A regenerable antifouling membrane bearing a photoresponsive crosslinked polyethylenimine layer

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ABSTRACT
We developed a stimuli-responsive polyvinylidene fluoride (PVDF) microfiltration (MF) membrane with a photoresponsive crosslinked layer. The photoresponsive crosslinked layer on the membrane surface can be removed with the foulant layer through a UV process after the membrane is fouled, thereby restoring the degraded performance due to membrane fouling. To achieve this, we synthesized a photoresponsive linker by coupling cinnamic acid with epichlorohydrin and coated the photoresponsive crosslinked polyethylenimine layer onto a PVDF membrane with 0.1 μm pore size. The combined results of Fourier-transform infrared spectroscopy, proton nuclear magnetic resonance, ultraviolet-visible spectrophotometry, and field-emission scanning electron microscopy investigations clearly showed that the photoresponsive linker was successfully synthesized and that the photoresponsive layer (PRL) was coated onto the PVDF MF membrane via photoresponsive crosslinking. The PRL-coated membrane exhibited hydrophilic surface properties in addition to a high fouling resistance, and the PRL recovered the water flux >45% of the initial flux after backwashing in dead-end fouling tests with silica particles, whereas the neat membrane recovered the water flux only <38% of the initial flux after backwashing. Moreover, the PRL recovered the water flux of the MF membrane more efficiently using a photoinduced regeneration process. Specifically, the flux recovery ratio achieved by the process was 77%, even after third cycle.

1. Introduction

Due to the ongoing issue of water shortages, various water-treatment techniques for obtaining clean water have recently attracted growing attention [1], with examples including distillation [2], chemical treatment [3], adsorption [4], and membranes [5]. Among these, membrane technology has attracted particular attention as an eco-friendly water-treatment technology because of its high energy efficiency, narrow usage area, and high processing speed. As a result, it has been applied to various fields, such as domestic water, wastewater, and groundwater treatment. However, in the membrane water-treatment process, fouling commonly occurs, in which contaminants block the pores and interfere with water permeation of the membrane. If the fouling issue becomes unsolved, this can lead to problems such as a reduction in the process energy efficiency, shortening of the membrane life, and additional cleaning requirements [6].

Thus, to delay the fouling of water-treatment membranes, various systems have been investigated, including the introduction of hydrophilic substances [7–10], stimulus-sensitive substances [11,12], and antimicrobial substances [8–10,13–15] to the surface of the separation membrane. More specifically, the introduction of hydrophilic or stimulus-sensitive materials can prevent contaminants from adhering to the membrane, delay membrane contamination, and allow the contaminants on the surface to be more easily removed [7–12]. In addition, the introduction of antimicrobial agents also prevents bacterial growth on the membrane surface and delays the performance reduction caused by biofouling [8–10,13–15]. However, even these methods cannot completely prevent fouling; thus, contaminants accumulate continuously on the membrane, gradually reducing its permeation performance. Research into the effective recovery of the membrane performance under harsh conditions is also necessary, as this is inevitably reduced by fouling.

In this context, a method based on the use of dynamic coupling as a means for restoring the performance of a reduced membrane has been reported [16,17]. Dynamic coupling refers to a bond that can be repeatedly formed and broken depending on the stimulus, with one typical example including a Diels–Alder (DA) cycloaddition reaction promoted by heat [18,19]. When a hydrophilic polymer or other...
functional substance is introduced onto the membrane surface using the DA reaction, thermal stimulation can decompose the covalent bond following membrane fouling, resulting in removal of both the functional substance and the foulants, thereby restoring the membrane performance [16][17]. Using this method, irreversible fouling that was not recoverable by backwashing was successfully removed, and a water permeability of 80% was recovered [16]. However, this DA-based membrane recovery method is severely limited with regard to the suitable membrane materials and applications due to the high temperatures required (i.e., >100 °C). Studies of membrane restoration following fouling are, therefore, required to develop a system that addresses the problems caused by harsh temperature conditions while maintaining the properties of the membrane. The cinnamoyl group is capable of reversible photochemical [2 + 2] cycloaddition through optical stimulation and has been studied in various ways, such as self-healing and shape memory materials [20-23]. It is expected that this photoinduced reaction will be able to replace the DA reaction and can be applied to the membrane under less severe conditions.

