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Anti-biofouling enhancement of a polycarbonate membrane with functionalized poly(vinyl alcohol) electrospun nanofibers: Permeation flux, biofilm formation, contact, and regeneration tests

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ABSTRACT

In this study, benzyl triethylammonium chloride (BTEAC)-functionalized poly(vinyl alcohol) (PVA) nanofibers were fabricated via electrospinning and deposited on a commercial polycarbonate (PC) membrane (f-PVA/PC membrane) in order to enhance the anti-biofouling activity of the membrane. Permeation flux, biofilm formation, contact, and regeneration tests were performed to evaluate the anti-biofouling potential of the f-PVA/PC membrane against bacteria, including *Klebsiella pneumoniae*, *Pseudomonas aeruginosa*, *Staphylococcus aureus,* and *Escherichia coli*. The permeation flux test showed that the normalized flux of the f-PVA/PC membrane was retained at 1.0 after filtration of 500 mL of the bacterial solution (*K. pneumoniae*), whereas the fluxes of the PC and PVA/PC membranes decreased to 0.57 and 0.84, respectively. In the biofilm formation test, the number of biofilm cells on the f-PVA nanofibers (*P. aeruginosa* = 4.21–4.98 log colony-forming unit (CFU), *S. aureus* = 3.74–4.39 log CFU) was less than those on the PVA nanofibers (*P. aeruginosa* = 5.68–6.89 log CFU, *S. aureus* = 4.72–5.82 log CFU). The contact test demonstrated that mortality rates (contact time = 60 min) on the f-PVA/PC membrane (*K. pneumoniae* = 94.08%, *S. aureus* = 99.99%, *E. coli* = 92.30%) were greater than those on the PC membrane (*K. pneumoniae* = 73.75%, *S. aureus* = 62.41%, *E. coli* = 76.80%). Fluorescence microscopy images illustrated that the population of red (dead) bacterial cells on the f-PVA/PC membranes was greater than that on the PVA/PC membrane. The regeneration test indicated that the f-PVA/PC membrane retained its anti-biofouling activity during regeneration and reuse over six cycles with mortality rates of 93.82–96.29% (*K. pneumoniae*), 74.27–85.15% (*S. aureus*), 91.68–95.19% (*E. coli*), and 94.94–96.90% (mixed-strain bacteria). The results demonstrated that the f-PVA nanofibers could enhance the anti-biofouling potential of the membrane through both anti-adhesive and anti-bacterial surface modifications.

1. Introduction

Polycarbonates (PCs) are thermoplastic polymeric materials containing carbonate groups (−O−(C=O)−O−). They are used to fabricate microfiltration membranes due to their excellent chemical resistance, high mechanical strength, and good thermal stability [1,2]. PC membranes are widely used in water filtration and wastewater treatment [3–8]. The fouling behavior of PC membranes has been examined by numerous researchers [9–15]. Ferrando et al. [16] employed confocal scanning laser microscopy to observe the fouling of PC membranes by bovine serum albumin conjugated with fluorescein and ovalbumin conjugated with Texas red. Choi et al. [6] examined the fouling behavior of PC membranes in a submerged membrane bioreactor treating municipal wastewater. Zator et al. [17] studied the fouling characteristics of PC membranes in response to foulants such as protein (bovine serum albumin) and polysaccharide (dextran) along with the effects of a chemical cleaning agent on the removal of foulants from the membrane surfaces. Dizge et al. [18] performed cross-flow microfiltration tests to investigate the biofouling of PC membranes by a biological suspension obtained from activated sludge wastewater treatment system.

Biofouling of polymeric membranes is a major obstacle in the application of membrane technology to water and wastewater treatment. Biofouling occurs through colonization and growth of biologically-active organisms, causing the formation of biofilms on the membrane surfaces [19]. Membrane biofouling results in permeate flux decline,

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more frequent chemical cleaning, membrane lifespan reduction, and an increase in operation costs [20,21]. In order to reduce membrane biofouling, polymeric membrane surfaces have been modified through surface grafting of macromolecular chains, deposition or entrapment of nanoparticles, and protective layer coating of hydrophilic polymers or surfactants [22].

