Long–term Durability of Desalination Performances of Dynamically Formed Membranes Using Poly(acrylic acid) and Tubular Ceramic Supports

Kazuki Akamatsu*, Takuma Usa, and Shin-ichi Nakao

Department of Environmental and Energy Chemistry, Faculty of Engineering, Kogakuin University, 2665-1 Nakano-machi, Hachioji-shi, Tokyo 192-0015, Japan

1. Introduction

The dynamic forming method was first developed by Marcinkowsky et al.1). This method incorporates membrane-forming materials, such as inorganic hydrous oxides, colloidal materials, and polymers, as active separation layers on porous supports2–9). The asymmetric structure of the resulting membrane is similar to that of reverse osmosis (RO)/nanofiltration (NF) membranes, which have a thin active separation layer on the porous support. Dynamically formed membranes using membrane-forming materials that feature an electric charge are expected to exhibit desalination properties. Historically, dynamically formed membranes were studied as substitutes to polymeric RO/NF membranes in the 1970s and 1980s. However, since the 1990s, the number of publications on dynamically formed membranes significantly decreased. This is probably because many types of novel RO/NF membranes with excellent desalination properties have been developed and subsequently commercialized. Regardless, the dynamic forming method remains attractive in terms of facile surface modification over a large area achieved within a single treatment. As exemplified, studies on the use of the dynamic forming method for the preparation of low-fouling membranes10–12), in oil/water separation systems13), in the food industry14), and in membrane bioreactors15, 16) were reported.

Dynamically formed membranes were prepared using poly(acrylic acid) (PAA) and tubular alumina supports. The performance of the membranes was arbitrarily tuned by varying the concentration of PAA and applied pressure during membrane forming. Compared with the commercial nanofiltration/reverse osmosis membranes, the dynamically formed membranes achieved higher permeability and lower salt rejection. Additionally, the effect of flow rate, which relates to the Reynolds number ($N_{Re}$), on the long-term durability of the membranes in crossflow operation was investigated. At $N_{Re}$ of $3.5 \times 10^4$, flux drastically increased with an associated reduced rejection performance owing to the detachment of the PAA layer from the membrane surface, whereas no severe decrease in the membrane performance was observed when $N_{Re}$ was $2.0 \times 10^4$. This finding indicated that the operation conditions influenced the durability of the membranes because of the physical attachment of the dynamically formed layer onto the alumina support.

Keywords: dynamic forming method / desalination / durability / poly(acrylic acid) / detachment

* Corresponding Author
Tel: +81-42-628-4584
Fax: +81-42-628-4542
E-mail: akamatsu@cc.kogakuin.ac.jp
dynamically formed membranes were extensively studied. However, in general, these experiments were only conducted over a few hours, and thus, the long-term durability of the dynamically formed membranes was rarely addressed. Unlike grafting methods, the dynamic forming method allows physical immobilization of the membrane-forming materials onto the base support. Thus, detachment of the membrane-forming material, in particular polymers, is possible over long-term operation, thereby resulting in the deterioration of the membrane performance with time. Pilot plant tests of brackish water treatment using dynamically formed membranes, involving 100–1000-h-long operations, were carried out. However, in these tests, some operation parameters, such as flow rate, were changed several times during each run. In some cases, some potentially fouling substances in the feed solution and a reduced flux were observed despite the recovery of flux upon detachment of the membrane-forming materials from the membrane surface. We should also take into account that polymeric base supports would undergo compaction. Hence, it is difficult to address the sole effect of long-term operation on the detachment of the dynamically formed layer and associated deterioration of the membrane performance.

In this study, we examined the changes in the membrane performance that were attributed to the detachment behaviors of the dynamically formed layers during long-term crossflow operations. We first developed dynamically formed membranes using PAA as the dynamically formed layer and tubular microfiltration (MF) ceramic membranes as porous supports. The desalination performance of the prepared membranes was compared with that of commercial polymeric flat NF membranes to demonstrate the characteristics of the performance of the dynamically formed membranes. Subsequently, long-term desalination tests were carried out to investigate the time-dependent desalination performance owing to the detachment of the PAA layer.

2. Experimental

2.1 Materials

PAA \((M_w 250 000)\), Na_2SO_4, NaCl, CaCl_2, and MgSO_4 were purchased from Wako Pure Chemical Industries Ltd. (Japan) and used without further purification. A tubular alumina MF membrane with pores of 70 nm was kindly supplied by Noritake Co., Ltd. (Japan) and used as a porous support. Two commercially available polymeric flat NF membranes (NTR-7450 and NTR-729HF) were kindly supplied by Nitto Denko Cor. (Japan).