Thus, we herein investigated the development of a fouling-resistant microfiltration (MF) membrane via the photoreversible crosslinking of branched-polyethylenimine (b-PEI) onto the membrane through the formation of photoreversible covalent bonds between the cinnamic acid units of the crosslinked b-PEI coating. The photoresponsive layer (PRL) should impart hydrophilicity to the membrane surface, and should be introducible and removable via a photoinduced process. We then examine the anti-fouling properties of the obtained membrane, and determine the flux recovery of the PRL-coated polyvinylidene fluoride (PVDF) membrane after a photo-induced regeneration.

2. Experimental

2.1. Materials

A hydrophobic PVDF membrane with 0.1 μm pore size (VVHP04700) was purchased from Merck Millipore (Burlington, USA). Cinnamic acid (C-COOH, 99%), epichlorohydrin (EP, 99%), benzyltriethylammonium chloride (99%), b-PEI (Mn = 25,000), and LUDOX SM-30 were purchased from Sigma–Aldrich (St Louis MO, USA). Dichloromethane (99.0%), sodium hydroxide (99%), sodium chloride (99%), ethyl acetate (99.8%) and were purchased from Daejung Chemical & Metals (Gyeonggi-do, Korea). In all experiments, distilled water was used to prepare aqueous solutions and suspension.

2.2. Synthesis of photoresponsive crosslinker (C-E)

Overall synthesis scheme is subscribed in Fig. 1. C-COOH (4 g), EP (25 g), and benzyltriethylammonium chloride (0.31 g) were put into a 250-mL three-necked flask equipped with a condenser and a magnetic stirrer bar and heated at 115 °C for 2 h. Then, the mixture was cooled to 30 °C, and an NaOH 20 wt% aqueous solution (10 g) and benzyltriethylammonium chloride (0.31 g) were added. After 6 h, water (50 mL) and ethyl acetate (100 mL) were added. The organic phase was washed with an NaCl 4 wt% aqueous solution (150 mL) three times and then dried over MgSO4 and concentrated by a rotary evaporator.

2.3. Preparation of PVDF membrane with photoresponsive crosslinked PEI layer

A PVDF membrane with a photoresponsively crosslinked PEI layer (PRL-coated membrane) was prepared via dip-coating and ultraviolet (UV) treatment in an N2 atmosphere. The coating solution was prepared by blending b-PEI, C-E, and dichloromethane. The composition of the coating solution is summarized in Table 1. A PVDF membrane was immersed in the coating solution and dried for 30 min. The membrane was then UV-treated for 1 h in an N2 atmosphere. The UV irradiation was performed by installing two 15 W UV lamps (BTD-150, wavelength 350 nm) each at a distance of 6 cm and 12 cm from the sample in the metal chamber. The UV-irradiation chamber was heated to 60 °C during the irradiation.

2.4. Removal of photoresponsively crosslinked PEI layer

The photoresponsively crosslinked PEI layer was removed via UV treatment for 4 h in an N2 atmosphere. The UV irradiation was performed by installing two 15 W UV lamps (BL-450, wavelength 250 nm) each at a distance of 6 cm and 12 cm from the sample in the metal chamber. Then, the membrane was rinsed with dichloromethane. The rinsed membrane was dried using a vacuum oven.

2.5. Characterization

The chemical structure of C-COOH, EP, b-PEI, and C-E was determined using Fourier-transform infrared (FT-IR) spectroscopy (Thermo Scientific Nicolet IS1) and proton nuclear magnetic resonance (1H NMR, Bruker AVANCE-E 600) spectroscopy in CDCl3. The photoresponsive crosslinking of C-E was confirmed by UV–visible (UV–vis) spectrophotometry (PerkinElmer, Lambda 25).

The chemical structure of the PVDF membranes with the photoresponsively crosslinked PEI layer were determined using attenuated total reflectance (ATR) FT-IR spectroscopy (Thermo Scientific Nicolet iS5). The surface morphologies of the membranes were examined using field-emission scanning electron microscopy (FE-SEM; SUPRA 55VP). The water contact angle of the membranes was measured by using a contact angle measuring instrument (Biolog scientific, Attention® THETA LITE).