Poly(vinyl alcohol) (PVA) is a synthetic polymer with a chemical formula of $[CH_2CH(OH)]_n$. PVA has been used by several researchers for modification of polymeric membranes due to its hydrophilicity and excellent chemical/thermal stability [23–25]. Brink and Romijn [26] have pretreated polysulfone ultrafiltration membranes with PVA to reduce membrane fouling by whey protein. Li and Barbari [27] have coated cellulose membranes with PVA hydrogels to prepare thin-gel composite ultrafiltration membranes and test the fouling behavior of the composite membranes in response to bovine serum albumin. Na et al. [28] prepared thin-film composite (TFC) membranes through modification of polyacrylonitrile (PAN) and poly(vinylidene difluoride) (PVDF) membranes with PVA and examined the anti-fouling characteristics of the TFC membranes using proteins such as pepsin and bovine serum albumin. Du et al. [29] modified PVDF flat sheet membrane surfaces with PVA to improve the fouling resistance of the membranes. Recently, electrospinning has been used to fabricate PVA-based hydrophilic electrospun nanofibers and composite nanofibrous membranes [30]. For instance, Wang et al. [31] fabricated ultrafiltration composite membranes through deposition of a hydrophilic PVA nanofiber layer on PAN nanofibrous membranes to enhance water flux and anti-biofouling. However, studies related to the deposition of functionalized PVA nanofibers on PC membranes for anti-biofouling enhancement are scarce.

In our previous studies [32,33], a PVA solution was mixed with benzyl triethylammonium chloride (BTEAC) as an antimicrobial agent and electrospun into functionalized PVA (f-PVA) nanofibers, which were shown to be effective in inhibiting bacterial growth on antibacterial tests. In the present study, BTEAC-functionalized PVA nanofibers were fabricated through electrospinning and deposited on a commercial PC membrane (f-PVA/PC membrane) in order to enhance the anti-biofouling activity of the membrane. Permeation flux, biofilm formation, contact, and regeneration tests were performed to evaluate the anti-biofouling potential of the f-PVA/PC membrane against bacteria, including *Klebsiella pneumoniae*, *Pseudomonas aeruginosa*, *Staphylococcus aureus*, and *Escherichia coli*.

2. Materials and methods

2.1. Preparation and characterization of the f-PVA/PC membrane

A commercial PC membrane (0.22 μm, Whatman, Maidstone, UK) was used as the raw membrane. PVA (99% hydrolyzed, molecular weight = 85,000–124,000) and BTEAC ($C_6H_5CH_2N(Cl)(C_2H_5)_3$) were purchased from Sigma Aldrich (St. Louis, MO, USA). In order to obtain the f-PVA/PC membrane, electrospinning was performed at room temperature using an electrospinning system (ESP200/ESP100, NanoNC, Seoul, Korea) with the following conditions: flow rate of 1 mL/h, tip-to-collector distance of 15 cm, and applied voltage of 15 kV. Based on our previous studies [32,33], a BTEAC-PVA solution was prepared by mixing a PVA solution (8 wt%) with 2.6% BTEAC. The BTEAC-functionalized PVA electrospun nanofibers were deposited on a PC membrane fixed to a rotating cylinder (diameter = 9 cm, speed = 1000 rpm) on a negative terminal. In order to gain the water stability of the electrospun nanofibers through crosslinking, the f-PVA/PC membrane was heat-methanol treated under the following conditions: heat treatment = 20 min at 150 °C, methanol treatment = 24 h) [33]. For comparison, a PVA/PC membrane was also prepared following the same procedures mentioned above without BTEAC.

