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Post-Treatment of Nanofiltration Polyamide Membrane through Alkali-Catalyzed Hydrolysis to Treat Dyes in Model Wastewater

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Abstract: This research focused on the influence of post-treatment using alkali-catalyzed hydrolysis with a full-aromatic nanofiltration (NF) polyamide membrane and its application to the efficient removal of selected dyes. The post-treated membranes were characterized through Fourier transform infrared spectroscopy, goniometry, and zeta-potential analysis to analyze the treatment-induced changes in the intrinsic properties of the membrane. Furthermore, the changes in permeability induced by the post-treatment were evaluated via the measurement of water flux, NaCl rejection, and molecular weight cutoff (MWCO) under different pH conditions and post-treatment times. Major changes induced by the post-treatment in terms of physicochemical properties were the enhancement of permeability, hydrophilicity, and negative charge due to the hydrolysis of the membrane’s amide bonds. Four different dyes were selected as representative organic pollutants considering the MWCO of the post-treated membranes. Compared with the pristine NF membrane, membranes post-treated at pH 13.5 showed better water flux with similar rejection of the target dyes. On the basis of these results, the proposed post-treatment method for NF membranes can be applied to the removal of organic pollutants of various size.

Keywords: dyes removal; post-treatment; alkali-catalyzed hydrolysis; polyamide membrane

1. Introduction

Nanofiltration (NF) membranes have been widely used to separate divalent ions, dyes, pharmaceutical compounds (PhACs), and natural organic matters [1,2]. Because NF membranes have physicochemical properties intermediate between those of ultrafiltration and reverse osmosis (RO) membranes, the separation mechanism of NF membranes has generally been explained on the basis of synergetic effects of both sieving and electrostatic interactions [3,4]. The molecular-weight cutoff (MWCO) of NF membranes is known to range from 300 to 500 Da; thus, the NF process has been conducted at relatively lower pressures than those used in RO processes [5,6]. Thus, because of the unique properties of NF membranes, high energy efficiency can be achieved if NF membranes are used to treat wastewater containing divalent ions or organic pollutants with molecular weights greater than 200 Da [5,7].

Treatment of wastewater containing organic/inorganic pollutants has become an urgent environmental issue because numerous pollutants have been detected in various water sources such as river, ground, and surface waters [8–13]. This pollution results from the inappropriate discharge of effluents [9,14]. In particular, colored effluents containing synthetic dyes lead to serious
environmental problems, such as (i) destruction of the ecosystem because of decreased dissolved oxygen, (ii) inhibition of photosynthesis for self-purification by aquatic organisms due to blocked sunlight, and (iii) toxic/carcinogenic effects to animals and plants living in polluted water bodies [8,15,16]. Therefore, the fabrication of high-performance NF membranes is a key factor in the cost-effective treatment of wastewater containing synthetic dyes.

Generally, NF membranes comprise two different layers—a support layer and an active layer—to optimize water flux and salt rejection [17]. The active layers of NF membranes have been fabricated through interfacial polymerization using reactions between an amine-based monomer in an aqueous phase and an acyl chloride-based monomer in an organic solvent phase [18]. The reaction between m-phenylenediamine (MPD) and trimesoyl chloride (TMC), in particular, is a well-known method for fabricating polyamide (PA) active layers with high water flux and salt rejection [19]. Previous studies have reported further improvement of water flux or salt rejection using various post-treatments. For example, surface grafting using hydrophilic monomers such as N-isopropylacrylamide [20] and poly(sulfobetaine methacrylate) were used to increase the surface hydrophilicity [21]. Another study attempted to improve the water flux of NF membranes through acid-catalyzed hydrolysis [22], leading to an increase in the pore size and hydrophilicity through conversion of amide bonds to amine and carboxylic acid bonds. We speculated that alkali-catalyzed hydrolysis could similarly be used to improve the pore size and hydrophilicity of NF membranes.

