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# High water permeable nanofiltration membranes via post pore expansion of polyamide thin layer introducing methoxycarbonyl groups

Daisuke Saeki <sup>a,b,\*</sup>, Hiroyuki Tsuchida <sup>b</sup>, Takahiro Kawakatsu <sup>c</sup>, Yukihisa Okumura <sup>b</sup>

<sup>a</sup> Research Initiative for Supra-Materials (RISM), Interdisciplinary Cluster for Cutting Edge Research, Shinshu University, 4-17-1 Wakasato, Nagano 380-8553, Japan <sup>b</sup> Department of Engineering, Graduate School of Science and Technology, Shinshu University, 4-17-1 Wakasato, Nagano 380-8553, Japan

<sup>c</sup> Kurita Water Industries Ltd., 3993-15 Haijima-cho, Akishima, Tokyo 196-0002, Japan

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### ABSTRACT

Improvement in the water permeability of nanofiltration (NF) membranes is desirable for saving energy in separation processes. Polyamide (PA) membranes formed via interfacial polymerization are commonly used as NF membranes because of their high water permeability and controllable selectivity. Typically, water permeability and rejection of target molecules are trade-offs, making simultaneous improvement challenging. In this paper, we demonstrate a new methodology called "post pore expansion" of PA NF membranes to enhance water permeability using a cleavable amine molecule, methyl 3,5-diaminobenzoate (MDAB). PA membranes were formed using piperazine, MDAB, and *m*-phenylenediamine as amine molecules. They were then treated with aqueous NaOH to convert the hydrophobic methoxycarbonyl groups to hydrophilic carboxyl groups via hydrolysis. Water permeability drastically increased after the NaOH treatment, reaching values 10 times higher than the initial value, while maintaining Na<sub>2</sub>SO<sub>4</sub> rejection. The fabricated membranes exhibited a maximum water permeability of 72.3 LMH/bar and Na<sub>2</sub>SO<sub>4</sub> rejection of 91.1 %. Various surface analyses confirmed the presence of carboxyl groups, and positron annihilation lifetime spectroscopy results indicated removing methoxycarbonyl groups and increasing pore size of the PA layer, suggesting that the pores were expanded. The presented "post pore expansion" methodology has the potential to drastically improve water permeability maintaining salt rejection in PA NF membranes.

#### 1. Introduction

Nanofiltration (NF) membranes have found diverse applications, including pretreatment for reverse osmosis (RO) membrane processes and separating and concentrating small organic molecules and multivalent ions, owing to their high energy efficiency [1]. Polyamide (PA) membranes formed via interfacial polymerization are widely used in NF applications because of their high water permeability [2]. Enhancing the water permeability of PA membranes is critical because it directly impacts the energy efficiency of separation processes.

The separation performance of PA membranes is influenced by several parameters during the membrane fabrication process, such as monomer structure, monomer concentration, additives, and support structure [3]. Amine monomers diffuse from the aqueous phase into the immiscible organic phase and react with acid halide molecules during interfacial polymerization, resulting in the formation of a threedimensional structure. Key factors that enhance the water permeability of PA membranes include density, hydrophilicity, and relative surface area. However, water permeability and the rejection of target molecules typically exhibit trade-offs, making simultaneous improvement challenging [4]. For instance, a reduction in PA density, which is primarily influenced by the monomer structure, enlarges pore size, thereby increasing water permeability while decreasing rejection.

Increasing the hydrophilicity of the PA layer represents an effective approach to enhance water permeability while maintaining rejection capabilities. The use of hydrophilic monomers in interfacial polymerization [5–12] or the surface modification of PA membranes with hydrophilic molecules [13–19] has been reported to increase hydrophilicity. Although hydrophilic monomers increase the hydrophilicity of the PA layer, they negatively affect the relative surface area because their low diffusivity in the organic phase can impede the growth of the PA layer [20]. These conflicting effects limit significant

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<sup>\*</sup> Corresponding author at: Research Initiative for Supra-Materials (RISM), Interdisciplinary Cluster for Cutting Edge Research, Shinshu University, 4-17-1 Wakasato, Nagano 380-8553, Japan.

E-mail address: dsaeki@shinshu-u.ac.jp (D. Saeki).