2.6. Membrane performance evaluation

Membrane filtration tests were performed using a 50-mL dead-end stirred cell (Amicon® 8050). Pressure was applied to the membrane cell through a pressure vessel connected to compressed nitrogen. To evaluate the change of the water flux and the separation property, a

Table 1

<table>
<thead>
<tr>
<th>b-PEI and C-E concentration</th>
<th>b-PEI (g)</th>
<th>C-E (g)</th>
<th>dichloromethane (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 wt%</td>
<td>0.25</td>
<td>0.25</td>
<td>49.5</td>
</tr>
<tr>
<td>2 wt%</td>
<td>0.50</td>
<td>0.50</td>
<td>49</td>
</tr>
<tr>
<td>3 wt%</td>
<td>0.75</td>
<td>0.75</td>
<td>48.5</td>
</tr>
<tr>
<td>5 wt%</td>
<td>1.25</td>
<td>1.25</td>
<td>47.5</td>
</tr>
<tr>
<td>10 wt%</td>
<td>2.50</td>
<td>2.50</td>
<td>45</td>
</tr>
</tbody>
</table>

Fig. 1. Schematic diagram of C-E preparation.
A rejection test for Globulin (92 kDa) was performed. The protein solution (1000 ppm) was first prepared as a feed solution and then filtrated by an ultrafiltration system at 0.6 bar. Permeate was collected in vial, and the mass of permeate was recorded every 20 s using a mass balance (CUW4200H, CAS corp.). Then, the water flux was calculated using Equation (1).

\[ J_w = \frac{V}{A \times \Delta t} \times 100 \]  

Here, \( J_w \) is the pure-water permeability (L/m²h, LMH), \( V \) is the volume of filtrated water (L), \( A \) is the effective membrane area (m²), and \( \Delta t \) is the permeation time (h). The concentration of proteins in the filtrated solution was estimated using a UV–vis spectrophotometer (PerkinElmer, Lambda 25) at a wavelength of 280 nm. The rejection ratio of each protein was calculated using the following equation.

\[ R(\%) = \frac{C_{\text{feed}} - C_{\text{permeate}}}{C_{\text{feed}}} \times 100 \]  

where \( C_{\text{feed}} \) is the protein concentration in the feed (ppm) and \( C_{\text{permeate}} \) is the protein concentration in the permeate (ppm).

2.7. Evaluation of fouling resistance

The filtration test of the neat and PRL-coated membranes was performed using a 50-mL dead-end stirred cell (Amicon® 8050). Pressure was applied to the membrane cell through a pressure vessel connected to compressed nitrogen. The pure water and silica suspension (500 ppm) was first prepared as a feed solution, and then filtrated by the ultrafiltration system at 0.6 bar. After each cycle of silica fouling, backwashing was performed at 0.6 bar for 5 min. The water flux was calculated using Equation (1). The flux recovery ratio (FRR) was calculated using the following equation:

\[ \text{FRR} = \frac{J_R}{J_0} \times 100 \]  

where \( J_R \) is the water flux of the cleaned membrane, and \( J_0 \) is the initial water flux. The reversible and irreversible fouling resistances were calculated using the following equation:

\[ R_r = \frac{J_R - J_P}{J_0} \times 100 \]  

\[ R_i = \frac{J_0 - J_R}{J_0} \times 100 \]  

where \( R_r \) and \( R_i \) are the reversible and irreversible fouling resistances,
respectively, and $J_P$ is the flux of the fouled membrane.

3. Results and discussion

3.1. Preparation of the C-E crosslinker

The photoresponsive crosslinker (C-E crosslinker) was synthesized via the reaction of cinnamic acid (C–COOH) and epichlorohydrin (EP), and the product was identified using FT-IR spectroscopy and $^1$H NMR studies. As shown in Fig. 2, the band at 1650 cm$^{-1}$ corresponding to the C–O stretching of the carboxylic acid moiety of C–COOH was shifted to 1714 cm$^{-1}$ following the reaction, confirming successful ester formation. In addition, signals corresponding to the C–C (1630 cm$^{-1}$) and epoxy moieties (910 cm$^{-1}$) were also observed, indicating the successful synthesis of the C-E crosslinker. Following UV treatment, the intensities of the C–C and epoxy signals were reduced in intensity, confirming that the photodimerization and epoxy-amine reaction had taken place. Fig. 3 shows the $^1$H NMR spectra of C–COOH, EP, and C-E, in which the main peaks from C–COOH (1, 2, 3, and 4) and EP (b, c, and d) are observed. The peak at 3.58 ppm (a) was split into two peaks at 4.5 ppm (a$'$) and 4.05 ppm (a$''$) in the case of C-E. This indicates that C–COOH and EP were successfully coupled, as depicted in Fig. 1. These results therefore confirm the successful synthesis of the photoresponsive C-E crosslinker, and that the linker reacted with b-PEI via the epoxy moiety.