The hydrolysis of polyamide bonds by acid or base has been explored in biological research because the skin of organisms contains polypeptides, which are chains of amino acids [23]. Amide bonds exhibit high chemical stability because of their resonance structure resulting from electronegative oxygen and lone-pair electrons of nitrogen [18]. However, the stable structure of amide bonds can be easily destroyed by acid or base under extreme pH conditions [24]. That is, hydrogen or hydroxide ions can weaken the resonance structure of an amide bond by reacting with oxygen/nitrogen or carbon atoms involved in amide bonding, respectively [24], enabling hydrolysis of the amide bond. These phenomena can be applied to amide-based membranes by the same logic, as demonstrated in a previous study [22]. That is, the pore size of an NF membrane can be controlled through manipulation of the experimental conditions related to hydrolysis of the polyamide layer. However, to the best of our knowledge, alkali-catalyzed hydrolysis of an MPD-based NF membrane to improve its permeability for treating dyes in model wastewater has not been previously reported.

Herein, we comprehensively studied the surface and permeability properties of an MPD-based NF membrane after the membrane was subjected to alkali-catalyzed hydrolysis as a post-treatment. To this end, we measured the intrinsic properties of the untreated membrane and compared them with the properties of previously reported membranes and post-treated membranes. We then used several characterization methods to investigate the effect of alkali-catalyzed hydrolysis on the chemical bonds, hydrophilicity, and surface charge of the treated membranes. We measured the MWCO of the post-treated membranes using several (poly)ethylene glycol solutions. Finally, the optimized membranes were used to remove four different aqueous-phase dyes and their removal performance was compared with that of previously reported membranes.

2. Materials and Methods

2.1. Chemicals

Sodium hydroxide (NaOH), hydrochloric acid (HCl), sodium chloride (NaCl), magnesium sulfate (MgSO₄), ethylene glycol (EG), polyethylene glycol (PEG, molecular weight of 200, 400, 600, 1000, and 2000 Da), Neutral red, Sunset yellow, Congo red, and Reactive red 120 were purchased from Sigma-Aldrich (St. Louis, MO, USA). Commercially available NF 90, which is a representative MPD-based polyamide, was obtained from DowFilmTec (Minneapolis, MN, USA). Furthermore, NF 270 was used as a representative loose NF membrane for control group, which was obtained from DowFilmTec (Minneapolis, MN, USA). Deionized (DI) water (approximately 18.2 MΩ·cm) was
used for all of the solutions prepared in this study. All chemicals were used as received without further purification.

2.2. Preparation of the Post-Treated Membranes

Preparation of the post-treated membranes was performed as referred to in a previous study [22]. In brief, coupons of an NF 90 membrane (coupon size: 10 cm (height) × 10 cm (width)) were soaked in glass bottles containing alkali solutions. This study focused on the effect of solution pH and contact time on the post-treatment of NF membranes; therefore, coupons of NF 90 membranes were exposed under pH 13, 13.5, and 14 for 7, 14, and 28 days. All of the samples were rinsed with DI water after post-treatment and then kept in DI water until used in permeability tests.

2.3. Confirmation of Physicochemical Properties of the Membranes

2.3.1. Surface Characterizations

The effect of the alkali-catalyzed hydrolysis on an NF 90 membrane was analyzed using a Fourier-transform infrared (FTIR) spectrometer, goniometer, and zeta-potential analyzer. In the case of the FTIR and goniometer, NF 90 and the post-treated membranes were dried in an oven at 333 K for 48 h. Dried samples were mounted in the FTIR spectrometer (Nicolet 6700; Thermo Scientific, Waltham, Ma, USA) equipped with an attenuated total reflectance accessory, and their chemical bonds were characterized in the wavenumber range from 4000 to 1000 cm\(^{-1}\) wavenumber [25,26]. Furthermore, the hydrophilicity of the membrane surface was measured by sessile drop method using a goniometer (VCA Optima system; AST Products, Inc., Billerica, MA, USA). Lastly, a wet membrane sample was mounted onto a zeta-potential analyzer (SurPASS, Anton Paar, Graz, Austria) to analyze its surface charge using 10 mM NaCl electrolyte solution at pH 5.6; the solution pH was adjusted with 0.1 N HCl, modified from previous studies [27,28].