The morphology and thickness of the f-PVA/PC membrane was measured by a field emission scanning electron microscope (FESEM, Supra 55VP, Carl Zeiss, Oberkochen, Germany). The characteristics of the PC, PVA/PC, and f-PVA/PC membranes were compared using various techniques. The tensile properties of the PC membrane and f-PVA nanofibers were measured with the universal testing machine (Instron 4467, Instron, Buckinghamshire, United Kingdom). The membrane samples were cut into the size of 10 mm × 40 mm. Stretching speed was 5 mm/min with the load cell of 20 N and the gauge distance of 10 mm. The mean and maximum pore sizes of the membranes were determined using a capillary flow porometer (CFP-1500AE, Porous Materials Inc., Ithaca, NY, USA). The porosity (ε) was determined by gravimetric method using the following equation [34].

$$\varepsilon(\%) = (m_w - m_d) \times 100/(\rho_w A l) \quad (1)$$

where m_w is the weight of the wet membrane, m_d is the weight of the dry membrane, ρ_w is the water density, A is the effective area of the membrane, and l is the membrane thickness.

The permeation fluxes of the membranes were determined at room temperature using a dead-end filtration system (transmembrane pressure = 70 kPa). Both pure (deionized) water and a bacterial solution (*K. pneumoniae* ATCC 4352, ~ 10^5 colony-forming unit (CFU)/mL) were used in the permeation flux tests. The permeation flux (J) was estimated based on the following relationship:

$$J = V/(S \times t) \quad (2)$$

where V is the total permeation volume (= 500 mL), S is the total permeation area (m^2), and t is the total permeation time (h). From the permeation flux tests, normalized fluxes of the PC, PVA/PC, and f-PVA/PC membranes obtained from permeation flux tests were obtained. In addition, FESEM was used to take images of *K. pneumonia* on the surfaces of the PVA/PC and f-PVA/PC membranes after filtration was performed.

2.2. Evaluation of the anti-biofouling activity of the f-PVA/PC membrane

First, a single-species biofilm formation test was performed to evaluate the anti-biofouling activity of the functionalized PVA nanofibers following the method described in literature [35]. In this test, *P. aeruginosa* ATCC 15442 and *S. aureus* ATCC 6538 were used as biofilm forming bacteria [36,37]. A stationary phase culture of bacteria (5.70 log CFU) was added to 5 mL of a sterilized Luria–Bertani (LB) media solution containing 0.01 g of PVA and f-PVA nanofibers. After 24, 48, and 72 h incubation at 37 °C, the nanofibers were removed from the medium to enumerate the planktonic cells present in the aqueous solution by inoculating on nutrient agar plates (incubation = 37 °C for 24 h). In order to enumerate the biofilm (sessile) cells using the spread plate technique, the nanofibers were rinsed gently in sterile deionized water and soaked in 1 mL of a NaCl solution (0.85%). The nanofibers were then vortexed at the highest setting for 30 s using a vortex mixer (Vortex Genie 2, VWR Scientific, Radnor, PA, USA) and sonicated for 30 s using an ultrasonic bath (Powersonic 420, Hwashin Technology Co., Seoul, Korea). These procedures were performed twice to disrupt the biofilm cells formed on the nanofiber surface.

The anti-biofouling activity of the f-PVA/PC membrane was evaluated by contact test using bacterial solutions of *K. pneumoniae*, *S. aureus*, and *E. coli* ATCC 11105 in a dead-end filtration system (transmembrane pressure = 0.7 bar). First, 100 mL of a solution containing 7.13–7.98 log CFU of each bacterium was filtered through the filtration system equipped with the PC, PVA/PC, and f-PVA/PC membranes (surface area = 11.34 cm^2), resulting in the loading of bacteria on the membrane surfaces. After the desired contact times (0–60 min), bacteria were recovered from the membrane surfaces by vigorously rinsing the membranes with a sterile phosphate-buffered saline (PBS) solution. Viable cells were enumerated by inoculation on a nutrient agar plate. The mortality rate (M, %) of bacteria on the membrane surface was calculated as follows: