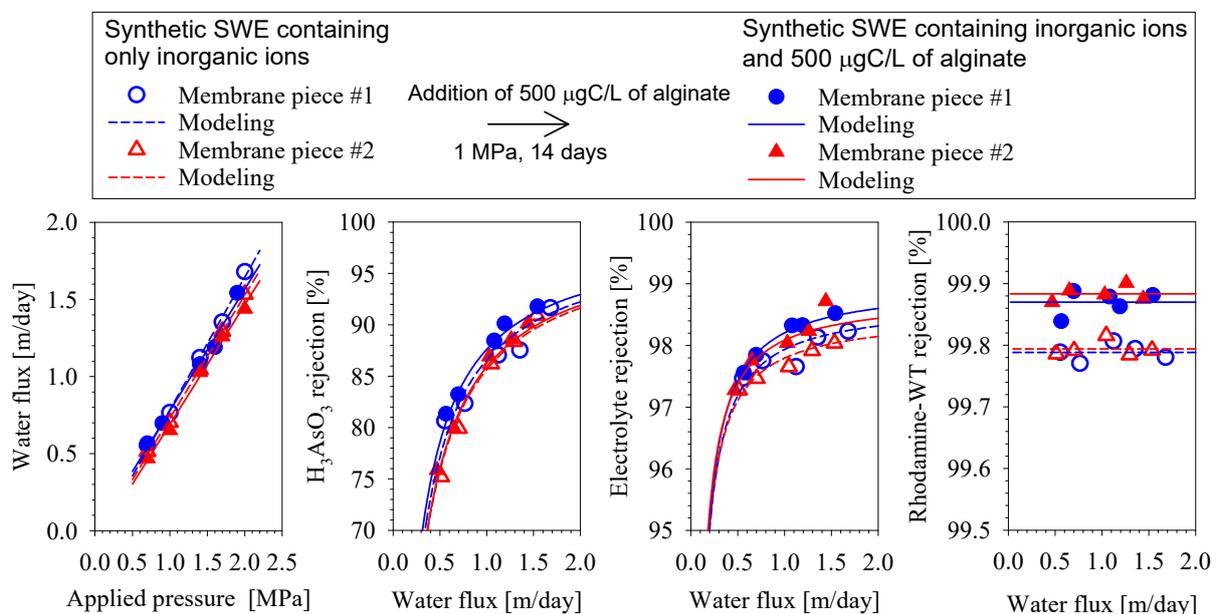


Fig. 1 Experimental (symbols) and modeling (lines) results of Membrane pieces #1 and #2. Open circles and triangles represent data obtained using synthetic SWE containing only inorganic ions, whereas closed circles and triangles represent data obtained using synthetic SWE containing inorganic ions and 500 µgC/L of alginate.