2.3.2. Membrane Performances

The membrane performance of the NF 90 and that of the post-treated membranes were characterized by water flux, NaCl or dye rejection, and MWCO value, as determined on the basis of their rejection of PEGs. The details of the experimental procedure are explained elsewhere [22,29]. In brief, a membrane coupon with 15 cm\(^2\) effective area was firstly compacted at 10 bars for 1 h, and stabilized at 5 bars for 30 min, followed by the permeability measurement of membrane samples. The concentrations of NaCl/MgSO\(_4\), dyes, and PEGs were measured using a calibrated conductivity meter (Accumet Excel XL30, Thermo Scientific, Waltham, MA, USA), an ultraviolet–visible spectrophotometer (Agilent Technologies, Santa Clara, CA, USA), and a total organic carbon analyzer (TOC-V\(_{CSN}\) analyzer; Shimadzu, Kyoto, Japan), respectively [30]. The concentrations of the four different dyes were obtained at their respective maximal adsorption wavelength [7]. The MWCO values of NF 90 and the post-treated membranes were calculated from the results of PEG experiments at the value of 90% rejection [22]. Water flux (L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\)) and rejection (%) were calculated using Equations (1) and (2):

\[
\text{Water flux} \left( \text{L m}^{-2} \text{h}^{-1} \text{bar}^{-1} \right) = \frac{\Delta W}{\Delta T \times A \times D \times P} \tag{1}
\]

where \(\Delta W\) is the weight of permeate, \(\Delta T\) is the operating time, \(A\) is the effective area of membrane, \(D\) is the density of water, and \(P\) is the operating pressure.

\[
\text{Rejection} \% = \left( 1 - \frac{C_p}{C_f} \right) \times 100 \tag{2}
\]

where \(C_p\) and \(C_f\) are the permeate and feed concentrations of NaCl/MgSO\(_4\), dyes, and PEGs, respectively.
3. Results and Discussion

3.1. Intrinsic Properties of the NF 90 Membrane

The commercial NF 90 membrane used in this work is a thin-film composite membrane comprising an MPD-based polyamide active layer and a polysulfone support layer. We characterized both layers because this study aims to investigate the influence of post-treatment alkali-catalyzed hydrolysis on the polyamide layer. Thus, the chemical bonds of the NF 90 membrane were analyzed by FTIR to characterize the bonding in both the polyamide layer and the polysulfone layer. Figure 1 describes the intrinsic chemical structure of the NF 90 membrane, as characterized by FTIR; four major peaks were selected to distinguish between polyamide (red text in Figure 1) and polysulfone (blue text in Figure 1) [31]. The characteristic FTIR peaks related to polyamide were the O–H/N–H stretching vibration at 3330 cm$^{-1}$, the C=O stretching vibration at 1663 cm$^{-1}$, and the N–H in-plane bending at 1541 cm$^{-1}$. In addition, FTIR peaks related to polysulfone were confirmed by the C–O–C stretching vibration at 1245 cm$^{-1}$. These peaks could be used to characterize the effect of alkali-catalyzed hydrolysis on the NF 90 membrane, as described in Section 3.2.1.

Table 1 summarizes the intrinsic performances, surface charges, and hydrophilicity of the membranes used in this study. First, the rejection rates of monovalent (NaCl) and divalent (MgSO$_4$) ions were greater than 92% and 98%, respectively. Second, the NF 90 membrane exhibited a negative charge at pH 5.6 because of deprotonation of the carboxylic acid groups on the active layer; this result is consistent with that of a previous study that reported pH 4.2 as the isoelectric point of the NF 90 membrane [32]. Third, the NF 90 membrane was hydrophilic (~45°) because of the charged species on the active layer, which were a result of both protonation of the amine and deprotonation of the carboxylic acid group [33]. All of the aforementioned experimental results are similar to those in a previous study in which the specifications of the NF 90 membrane were reported [34].
Table 1. Properties of NF 90 membrane reported in a previous study and in this study [34].

| NF 90 Membrane Property | Previous Study | Measured in This Study (n = 3) |
|-------------------------|----------------|--------------------------------|
| Pure water permeability (L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\)) | 15.8 at 5 bar | 14.6 ± 0.9 at 5 bar |
| NaCl rejection (%) | 85–95 | 92.8 ± 1.3 |
| MgSO\(_4\) rejection (%) | >97 | 98.3 ± 0.6 |
| Zeta potential at pH 5.6 (mV) | −20.3 | −15.2 ± 2.1 |
| Contact angle (°) | 48.7 | 44.9 ± 4.5 |

3.2. Effect of Alkali-Catalyzed Hydrolysis on the NF 90 Membrane

3.2.1. Change of Surface Properties

The effect of alkali-catalyzed hydrolysis on the surface properties of the NF membrane was characterized by FTIR, surface charge, and surface hydrophilicity. Figure 2 shows the effect of alkali hydrolysis on the FTIR spectra of the pristine and post-treated NF 90 membranes. The polyamide peaks (i.e., the C=O stretching vibration at 1663 cm\(^{-1}\) and the N–H in-plane bending vibration at 1541 cm\(^{-1}\)) continuously decreased in intensity with increasing contact time and solution pH; however, the intensity of the polysulfone peak was constant, as exemplified by the C–O–C stretching vibration at 1245 cm\(^{-1}\). That is, the polysulfone groups exhibited greater chemical stability than the polyamide groups; this result reveals a tendency similar to that reported in a previous study in which sulfuric acid was used for the post-treatment of an NF membrane [22]. In particular, the polyamide peaks completely disappeared when the membrane was post-treated at pH 14 for 28 days.

![Figure 2. Effect of alkali hydrolysis on the peaks in FTIR spectra of NF 90 pristine and post-treated membranes.](image)

As previously mentioned, the alkali-catalyzed hydrolysis of an amide bond results in the formation of a carboxylic acid group and an amine bond [24], possibly leading to an increase in the absolute value of the surface charge. The authors of a previous study reported that the absolute value of...
the surface charge was increased after acid-catalyzed hydrolysis of a semi-aromatic NF membrane with almost the same isoelectric point as that of the membrane used in the present study [18]. In the present study, we measured the surface charge of the pristine and post-treated NF 90 membranes and found that the absolute value of the surface charge at pH 5.6 tended to increase with increasing post-treatment time (Table 2). That is, this phenomenon can be explained by an increase in protonated carboxylic acid groups due to the conversion of amide groups to carboxylic acid and amine groups; this result is consistent with the FTIR results showing a decrease in polyamide peaks with increasing post-treatment time.

| Membrane | NF 90 Pristine | Post-Treated at pH 13.5 for 7 D | Post-Treated at pH 13.5 for 14 D | Post-Treated at pH 13.5 for 28 D |
|----------|----------------|-------------------------------|-------------------------------|-------------------------------|
| Zeta potential (mV) | $-15.2 \pm 2.1$ | $-17.2 \pm 1.6$ | $-18.2 \pm 1.2$ | $-18.9 \pm 1.4$ |

In addition, we measured the contact angle of the membrane before and after the post-treatment to investigate the effect of alkali-catalyzed hydrolysis on the surface hydrophilicity due to depolymerization of the amide bond. Figure 3 presents the contact angles of the pristine NF 90 and post-treated membranes; the contact angle decreased from $44.9^\circ$ to $38.6^\circ$ with increasing post-treatment time at pH 13.5. That is, surface hydrophilicity increased with increasing amount of conversion from neutral (i.e., amide bond) to charged form (i.e., carboxyl acid and amine bond). This phenomenon has been reported in other studies, and it can be used to analyze the pK$_a$ value of the membrane surface [9,35]. In the case of the membrane post-treated at pH 14 for 28 days, hydrophilicity evidently decreased because of the relatively hydrophobic characteristic of the polysulfone layer [36]; this result is in good agreement with the FTIR results (Figure 2).

Figure 3. Contact angles of pristine NF 90 and post-treated membranes ($n = 10$).

3.2.2. Change of Membrane Performances

The influence of the alkali-catalyzed hydrolysis on the membrane performance of the NF membrane was investigated by measurement of water flux, NaCl rejection, and MWCO value from PEGs rejection. Figure 4a describes the effect of the post-treatment on the water flux of the NF 90 membrane. The water flux was dependent on the post-treatment conditions (i.e., the solution pH and contact time). In the case of the membrane treated at pH 13 and 14, depolymerization of the polyamide layer was too
slow and fast, respectively, as determined from the increase in the water flux. Thus, an experimental condition of pH 13.5 would be appropriate to further investigate the change in water flux resulting from post-treatment with increasing contact time. Similarly, NaCl rejection was constant or dramatically decreased for experimental conditions at pH 13 and 14, respectively (Figure 4b). According to the change in water flux and NaCl rejection, both the concentration of hydroxide ions and the contact time were critical factors affecting membrane performance because the hydrolysis reaction rate is likely proportional to the degree of reaction between hydroxide ions and amide bonds [37].