Fig. 1. Concept of "post pore expansion" of polyamide (PA) nanofiltration (NF) membranes to improve the water permeability using cleavable amine, methyl 3,5diaminobenzoate (MDAB).

improvements in water permeability. Conversely, surface modification can alter the hydrophilicity of the pre-formed PA surface and enhance water permeability. Nevertheless, surface modification primarily affects the PA surface and not the interior, resulting in limited improvements in water permeability.

In another approach, various nanomaterials, such as carbon nanotubes [21–23], metal nanotubes [24], cellulose nanofibers [25], nanoparticles [26,27], and graphene [23,28,29] have been employed as additives in PA membranes to form water channels [30,31]. Computer simulations have indicated that PA membranes incorporating these nanomaterials as water channels could theoretically achieve 10 to hundred times higher water permeability than conventional PA membranes [32]. These materials effectively improve the water permeability of PA membranes, but they also come with significant challenges such as high production costs [33,34], biological toxicity [35,36], and membrane fabrication complexity [34].

In this study, we propose an advanced fabrication method for PA NF membranes to drastically improve water permeability maintaining salt rejection. During interfacial polymerization, hydrophobic amine molecules increase the roughness of the PA layer due to their high diffusivity from the aqueous to the organic phase, while they decrease the hydrophilicity of the PA layer. Our concept involves increasing the hydrophilicity of the PA layer through "post-treatment" after the formation of a rough PA layer via interfacial polymerization (Fig. 1). This method simultaneously enhances the hydrophilicity and surface roughness of the PA layer, which are essential for achieving high water permeability. Methyl 3,5-diaminobenzoate (MDAB), the focus of this study, has a methoxycarbonyl group, which is less hydrophilic than a carboxyl group. Interfacial polymerization using hydrophobic MDAB as the amine molecule forms a polyamide layer with a rough structure. The methoxycarbonyl groups in the formed polyamide hydrolyze into hydrophilic carboxyl groups upon exposure to basic conditions, thereby increasing water permeability due to the enhanced hydrophilicity and pore expansion by reduced molecular size of side chains. The novel point of this concept is that the membrane performance is regulated not by functional additives or surface modification but by changing the molecular structure of the pre-formed PA layer through "post-treatment". Water permeability and salt rejection were evaluated in terms of membrane performance, and various surface analyses were performed to confirm the hydrolysis of the methoxycarbonyl groups and pore expansion in the polyamide layer.

# 2. Experimental

# 2.1. Materials

Aqueous solutions were prepared using Milli-Q water (>18.2 M $\Omega$  cm; Merck; Darmstadt, Germany). MDAB and trimesoyl chloride (TMC) were

purchased from Alfa Aesar (Massachusetts, USA) and Tokyo Chemical Industry (Tokyo, Japan), respectively. A commercial polysulfone ultrafiltration membrane (CF-30 K; MWCO = 500 kDa), used as the support membrane for the PA layer, was obtained from Nitto Denko (Osaka, Japan). A silicone wafer was purchased from Global Top Chemical (Tokyo, Japan). All other chemicals were purchased from Fujifilm Wako Pure Chemical Industries (Osaka, Japan).

# 2.2. Fabrication of PA membranes via interfacial polymerization

PA membranes were fabricated using conventional interfacial polymerization [37]. An amine solution was prepared by adding piperazine (PIP), MDAB, and *m*-phenylenediamine (MPD) at a total concentration of 2.0 wt% to an aqueous solution containing 0.25 wt% sodium dodecyl sulfate and 5.0 wt% isopropyl alcohol to solubilize MDAB. The solution was heated at 70 °C for one hour in the dark and cooled to room temperature owing to the low solubility of MDAB. A support membrane stored in Milli-Q water was immersed in the amine solution for 1 min and subsequently in a hexane solution containing 0.15 wt% trimesoyl chloride (TMC) for 15 s to form a PA layer. Excess solution at each immersion step was removed using airflow. The obtained membrane was dried at 100 °C for 10 min, rinsed with Milli-Q water, and stored in Milli-Q water at 5 °C. The membrane fabricated with an x:y:z weight ratio of PIP:MDAB:MPD was designated as PIP<sub>x</sub>MDAB<sub>y</sub>MPD<sub>z</sub>.

#### 2.3. Hydrolysis of methoxycarbonyl groups in PA layer

The fabricated membrane was placed in contact with an aqueous solution of 0.1 mol/L NaOH at a flow rate of 1.0 or 3.0 mL/min under stirring at 300 or 1000 rpm using the membrane test unit described in the following section. Subsequently, Milli-Q water was fed at 9.9 mL/min with stirring at 1000 rpm and a transmembrane pressure of 3.0 bar to rinse the membrane.