3.2. Photoinduced dynamic bond formation

The reversible photo-crosslinking reaction involving dimerization of the cinnamic acid moiety was monitored by UV–vis spectroscopy, where Fig. 4a and b shows the UV–vis absorbance changes of the b-PEI-C-E coating. More specifically, the UV absorbance intensity at 280 nm decreased with 350 nm light irradiation, indicating that photoinduced crosslinking took place, and an increase in the absorbance intensity was observed upon irradiation with 256 nm light, which signified cracking of the bond. These results confirm the successful preparation of a linker capable of reversible crosslinking by optical stimulation through the cinnamic acid moiety.
3.3. Fabrication of the PVDF membrane with a photoresponsive crosslinked PEI layer

Fig. 5 shows the ATR FT-IR spectra of the membranes. Following introduction of the photoresponsive crosslinked PEI layer, the infrared band at 3300 cm⁻¹, corresponding to the N–H stretching of b-PEI, was observed in the spectrum of the PRL-coated membrane, and the band at 2870 cm⁻¹ corresponding to CH stretching, the shoulder at 1710 cm⁻¹ corresponding to C=O stretching were observed with the peaks of the neat PVDF membrane. These observations confirm the successful coating of the photoresponsive crosslinked PEI layer on the PVDF membrane surface.

The surface FE-SEM images of the neat PVDF membrane and the PRL-coated membranes are shown in Fig. 6. As indicated, the morphologies were preserved until the PEI and C-E contents in the coating solution reached 1 wt%, while above 2 wt%, agglomerates and pore clogging were observed on the membrane surface. Such changes in the pore structure are expected to affect the permeation characteristics of the membrane.
membrane.

3.4. Hydrophilicity changes in the PRL-coated membranes

Results for the water contact angle measurements of the PRL-coated membranes are shown in Fig. 7. More specifically, the contact angle of the neat PVDF membrane was 136°, and this value decreased to 57° on increasing the coating solution concentration. These results were attributed to the hydrophilicity of the b-PEI component of the coating layer, and the continuous decrease in the contact angle was also affected by the increase in the amount of coated PRL. The decrease in contact angle over time accelerated while the concentration of the coating solution increased to 5 wt%. For 5 wt% and 10 wt%, the contact angles after 40 s were the same; however, the decrease in the contact angle for 5 wt% with time was faster than that for 10 wt%. This is interpreted to be because overcoated PRL materials block the pores, and the pore water absorption rate decreases at 10 wt%. This phenomenon has also been observed in other membrane modification studies [24].

3.5. Membrane performance

Fig. 8 shows the water permeability and rejection properties of the neat PVDF and PRL-coated membranes. As the concentration of the coating solution was increased, the water permeability decreased, and the globulin rejection rate tended to increase. This reduction in the water permeability accompanied by an increase in the rejection rate can be regarded as a change in the pore size of the membrane. However, the amount of the coating layer introduced influences not only the pore size of the membrane but also the surface properties and resistance to fouling. Subsequent experiments were performed using the 2 wt% coated membrane with the least membrane performance change among the membranes with reduced initial contact angle.

3.6. Photo-induced regeneration process

Fig. 9 shows the ATR FT-IR spectra, FE-SEM images, and water contact angles of the PRL-coated membrane during the regeneration procedure. ATR FT-IR spectroscopy of the PRL-coated membrane during the photo-induced regeneration procedure are shown Fig. 9a. The band at
3300 cm\(^{-1}\), corresponding to the N–H stretching and the shoulder at 1710 cm\(^{-1}\), corresponding to C=O stretching of the PRL, disappeared following the photoinduced removal process, which was attributed to detachment of the PRL. These N–H stretching band and shoulder reappeared after the recoating of the PRL via coating and UV treatment with 350 nm light. This indicates the successful detachment and recoating of the PRL on the PVDF membrane via photoreversible crosslinking reactions.