![Graphs showing water flux and NaCl rejection](image)

**Figure 4.** Effect of alkali hydrolysis on the permeability of NF 90 pristine and post-treated membranes in terms of (a) water flux and (b) NaCl rejection (experimental conditions: 2000 mg L\(^{-1}\) NaCl and 5 bar).

Increased water flux and decreased salt rejection with increasing solution pH and post-treatment time would result from an increase in pore size due to depolymerization of the polyamide layer. Thus, the MWCO values of the pristine NF 90 and post-treated membranes were measured to confirm the pore size of the membrane indirectly. The MWCO value was obtained by rejection of PEG solutions, as shown in Figure 5. The MWCO value of pristine NF 90 was in the range from 62 to 200 Da, and the value continuously increased when the membranes were exposed to pH 13.5 for 7 to 28 days.
(Figure 5). This result clearly confirms an increase in both water and salt permeability with increasing post-treatment time at pH 13.5, as shown in Figure 4.

![Figure 5. Effect of alkali hydrolysis on the molecular weight cutoff (MWCO) of NF 90 pristine and post-treated membranes (experimental conditions: 1000 mg L⁻¹ polyethylene glycol (PEG) solutions and 10 bar).](image)

3.3. Removal of Dyes in Model Wastewater by the NF 90 and Post-Treated Membranes

This study focused on the feasibility of alkali-catalyzed hydrolysis of NF membranes used to treat dyes in model wastewater; thus, four different dyes were selected considering the MWCO value of the post-treated membranes: (i) Neutral red (\(M_w \approx 288\)), (ii) Sunset yellow (\(M_w \approx 452\)), (iii) Congo red (\(M_w \approx 696\)), and (iv) Reactive red 120 (\(M_w \approx 1469\)). Figure 6 shows the effect of alkali hydrolysis on the membrane performance of the pristine and post-treated NF 90 membranes. The water flux of the pristine NF 90 membrane was relatively lower than that of the post-treated membranes, as shown in Figure 6a; it demonstrates better than 99% rejection for all of the dyes (Figure 6b). To overcome the low water flux of the pristine NF 90 membrane, the post-treated membranes were applied to each dye considering their MWCO values. That is, the membranes post-treated at pH 13.5 for 7, 14, and 28 days achieved higher water flux with similar rejection in the case of Sunset yellow, Congo red, and Reactive red 120 removal, respectively. Interestingly, the membrane post-treated at pH 13.5 for 28 days achieved greater than 98% removal of Reactive red 120, even though the MWCO of the membrane (i.e., \(\approx 1470\)) was similar to the dye \(M_w\) (i.e., \(\approx 1469\)). This result is explained by the effect of electrostatic repulsion between the increased negative charge of the membrane and the negative charge of the dye. Table 3 summarizes a comparison of dye removal between previous studies and this study in terms of water flux and rejection. Particularly, post-treated membranes had higher water flux with comparable dye rejection compared to the NF 270 loose NF membrane. The membranes post-treated under each optimized condition exhibited a higher water flux with comparable dye rejection compared with the pristine NF 90 membrane and previously reported membranes. Finally, Figure 7 shows photos of the dye removal process using the NF 90 pristine and post-treated membranes; these photos support our hypothesis that the alkali-catalyzed hydrolysis can be used as a post-treatment method for polyamide-based NF membranes to improve their performance in the removal of dyes. In addition, this technique could be used to remove various organic pollutants, depending on their molecular size and surface charge, through optimization of the post-treatment conditions for polyamide-based NF membranes.
Figure 6. Effect of alkali hydrolysis on the permeability of NF 90 pristine and post-treated membranes in terms of (a) water flux and (b) dye rejection (experimental conditions: 50 mg L\(^{-1}\) dye solutions and 5 bar).
### Table 3. Comparison of dye removal between previous studies and this study in terms of water flux and rejection.