#### 2.4. Evaluation of separation performance

The pure water permeability and salt rejection of NaCl, MgSO<sub>4</sub>, and Na<sub>2</sub>SO<sub>4</sub> were evaluated using a laboratory-scale cross-flow membrane test unit, as described in our previous study [37]. The average values and standard deviation were obtained from the measurements of three pieces of each membrane. Aqueous 0.05 wt% salt was used as the feed water for the salt rejection measurements. The effective area of the membrane cell was 8.0 cm<sup>2</sup>. The flow rate and applied pressure were set to 9.9 mL/min and 3.0 bar, respectively. The feed-water side at the bottom of the membrane cell was magnetically stirred at 1000 rpm. Water permeability and salt rejection were calculated from the accumulated mass and electrical conductivity of the permeated water; the latter was measured using a conductivity meter (B771; Horiba, Tokyo,



Fig. 2. Time course of the membrane performance of  $PIP_{50}MDAB_{50}$  during treatment with the NaOH aqueous solution at 1.0 mL/min and 300 rpm of the stirring rate.

Japan). Each measurement was carried out at room temperature after rinsing the membranes with Milli-Q water.

The water permeation resistance of the support and PA layer was calculated with a simple resistances-in-series model using the following equations [38,39]:

$$P_{\text{Total}} = \frac{1}{R_{\text{Total}}} = \frac{1}{(R_{\text{support}} + R_{\text{PA}})}$$
(1)

$$P_{\text{support}} = 1/(R_{\text{support}}) \tag{2}$$

 $P_{\text{Total}}$  and  $P_{\text{support}}$  are the water permeability of the fabricated membrane and support membrane, LMH/bar.  $R_{\text{support}}$  and  $R_{\text{PA}}$  are the resistance of the support membrane and PA layer in the fabricated membrane, h bar/m.  $P_{\text{support}}$  is 451.5 LMH/bar.

# 2.5. Characterization of surface properties

The chemical composition of the membrane surface was analyzed using X-ray photoelectron spectroscopy (XPS; QuanTera II; Ulvac-Phi, Kanagawa, Japan). XPS spectra were analyzed using computer-aided surface analysis with X-ray photoelectron spectroscopy (CasaXPS) software. Membrane morphology was observed using field emission scanning electron microscopy (FE-SEM; JSF-7000F; JEOL, Tokyo, Japan) and atomic force microscopy (AFM; Hitachi High-Tech Science, Tokyo, Japan). For these analyses, membrane samples after the separation performance measurements were freeze-dried under vacuum (FDU-1200; Tokyo Rikakikai, Tokyo, Japan). Additionally, samples were coated with osmium (Neoc-AN; Meiwafosis, Tokyo, Japan) prior to FE-SEM. AFM was carried out with an OMCL-AC160TS-C3 cantilever (Olympus, Tokyo, Japan) in tapping mode. The thickness of the PA layer was also measured by using AFM. Membrane samples were immersed in N,N-dimethylformamide for 30 min to detach the PA layer from the support membrane. The PA layer was immersed in isopropyl alcohol. transferred to the surface of a silicon wafer, and dried in the atmosphere. Water contact angles of the wet membrane samples were obtained from ten-times measurements using a contact angle meter (DM-100; Kyowa Interface Science, Saitama, Japan).

# 2.6. Measurement of pore size of PA layer

The pore sizes of the PA layers of the fabricated membranes were evaluated via positron annihilation lifetime spectroscopy (PALS) using a pulsed-beam-type PALS apparatus (PALS-200A; Fuji Imvac, Kanagawa, Japan) [40]. Membrane samples after the separation performance measurements were freeze-dried under vacuum and then placed in the apparatus. The positron beam output was set at 1.0 keV, and a total count of  $1.5 \times 10^7$  gamma rays was used. The obtained PALS spectra were analyzed using the PALSFit method to determine the average pore size [41], and the CONTIN method was used to obtain the pore size distribution.

# 3. Results and discussion

# 3.1. Membrane performance

First, we investigated the effect of NaOH treatment time on membrane performance. Fig. 2 illustrates the change in the membrane



**Fig. 3.** Change in the membrane performance of  $PIP_{50}MDAB_{50}$  (A) and  $PIP_{50}MPD_{50}$  (B) during treatment with the NaOH aqueous solution at 3.0 mL/min and 1000 rpm of the stirring rate. W\* indicates the data after the NaOH treatment and two days of the Milli-Q water washing.