The surface morphology of PRL-coated membrane during the photoinduced regeneration process were then observed using FE-SEM (Fig. 9b). As indicated, the aggregates on the PRL-coated membrane surface disappeared after the removal process and reappeared after recoating. This indicates that the PRL could be detached and recoated by photostimulation. Fig. 9c shows the change of water contact-angle of the membranes during the photo-induced regeneration process. The water contact angle of the PRL-coated membrane was 113°, and this value increased to 132° after detachment of the PRL. This contact-angle result was similar to a neat PVDF membrane, indicating that the surface of the PVDF is exposed. Regeneration of the hydrophilicity through recoating of the PRL then gave a water contact angle of 107°. These changes in hydrophilicity during the photoreversible coating process provide clear evidence of the peeling and sticking of the PRL through photoresponsive crosslinking, and so our results indicate that a photoresponsive membrane was successfully prepared via photoreversible crosslinking of the PRL.

3.7. Evaluation of fouling resistance

Fig. 10 shows the result of filtration tests on the neat PVDF membrane and the PRL-coated membrane using a 500 ppm silica colloidal aqueous suspension. The water flux of the neat PVDF membrane and PRL-coated membrane decreased to ~10% of the initial flux after silica suspension filtration. After backwashing for 5 min, the neat PVDF membrane recovered 38% of the initial flux. The PRL-coated membrane showed better fouling recovery performance, the FRR achieved by backwashing was 45%. In addition, the \(R_r\) values of the PRL-coated membrane showed an increase of ~33%, while the \(R_{ir}\) values showed a decrease of ~55%. These results indicate that the PRL coating effectively enhanced the cleaning efficiency due to its hydrophilic nature. However, in the second cycle after washing, when only backwashing was used, the membrane exhibited a water permeability slightly lower than that in the first cycle, even for the PRL-coated membrane, likely due to accumulated irreversible fouling. The use of continuous membranes was accompanied by a steady increase in irreversible membrane contamination that was not removed by backwashing. In contrast, following the detachment and recoating of the PRL via the
photoreversible process, $R_p$ of the PRL-coated membrane decreased to 23%, and the FRR reached 77%, whereas $R_0$ of the neat PVDF membrane increased to 74%, and the FRR was only 16%. The recovery of the water flux for the PRL-coated membrane was therefore attributed to removal of the adsorbed silica particles on the membrane surface, which was not detached during backwashing. This was because the adsorbed particles were removed on the membrane surface with the PRL. These results show that the MF membrane coated with the photoreversible cross-linked layer enhanced the water-treatment efficiency by improving the irreversible fouling removal rate.

4. Conclusion

We herein reported the successful development of a stimuli-responsive polyvinylidene fluoride (PVDF) microfiltration (MF) membrane with a photoreversible crosslinked layer. To achieve this, a photoresponsive linker was synthesized using cinnamic acid and epichlorohydrin, and a polyethylenimine layer (PRL) was coated onto a PVDF membrane using the linker. The combined results of Fourier transform infrared spectroscopy, proton nuclear magnetic resonance spectroscopy, ultraviolet–visible spectrophotometry, and field emission scanning electron microscopy showed that the photoresponsive linker was successfully synthesized and that the PRL was coated onto the PVDF MF membrane via photoreversible crosslinking. In addition, the PRL-coated membrane exhibited hydrophilic surface properties in addition to a high fouling resistance, and recovered the water flux >45% of the initial flux after backwashing. In contrast, the neat membrane recovered the water flux only <38% of the initial flux after backwashing. Furthermore, the photoinduced regeneration process yielded a FRR of 77%, even after third cycle. These results are of importance as they indicate new type of membrane modification technology for the preparation of smart anti-fouling membranes.

CRediT authorship contribution statement

Taeseen Yun: Conceptualization, Methodology, Validation, Investigation, Writing - original draft. Seung-Yeop Kwak: Conceptualization, Methodology, Writing - review & editing, Supervision, Project administration, Funding acquisition.

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References