| Membrane                          | Target Dye       | Experimental Conditions | Water Flux (L m⁻² h⁻¹ bar⁻¹) | Rejection (%) | Reference |
|-----------------------------------|------------------|-------------------------|-----------------------------|---------------|-----------|
| NF 90 pristine                    | Sunset yellow    | 50 mg L⁻¹ dye at 5 bar  | 14.9                        | >99           | This work |
| Post-treated at pH 13.5, 7D       | Sunset yellow    | 50 mg L⁻¹ dye at 5 bar  | 16.0                        | >99           | This work |
| DEA-modified PA-TFC               | Sunset yellow    | 50 mg L⁻¹ dye at 5 bar  | 14.8                        | 97.5          | [7]       |
| PA-TFC                            | Sunset yellow    | 100 mg L⁻¹ dye at 5 bar | 9.3                         | >99           | [8]       |
| CMCNa/PP composite membrane      | Sunset yellow    | 100 mg L⁻¹ dye at 0.8 bar | 8.6                    | 82.2          | [1]       |
| Sericin-TMC membrane              | Sunset yellow    | 100 mg L⁻¹ dye at 5 bar | 12.4                        | 95.4          | [3]       |
| NF 90 pristine                    | Congo red        | 50 mg L⁻¹ dye at 5 bar  | 18.3                        | >99           | This work |
| Post-treated at pH 13.5, 14D      | Congo red        | 50 mg L⁻¹ dye at 5 bar  | 28.0                        | >99           | This work |
| NF 270 pristine                   | Congo red        | 50 mg L⁻¹ dye at 5 bar  | 22.3                        | >99           | This work |
| DEA-modified PA-TFC               | Congo red        | 50 mg L⁻¹ dye at 5 bar  | 15.7                        | >99           | [7]       |
| PA-TFC                            | Congo red        | 100 mg L⁻¹ dye at 5 bar | 9.2                         | >99           | [8]       |
| CMCNa/PP composite membrane      | Congo red        | 100 mg L⁻¹ dye at 0.8 bar | 7.8                    | >99           | [1]       |
| Sericin-TMC membrane              | Congo red        | 100 mg L⁻¹ dye at 5 bar | 12.6                        | >99           | [3]       |
| NF 90 pristine                    | Reactive red 120 | 50 mg L⁻¹ dye at 5 bar  | 19.8                        | >99           | This work |
| Post-treated at pH 13.5, 28D      | Reactive red 120 | 50 mg L⁻¹ dye at 5 bar  | 65.7                        | 98.1          | This work |
| NF 270 pristine                   | Reactive red 120 | 50 mg L⁻¹ dye at 5 bar  | 25.8                        | >99           | This work |
| Brij-58 contained PVDF membrane   | Reactive red 141 | 15 mg L⁻¹ dye at 6 bar  | 5.2 (PWP)                   | 90.0          | [38]      |
| PEI-enhanced UF membrane          | Reactive red 120 | 50 mg L⁻¹ dye at 4 bar  | 37.0                        | 99.0          | [15]      |
4. Conclusions

This research comprehensively investigated the effect of alkali-catalyzed hydrolysis on NF 90 membranes in terms of changes in the membranes’ physicochemical properties and permeability. FTIR analyses indicated that extreme alkali conditions mainly affected the polyamide active layer rather than the polysulfone support layer. The FTIR results were consistent with the results of other characterizations, such as measurements of the surface hydrophilicity, surface charge, and MWCO value. In addition, the post-treated membranes exhibited higher water and salt permeability compared with the pristine NF 90 membrane because of hydrolysis of the polyamide active layer. Optimization of the post-treated membranes was conducted at pH 13.5 with post-treatment times of 7, 14, and 28 days, and four different dyes were selected on the basis of the enhanced MWCO value of each post-treated membrane. The membranes optimized by alkali-catalyzed hydrolysis exhibited better water flux with comparable dye rejection compared with a pristine NF 90 membrane and other membranes reported elsewhere. The characterization and performance results presented here indicate that post-treatment of polyamide membranes can be efficiently used in the wastewater treatment of organic pollutants with different molecular size.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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