Fig. 4. Membrane performance of  $PIP_xMDAB_y$  after NaOH treatment and Milli-Q water washing. Each value was obtained from three pieces of the membrane samples. Error bars indicate the standard deviation.

performance of PIP<sub>50</sub>MDAB<sub>50</sub> during NaOH treatment at 1.0 mL/min and 300 rpm of the stirring rate. After 6 days of NaOH treatment, water permeability gradually increased and was 10 times higher than the initial value. In contrast, the rejections of NaCl and MgSO<sub>4</sub> decreased. The increased water permeability and decreased salt rejection suggest that the pores of PIP<sub>50</sub>MDAB<sub>50</sub> were expanded by NaOH treatment. The membrane performance can be controlled by varying the NaOH treatment time. The long duration of the increase in water permeability implies that the influence of NaOH treatment on the membrane performance is quite slow. Methoxycarbonyl groups exist not only on the PA surface but also within the PA layer. NaOH gradually penetrated the inner part of the PA layer, hydrolyzed the ester bond of the methoxycarbonyl group, and reduced the size of side chains of PA.

Further, we investigated the effect of the methoxycarbonyl group incorporation ratio on the membrane performance. The time course of the membrane performance of PIP<sub>50</sub>MDAB<sub>y</sub>MPD<sub>z</sub> during the NaOH treatment is depicted in Fig. S1. The water permeabilities of PIP<sub>50</sub>M-DAB<sub>50</sub> (Fig. 2) and PIP<sub>50</sub>MDAB<sub>45</sub>MPD<sub>5</sub> (Fig. S1A) increased during NaOH treatment, while those of PIP<sub>50</sub>MDAB<sub>37.5</sub>MPD<sub>12.5</sub> and PIP<sub>50</sub>M-DAB<sub>25</sub>MPD<sub>25</sub> changed slightly. Generally, MPD-based PA membranes perform lower water permeability and higher salt rejection than PIPbased PA membranes due to the relatively high reactivity of MPD with TMC [42,4]. The high-degree crosslinking by MPD likely restricts the NaOH penetration into the PA layer to hydrolyze methoxycarbonyl groups resulting in decreasing the water permeability and its change degree, and the change in the PA network structure due to electrostatic repulsion between the carboxyl groups generated by the hydrolysis of the methoxycarbonyl groups, as described below.

When  $PIP_{50}MDAB_{50}$  underwent treatment with an aqueous NaOH solution at a flow rate of 3.0 mL/min and a stirring rate of 1000 rpm to expedite fabrication, the water permeability stabilized within 2 days of NaOH treatment (Fig. 3A). The hydrolysis of methoxycarbonyl groups was accelerated with an increase in stirring rate, facilitating NaOH penetration into the PA layer. If NaOH cleaves the amide bonds within the PA layer, water permeability should also increase. Conversely, when

PIP<sub>50</sub>MPD<sub>50</sub>, devoid of methoxycarbonyl groups, underwent treatment under identical NaOH conditions, minimal changes in water permeability and salt rejection were observed (Fig. 3B). As documented, salt rejection decreases upon cleavage of amide bonds between the diamine and TMC [43]. Therefore, the enhanced water permeability post NaOH treatment stemmed from methoxycarbonyl group cleavage while preserving the PA structure's integrity via amide bond binding. The membrane fabrication process employed an aqueous NaOH solution at 3 mL/ min and a stirring rate of 1000 rpm for the following experiments.

Subsequent treatment of  $PIP_{50}MDAB_{50}$  with Milli-Q water led to a decrease in its water permeability. During NaOH treatment at elevated pH levels, the deprotonation of carboxyl groups induced electrostatic repulsion among them, thereby expanding the pores and enhancing water permeability even more. However, upon washing with Milli-Q water, the carboxyl groups underwent protonation at a neutral pH, resulting in the cancellation of electrostatic repulsion among the deprotonated carboxyl groups, leading to the contraction of the PA layer.

Since the results presented in Fig. 3B and Fig. S1 indicate that MPD strongly prevented the water permeability increase of the MDABincorporated membranes during NaOH treatment, PIP<sub>x</sub>MDAB<sub>y</sub> membranes were fabricated without MPD, and the impact of MDAB incorporation degree on membrane performance was examined Fig. S2. illustrates the variation in water permeability of PIP<sub>x</sub>MDAB<sub>y</sub> during NaOH treatment. Across all compositions, water permeability increased with NaOH treatment duration, reaching a steady state within three days and declining post washing with Milli-Q water. The increasing rate of the water permeability of PIP70MDAB30 was lower than that of other compositions, caused by the small amount of MDAB. When enough MDAB exists in the PA layer, NaOH efficiently hydrolyzes methoxycarbonyl groups and increases the water permeability. Fig. 4 provides an overview of membrane performance of PIPxMDABy after NaOH treatment and Milli-Q water washing. The PIPxMDABy membranes showed higher rejection against Na<sub>2</sub>SO<sub>4</sub> than NaCl and MgSO<sub>4</sub> regardless of the MDAB composition owing to Donnan exclusion mechanism of the negatively charged NF membranes [44]. Although salt rejection against NaCl and MgSO4 remained largely consistent with MDAB ratio, rejection against Na<sub>2</sub>SO<sub>4</sub> increased with MDAB ratio. The increases in Na<sub>2</sub>SO<sub>4</sub> rejection and water permeability with MDAB ratio stemmed from the increased number of hydrophilic carboxyl groups. Notably, PIP<sub>30</sub>MDAB<sub>70</sub> achieved 72.3 LMH/bar keeping over 90 % of Na<sub>2</sub>SO<sub>4</sub> rejection. Conversely, PIP<sub>60</sub>MDAB<sub>40</sub> exhibited the highest water permeability (72.9 LMH/bar) albeit with lower salt rejection compared to other membranes. This underscores the balance between the flexibility of PIP's polymeric network structure and the number of MDAB's carboxyl groups, resulting in the highest water permeability.

Table 1 shows the permeation resistance of the fabricated membranes before and after the NaOH treatment and Milli-Q water washing. The NaOH treatment drastically decreased PA layer resistance  $R_{PA}$  by less than 6 % of the initial values for all MDAB compositions. The resistance ratio between the PA layer and fabricated membrane ( $R_{PA}/R_{Total}$ ) was minimally 84 %, indicating the permeability was restricted to the PA layer resistance despite the high water permeability of PIP<sub>30</sub>MDAB<sub>70</sub>.

The chemical stability and fouling property are both essential for the

Table 1

The permeation resistance composition of the fabricated membrane before and after the NaOH treatment and Milli-Q water washing.

	R <sub>PA</sub> before NaOH treatment [h bar/m]	R <sub>PA</sub> after NaOH treatment [h bar/m]	R <sub>PA</sub> after Milli-Q water washing [h bar/m]	R <sub>PA</sub> before NaOH treatment [%]	R <sub>PA</sub> /R <sub>Total</sub> after NaOH treatment [%]	R <sub>PA</sub> /R <sub>Total</sub> after Milli-Q water washing [%]
PIP70MDAB30	0.2026	0.0106	0.0184	98.9	82.8	89.3
PIP <sub>60</sub> MDAB <sub>40</sub>	0.1663	0.0068	0.0115	98.7	75.4	83.9
PIP <sub>50</sub> MDAB <sub>50</sub>	0.1972	0.0090	0.0148	98.9	80.2	87.0
PIP40MDAB60	0.1333	0.0074	0.0123	98.4	76.9	84.8
PIP30MDAB70	0.1414	0.0071	0.0116	98.5	76.1	84.0

#### Table 2

Elemental composition of the surface of the fabricated membranes obtained by XPS analysis.

	C1s [at %]	N1s [at %]	01s [at %]	C/N [-]	0/C [-]	O/N [-]
Before NaOH treatment	72.34	11.15	16.51	6.49	0.23	1.48
After NaOH treatment	68.78	11.52	19.70	5.97	0.29	1.71
After Milli-Q water washing	68.25	11.80	19.95	5.78	0.29	1.69



**Fig. 5.** Water contact angle measurement of  $PIP_{50}MDAB_{50}$  before (A) and after the NaOH treatment and Milli-Q water washing (B). Each value was obtained from ten times measurements.

practical use of water purification membranes. MDAB-containing membranes maintained constant water permeability and Na<sub>2</sub>SO<sub>4</sub> rejection after two days during the 0.1 mol/L NaOH treatment. When PIP<sub>50</sub>MDAB<sub>50</sub> was exposed to 0.1 mol/L HCl aqueous solution, no noticeable decrease in the water permeability was observed (Fig. S3). From these results, MDAB-containing membranes have enough chemical stability to wash with acidic and basic solutions.

Fig. S4 shows the fouling behavior of  $PIP_{50}MDAB_{50}$  after NaOH treatment and Milli-Q water washing against bovine serum albumin (BSA) as a model of organic foulants.  $PIP_{50}MPD_{50}$  was also evaluated as a model of conventional NF membranes. The water permeability of  $PIP_{50}MDAB_{50}$  and PIP50MPD50 similarly decreased after feeding the BSA aqueous solution; however, it didn't decrease further and maintained the constant value after 20 min. Although the fouling degree of  $PIP_{50}MDAB_{50}$  was slightly worse than that of  $PIP_{50}MPD_{50}$ , the actual water permeability of the former was ten times higher than that of the latter despite the fouling.

# 3.2. Chemical analysis

To confirm the conversion of methoxycarbonyl groups to carboxyl groups through hydrolysis, surface analyses of PIP<sub>50</sub>MDAB<sub>50</sub>, which performed the highest salt rejection, were conducted using XPS, FE-

SEM, and AFM. Table 2 presents the elemental composition of the PIP<sub>50</sub>MDAB<sub>50</sub> surface before and after NaOH treatment and Milli-Q water washing, as obtained from the XPS spectra (Fig. S5). O/C increased following NaOH treatment. Theoretically, the relative oxygen ratio of carboxyl groups surpasses that of methoxycarbonyl groups. Fig. S6 displays the peak separation results of C1s, revealing an increase in C-N and a decrease in C-O bonding areas post NaOH treatment, signifying methoxycarbonyl group reduction. The decreased C/N and increased O/N indicate the conversion of methoxycarbonyl groups to carboxyl groups in the PA layer because it causes a decreased carbon amount and increased oxygen amount maintaining a nitrogen amount. These findings suggest the removal of methyl groups from methoxycarbonyl groups in the PA layer via hydrolysis. Notably, Milli-Q water washing did not alter the elemental composition but led to a reduction in water permeability (Fig. 3A). This decline in water permeability post Milli-Q water washing was attributed to structural changes such as polymer shrinking canceling the electrostatic repulsion. The generation of carboxyl groups or decomposition of methoxycarbonyl groups could not be distinguished by Fourier transform infrared spectroscopy because polyamide has carboxyl groups natively.

Fig. 5 illustrates the water contact angles of  $PIP_{50}MDAB_{50}$  before and after NaOH treatment and washing with Milli-Q water. Following NaOH treatment, the membrane surface exhibited increased hydrophilicity compared to the pristine membrane. Methoxycarbonyl groups are more hydrophobic than the carboxyl groups generated by hydrolysis, resulting in a hydrophilic surface.

Fig. 6 shows the AFM images of PIP<sub>50</sub>MDAB<sub>50</sub> before and after NaOH treatment, revealing a nodular structure characteristic of polyamide membranes containing PIP [45]. Similar structures were observed in SEM images (Fig. S7). These findings suggest that NaOH treatment maintained the macroscopic structure of the polyamide. The specific surface area values, calculated from the AFM images, for PIP<sub>50</sub>MDAB<sub>50</sub> before and after NaOH treatment were 38.0 and 40.3  $\mu$ m<sup>2</sup>, respectively, exhibiting a slight increase post treatment. The thickness also increased from 159 nm to 201 nm by the NaOH treatment (Fig. S8). These increase can be attributed to the swelling of the polyamide layer induced by water molecule adsorption to carboxyl groups, resulting in a drastic increase in water permeability (Fig. 3A).

PALS measurements offer insights into the actual pore structure of the PA layer [40], a parameter challenging to quantify through water permeability measurements and surface analysis alone. Fig. 7A shows the obtained PALS spectra. The lifetime shifted to the long region after the NaOH treatment and Milli-Q water washing, indicating the increase of the pore size. The pore size values, derived from PALSFit analysis of PALS spectra, for PIP<sub>50</sub>MDAB<sub>50</sub> before and after NaOH treatment and Milli-Q water washing were 0.554, 0.620, and 0.591 nm, respectively. The NaOH treatment significantly increased the pore size. The pore size distribution, obtained through CONTIN analysis of PALS spectra, also



Fig. 6. AFM images of PIP<sub>50</sub>MDAB<sub>50</sub> before (A) and after the NaOH treatment and Milli-Q water washing (B).



