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Preparation and application of patterned hollow-fiber membranes to membrane bioreactor for wastewater treatment

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A B S T R A C T

Hollow-fiber membranes have been widely used in membrane processes for water and wastewater treatments, but membrane fouling in commercialized hollow-fiber membranes still remains a challengeable task to be solved. In this study, we introduced patterned morphology to the membrane surface of a polyvinylidene fluoride (PVDF) hollow-fiber module using a lithographic method. Two types of patterned hollow-fiber (PHF) PVDF membranes (prism and pyramid) were prepared respectively, and their anti-biofouling characteristics were tested in a membrane bioreactor (MBR) for wastewater treatment. PHF membranes with high pattern fidelity were fabricated under the pressurized injection of the non-solvent for phase inversion. The PHFs showed not only higher water flux due to the increase of the effective membrane surface, but also enhanced anti-fouling property in comparison to a non-patterned hollow-fiber membrane. The effect of the PVDF concentration and non-solvent injection rate were also investigated on the morphology and pattern fidelity of PHF membranes.

1. Introduction

Over the last few decades, hollow-fiber membranes have been extensively used in membrane processes for water and wastewater treatments. One of the advantages of hollow-fiber membranes over flat-sheet membranes lies in high membrane surface area per a given module volume, leading to high module packing density [1,2]. However, membrane fouling, a critical problem limiting the lifespan of membranes, allows no exceptions to the hollow fiber module [3–7].

Recently, along with the development of lithographic technology, novel approaches to fouling reduction have been developed by adopting patterns on the membrane surface. In the series of studies reported by Culfaz et al., micro-structured UF hollow-fiber membranes were prepared using a patterned spinneret [8–12]. They observed reduced fouling and thus higher water productivity of the micro-structured membranes because the initial deposition rate on the fins of the micro-structure was much lower than that in the grooves between the fins. This result was attributed to the shear-induced migration from high-shear region of the fins to low-shear region of the grooves. Even though the micro-structured membranes had good potential for mitigating membrane fouling, however, the method to form patterns on the membrane surface was inadequate to prepare diverse patterns because the patterns on the membrane surface were embedded by converting the patterned spinneret.

In order to fabricate diverse patterns on the membrane surface, Won et al. modified the conventional method and developed a modified immersion precipitation method to relieve the formation of a dense layer at the solvent and non-solvent interface, that is, the opposite side of the patterned surface [13]. They successfully prepared prism- and pyramid-patterned membranes and demonstrated that the patterned membranes effectively mitigated the deposition of microbial cells in a membrane bioreactor (MBR) for wastewater treatment. They also showed a patterned surface on a membrane could increase pure water permeability in comparison to a non-patterned membrane due to the increase in actual area of the membrane with a patterned surface. The preparation method in their study, however, was not directly applicable to a hollow-fiber membrane surface, but was limited to a flat sheet membrane surface.

It would be desirable to fabricate diverse patterned hollow-fiber membranes that would gain the merits of both the hollow-fiber membrane and the patterned surface. The aim of this study was to develop patterned hollow-fiber (PHF) membranes with multidirectional patterns in order to enhance actual membrane surface area per projected area and to alleviate membrane fouling. Prism and pyramid patterns were introduced in an outside-in

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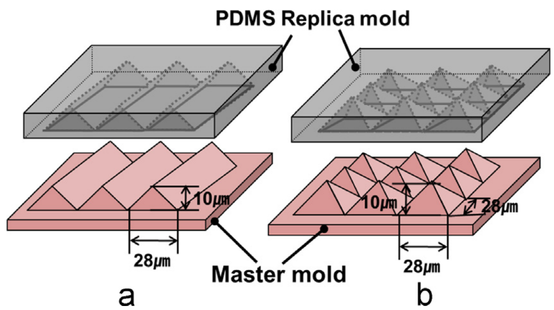

Fig. 1. Schematic diagrams of replicating (a) prism and (b) pyramid patterns from master molds to PMDS replica molds.

hollow-fiber membrane surface. It was also investigated how parameters such as polymer concentration and non-solvent injection rate would affect the pattern fidelity and macro-void fraction of PHF. Finally, pure water flux and anti-fouling effects were tested with the PHF membranes compared with a non-patterned hollow-fiber membrane. Particularly, the latter was conducted in a membrane bioreactor (MBR) for wastewater treatment.