2.2 Preparation of dynamically formed membranes

PAA aqueous solutions at varying concentrations of 200, 500, and 1000 ppm were filtered using the MF support in a crossflow until the flux became constant to produce the dynamically formed PAA layer on the support. During preparation, the flow rate and temperature were maintained at 3 L min\(^{-1}\) and 25 °C, respectively. The applied pressure was 0.2, 0.5, or 1.0 MPa.

2.3 Evaluation of the performance of the dynamically formed membranes

2.3.1 Effect of preparation conditions on the membrane performance

The flux and rejection properties of the membranes were measured in a crossflow mode using aqueous solutions containing 100 ppm Na_2SO_4 as the feed solutions. The flow rate and temperature were maintained at 6 L min\(^{-1}\) and 25 °C, respectively. The pressure was 0.5, 0.7, or 1.0 MPa. The concentration of Na_2SO_4 in the permeate solution was measured using a conductivity meter and the observed rejection \(R_{obs}\) was calculated as follows:

\[
R_{obs} = 1 - \frac{C_p}{C_b} \tag{1}
\]

where \(C_p\) and \(C_b\) are the concentrations of the salt in the permeate solution and bulk solution, respectively.

2.3.2 Comparison of the performance of the prepared membranes with that of commercial NF membranes

Two NF membranes (NTR-7450 and NTR-729HF) and one dynamically formed membrane, using 1000 ppm PAA and at 1.0 MPa, were employed in this study. Aqueous solutions containing Na_2SO_4, NaCl, CaCl_2, and MgSO_4 at known concentrations were used as feed solutions, and the membrane performances were evaluated at a flow rate of 6 L min\(^{-1}\) at 25 °C. The difference between the membrane configurations was ignored by discussing the real rejection \(R_{real}\), as defined:

\[
R_{real} = 1 - \frac{C_p}{C_m} \tag{2}
\]
where $C_m$, $J_v$, and $k$ are the concentration of the salt at the membrane surface, flux, and mass transfer coefficient, respectively. $C_m$ was calculated according to the concentration polarization equation. $k$ was obtained using the Deissler’s equation.

### 2.3.3 Long-term operation of the dynamically formed membranes

Two dynamically formed membranes, which were prepared with 1000 ppm PAA and at 1.0 MPa, were employed, and the time-dependent membrane performance was evaluated using aqueous solutions containing 100 ppm Na$_2$SO$_4$ as feed solutions at 25 °C. The flow rate was set at 6 L min$^{-1}$ or 3.5 L min$^{-1}$. To maintain the level of freshness of the feed solutions and to avoid the formation of potential fouling substances, the feed solutions were exchanged twice a week. The process only lasted for less than 5 min.

### 3. Results and discussion

#### 3.1 Effect of the preparation conditions on the performance of the dynamically formed membranes

The relationship between the pressure and flux of the dynamically formed membranes at varying PAA concentrations of 200, 500, and 1000 ppm under varying applied preparation pressures of 0.2, 0.5, and 1.0 MPa is shown in Fig. 1. In all cases, a linear relationship was observed. The slope became smaller when the pressure of the dynamic forming method was higher and when the concentration of PAA used was larger. For example, the slope obtained for the membrane prepared with 200 ppm PAA and at an applied pressure of 0.2 MPa was approximately three times larger than that obtained for the membrane prepared with 1000 ppm PAA and at an applied pressure of 1.0 MPa. This finding suggests that the amount of PAA deposited onto the substrate increased with increasing applied pressures and increasing concentrations of PAA in the feed solution.

The relationship between the applied preparation pressure (0.2, 0.5, and 1.0 MPa) and $R_{obs}$ of the dynamically formed membranes at varying PAA concentrations of 200, 500, and 1000 ppm is shown in Fig. 2. $R_{obs}$
of the unmodified alumina support was 0.26, and increased for all dynamically formed membranes. $R_{\text{obs}}$ became larger at increasing preparation pressures and PAA concentrations. For example, $R_{\text{obs}}$ of the membrane prepared with 1000 ppm PAA and at 1.0 MPa was 0.98. Accordingly, $R_{\text{obs}}$ could be tuned over a wide range of values. These results indicated that the amount of PAA deposited onto the substrate increased with increasing preparation pressures and PAA concentrations in the feed solution, thereby achieving higher $R_{\text{obs}}$ values. Thus, the membrane performance can be arbitrarily tuned by varying the preparation pressure and PAA concentration.

3.2 Comparison of the performance of the prepared membranes with that of commercial NF membranes

Fig. 3 shows the relationship between the pressure and the pure water flux of a dynamically formed membrane (at 1000 ppm PAA and 1.0 MPa) and two NF membranes (NTR–7450 and NTR–729HF). Among these three membranes, NTR–729HF showed superior desalination properties, regardless of the salt species tested, and $R_{\text{real}}$ was consistently higher than 0.9. NTR–7450 displayed the second best desalination properties. NTR–7450 and NTR–729HF displayed comparable $R_{\text{real}}$ values for Na$_2$SO$_4$. However, the $R_{\text{real}}$ values of NTR–7450 for other salts were lower than those of NTR–729HF, and decreased with increasing salt concentrations. In contrast, the dynamically formed membrane showed the lowest $R_{\text{real}}$ values. An $R_{\text{real}}$ value of 0.92 was obtained for Na$_2$SO$_4$ ($C_m = 250$ ppm), and decreased to 0.83 when $C_m$ of Na$_2$SO$_4$ increased to 570 ppm. Additionally, the dynamically formed membrane displayed lower $R_{\text{real}}$ values for other salts studied at low salt concentrations. The opposite trend was obtained for the water permeability. Such a trade–off between the flux and rejection can be observed in various membranes, and in this case the dynamically formed layers onto the porous support would be loosely attached when compared with the active separation layers in commercial NF membranes that generated higher flux and lower rejection. However, at relatively low concentrations ($\approx 100$ ppm), concurrent high flux and $R_{\text{real}}$ values comparable with those of commercial NF membranes could be achieved. Thus, the dynamically formed membranes present potential in water desalination at relatively low saline water concentrations as the desalination processes employed for industrial water recycling purposes.
3.3 Long-term operation studies of the dynamically formed membranes

Fig. 5 shows the time-dependent flux and rejection profiles obtained under two different crossflow conditions (6.0 L min$^{-1}$ and 3.5 L min$^{-1}$) during long-term operations.

A 500-h operation was then examined under a pressure of 0.6 MPa and a flow rate of 3.5 L min$^{-1}$. The flow rate corresponds to an $N_{Re}$ of $2.0 \times 10^4$ in this system. For comparison purposes, this pressure was selected as it afforded the generation of an initial flux of $4.0 \times 10^{-5}$ m$^3$ m$^{-2}$ s$^{-1}$. Thus, the effect of flux could be ignored and the sole influence of flow conditions on the durability of the membranes could be examined. As shown in Fig. 5(a), no significant increases in the flux were observed during the 500-h operation. Additionally, as shown in Fig. 5(b), the extent of decrease in rejection performance was significantly smaller than that in the system with $N_{Re}$ of $3.5 \times 10^4$ though temporal recovery upon replacement of the feed solution with a fresh solution was observed. Compared with the former case study ($N_{Re} = 3.5 \times 10^4$), the amount of detached PAA during the operation was considerably smaller. These results clearly indicated that the flow rate influenced the durability of the dynamically formed membranes using PAA and tubular ceramic supports. This was because the PAA layer which was originally formed on the support detached from the surface in the presence of a crossflow stream under higher $N_{Re}$ conditions that induced higher shear near the membrane surface. Moreover, the dynamical-
4. Conclusions

In this study, a dynamic forming method was employed to prepare membranes using PAA and tubular alumina supports; the dynamically formed membranes can be used in water desalination applications. The membrane performance was tuned by varying the concentration of PAA and applied pressure used during the dynamic forming method. Higher concentrations of PAA and applied pressures resulted in improved rejection performance and reduced permeability. When the concentration of PAA and the applied pressure during the preparation were set at 1000 ppm and 1.0 MPa, respectively, $R_{\text{obs}}$ of the resulting membrane for 100 ppm Na$_2$SO$_4$ solution was as high as 0.98, while the $R_{\text{obs}}$ of the unmodified alumina support was only 0.26. Compared with commercial polymeric NF membranes (NTR–7450 and NTR–729HF), the dynamically formed membranes exhibited higher flux and lower rejection performance, and the dynamically formed membranes show potential in water desalination applications at low saline water concentrations such as desalination processes for industrial water recycling purposes. Additionally, long-term desalination tests under different flow rate conditions in crossflow modes were carried out. The flow rate during operation significantly influenced the membrane performance over time. Using a flow rate of 6.0 L min$^{-1}$ ($N_{\text{Re}} = 3.5 \times 10^4$), the PAA layer detached from the membrane surface, resulting in higher flux and reduced rejection performance over a 1000–h crossflow operation. In contrast, using a flow rate of 3.5 L min$^{-1}$ ($N_{\text{Re}} = 2.0 \times 10^4$) did not lead to considerable reduction in the membrane performance. This was because the amount of the detached PAA was relatively smaller. Hence, we can say that $N_{\text{Re}}$ is one of the most important parameters influencing the durability of dynamically formed membranes.

Acknowledgments

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