Fig. 7. (A) PALS spectra and (B) pore size distribution of PIP<sub>50</sub>MDAB<sub>50</sub> before and after the NaOH treatment and Milli-Q water washing obtained by CONTIN analysis of PALS spectra.



Fig. 8. Comparison of membrane performance. The raw values of the membrane performance of previously reported systems are shown in Table S1.

exhibited an enlargement in pore size (Fig. 7B). The emergence of carboxyl groups in the PA layer via methoxycarbonyl group hydrolysis induced by NaOH treatment resulted in pore size enlargement through the hydration of carboxyl groups and/or molecular size decrease from methoxycarbonyl to carboxyl groups, consequently augmenting the water permeability of  $PIP_{50}MDAB_{50}$ . The subsequent Milli-Q water washing slightly reduced the pore size, suggesting the cancellation of the electrostatic repulsion between carboxyl groups.

#### 3.3. Comparison of membrane performance

Over the last decade, various innovative approaches have been reported to improve the water permeability of PA membranes, including monomer modification [5–12,46], surface modification [13–19], nanomaterial composites [21–31], and support material modification [47]. Notably, support material modification methods, such as polymer

interlayers[48–54], nanocarbon material interlayers [55–59], inorganic material interlayers [60], and sacrificial layers [61,62], offer avenues for fabricating high-performance membranes by augmenting the relative surface area of the PA layer without altering its chemical structure. To contextualize the present study within the landscape of PA NF membrane fabrication methods, the membrane performance of previously reported systems is compared with that of membranes fabricated via the post pore expansion method in this study (Fig. 8). Our membranes exhibit water permeability exceeding three times that of commercial counterparts and rival or surpass most reported membranes. Moreover, their performance matches that of nanocomposite membranes [21–28]. In terms of fabrication cost, our proposed method not only eliminates the need for expensive nanomaterials but also aligns with the conventional PA membrane fabrication process. Additionally, our methodology possibly integrates support material modification techniques, recognized as potent means to enhance water permeability [47]. Membrane performance was flexibly modulated by NaOH treatment duration (Fig. 3) and monomer composition (Fig. 4). The PA layer, formed via "post pore expansion" using methoxycarbonyl groups, holds promise as next-generation PA materials.

#### 4. Conclusions

A novel fabrication method for PA NF membranes, termed "post pore expansion," was developed, involving the hydrolysis of methoxycarbonyl groups within a pre-formed PA layer to achieve high water permeability. PA membranes containing methoxycarbonyl groups were produced through conventional interfacial polymerization using MDAB, a relatively hydrophobic and cleavable amine molecule. Subsequent hydrolysis of methoxycarbonyl groups within the formed PA layer using aqueous NaOH resulted in the formation of hydrophilic carboxyl groups. Water permeability exhibited a remarkable increase with NaOH treatment duration, reaching values 10 times higher than the initial levels while maintaining Na<sub>2</sub>SO<sub>4</sub> rejection. Notably, a maximum water permeability of 72.3 LMH/bar was achieved, alongside a high Na<sub>2</sub>SO<sub>4</sub> rejection of 91.1 %. Membrane performance can be flexibly modulated by NaOH treatment duration and MDAB ratio. Surface analyses using AFM, XPS, and water contact angle measurements indicated minimal impact on the macroscopic surface morphology of the PA layer post NaOH treatment, while effectively converting methoxycarbonyl groups into carboxyl groups. PALS revealed pore expansion within the fabricated PA membranes, validating the concept of "post pore expansion." This methodology will lead to a breakthrough in reconciling the tradeoff between water permeability and rejection in PA NF membranes.

# CRediT authorship contribution statement

Daisuke Saeki: Conceptualization, Methodology, Validation, Formal analysis, Resources, Data curation, Writing – original draft, Writing – review & editing, Visualization, Supervision, Project administration, Funding acquisition. Hiroyuki Tsuchida: Methodology, Validation, Formal analysis, Investigation, Visualization. Takahiro Kawakatsu: Methodology, Investigation, Resources. Yukihisa Okumura: Validation, Writing – review & editing, Supervision.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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# Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.seppur.2024.130265.

#### Data availability

Data will be made available on request.

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