2. Materials and methods

2.1. Preparation of master and replica molds

Polyvinylidene fluoride (PVDF) and dimethylformamide (DMF) (Sigma-Aldrich Korea, Republic of Korea) were used as membrane material and solvent, respectively. Master molds with prism and pyramid patterns were fabricated by photolithography (Nanopatterning Organic Devices Laboratory in Seoul National University, Republic of Korea). As the master molds could swell on contact with organic solvents such as DMF, replica molds were prepared separately (Fig. 1). The replica molds were prepared with polydimethylsiloxane (PDMS) using the PDMS pre-polymer and crosslinking agent (Sylgard 184 kit, Dow Corning, USA). A commercialized cylindrical polyester braid (Mitsubishi, Japan) was used as a support layer for the PHF membranes. The braid had an internal diameter of 0.9 mm and a thickness of 0.45 μm. Commercial polyethylene terephthalate (PET) film (Kolon industries, Inc., Republic of Korea) and commercial drinking straws with an internal diameter of 5 mm were used to fix the replica molds in a cylindrical shape.

2.2. Fabrication of patterned hollow-fiber membranes

PHF membranes were prepared with the process shown in Fig. 2 after the PVDF solution had been prepared in advance by dissolving PVDF pellets in DMF at 60 °C for 6 h and then at room temperature overnight for complete mixing. The concentration of the resulting PVDF solution ranged from 10% to 25% as a mass percentage. The patterned PDMS replica mold was rolled up with PET film and inserted into the straw. Next, a braid was positioned as a support layer in the center of the rolled mold. An empty space between the PDMS replica mold and braid was filled with the PVDF solution prepared previously. After that, one end of the braid was clamped, and deionized water as non-solvent was injected into the lumen of the braid to induce the phase inversion of the PVDF solution. The injection rate was changed from 5 to 40 L/min. The coagulation was completed in a water bath overnight. Finally, a PHF membrane was acquired by removing the straw, PET film and PDMS replica mold.

2.3. Calculation of pattern fidelity

As shown in Fig. 1, the prism-patterned master mold had a width of 28 μm and a height of 10 μm for a cross section of one prism, while the dimensions of the pyramid patterns were 28 μm × 28 μm × 10 μm. In soft lithography, the degree of pattern transferring from a master mold to a replica mold is often evaluated by pattern fidelity [14,15]. The definition of pattern fidelity is the ratio of pattern length in a replica mold to that of a master mold [16]. However, this definition of pattern fidelity is applicable only to one-directional patterns such as a simple line pattern, while the pyramid and prism patterns in this study are two dimensional objects. As the fidelity based on two dimensions of a finalized PHF membrane and corresponding replica mold would be more reasonable, the width and height fidelities were defined as follows and the average values of each fidelity were calculated as [16]:

$$\text{Width fidelity} = \frac{\text{Width of pattern in } a \text{ PHF membrane}}{\text{Width of pattern in } a \text{ replica mold}}$$

$$\text{Height fidelity} = \frac{\text{Height of pattern in } a \text{ PHF membrane}}{\text{Height of pattern in } a \text{ replica mold}}$$

2.4. Analysis of membrane surface morphology and pore size

The morphology of the PHF membranes was observed using a scanning electron microscopy (SEM) (JSM-6701F, Jeol Korea Ltd., Republic of Korea). To obtain cross-sectional images, a piece of a PHF membrane was immersed in liquid nitrogen and then fractured. The fractured sample was attached to a metal mount and sputter-coated with gold–platinum by using a sputtering machine (Cressington 108 auto, Cressington, UK). Two-dimensional macro-void fractions within the membrane cross-section area were calculated by using an imaging software program (Image J, 1.46r, US National Institutes of Health, USA).

The pore size distribution of a PHF membrane was measured using a mercury porosimeter (AutoPore VI 9500, Micromeritics Instrument, USA). A weighed amount of the membrane was introduced into a chamber filled with mercury. Then, pressure was increased to fill the micropores of the membrane with mercury. By monitoring the volume change of the mercury and the corresponding pressure, the pore size distribution of the patterned hollow-fiber membrane was obtained.

2.5. Analysis of membrane filtration performance

The pure water flux of the patterned and non-patterned hollow-fiber membranes was evaluated under various pressures of 20, 30, 40, and 50 kPa after pre-compaction with distilled water at 50 kPa for 3 h.

Patterned and non-patterned hollow-fiber membranes were tested by being immersed at the same time in a laboratory-scale membrane bioreactor (MBR) with an 18-L working volume, shown in Fig. 3. The effective membrane surface area of each membrane was 2.4×10^{-3} m^2. Activated sludge in the MBR was taken from a wastewater treatment plant (Tancheon wastewater treatment plant, Republic of Korea). Mixed liquor suspended solid in the MBR was 8000–9000 mg/L, and hydraulic retention times and sludge retention times were maintained at 13 h and 40 d, respectively, by using a maintaining membrane module made of commercialized polyethylene membranes (Econity Co., Ltd., Republic of Korea). The MBR was operated at a constant flux of 10 L/(m^2 h). Detailed operating conditions and the composition of the synthetic wastewater are shown in Tables S1 and S2 in the supporting information.

3. Results and discussion

3.1. Factors affecting the morphology and pattern fidelity of PHF membranes

It is known that the properties of membranes prepared with non-solvent-induced phase inversion are controlled by several parameters