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Structure design and performance study on braid-reinforced cellulose acetate hollow fiber membranes

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ABSTRACT

A novel braid-reinforced (BR) cellulose acetate (CA) hollow fiber membrane consisting of separation layer and 'hybrid' braid was reported in this study. The 'hybrid' braid containing CA and polyacrylonitrile (PAN) fiber not only provided the membrane well interfacial bonding state but also overcame the negative effect of CA fiber's swelling on membrane permeability. The influences of braid composition and CA concentration on the structure and performance of BR CA membranes were investigated. There were two kinds of interfaces between the braid and the separation layer, which were named homogeneous-reinforced (HMR) interface and heterogeneous-reinforced (HTR) interface. Taking into account both interfacial bonding state and membrane permeability, the best ratio of the fibers in the braid was 2/1(CA/PAN). Increased CA concentration brought about reduced permeate flux and increased protein rejection. The BR CA membranes exhibited excellent anti-fouling property with flux recovery rates higher than 80%. The tensile strength of BR CA hollow fiber membranes varied from 16.0 MPa to 62.9 MPa by adjusting the braid composition. The BR CA membrane showed similar performance with the commercial hydrophilic polyvinylidene fluoride (PVDF) hollow fiber membrane during the filtration of milk solution, and the flux could be recovered by chemical cleaning.

1. Introduction

Membrane technology had grown with cellulosic materials [1]. Cellulose acetate (CA), the most important derivative of natural cellulose, had played an important role in membrane separation because of its good film forming performance [2,3] and relatively low cost [4]. The merits of the CA membranes were inert to proteins [5] i.e., a high recovery from a filtrate, and a high flux, which made them better suitable for dairy wastewater treatment. Water was used throughout all steps of the dairy industry, including cleaning, sanitization, heating, cooling, and floor washing; naturally the industry's need for water was huge [6]. As we known, the industrial dairy waste contained a high concentration of organic material such as proteins, which had high levels of chemical oxygen demand (COD), total Kjeldahl nitrogen (TKN), and high concentrations of suspended solids (SS) [7]. Through CA membrane filtration, the wastewater could be reused partially or followed by deep filtration.

Most CA hollow fiber membranes were prepared by a dry–wet phase inversion method [8–11], where the poor mechanical property limited their application in engineering practice, especially in the membrane bioreactor (MBR). The hollow fiber membrane used in the submerged MBR was easy to be damaged and broken by the disturbance of the aerated airflow or a back-washing process [12]. Therefore, it required the hollow fiber membrane with high mechanical property.

Plenty of researches had been employed to improve the mechanical properties of hollow fiber membranes. The relatively simple and effective method was coating a separation layer on the high-strength hollow tubular braid. Zenon Environmental Inc. [13] produced a reinforced semipermeable membrane involving a tubular braid microporous support coated on its outer surface with a thin tubular asymmetric polymer semipermeable film. Kolon Industries, Inc. [14] developed a braid-reinforced (BR) hollow fiber membrane which included a reinforced material of tubular braids and a resinous thin film coated on the surface of the reinforced material. However, such a hollow fiber membrane had some drawbacks that the surface layer was easily peeled from the tubular braid due to thermodynamically incompatibility between the porous membrane and reinforced fiber [12]. The higher interfacial bonding strength between the porous membrane and the reinforced braid was desirable because of the techniques of aeration and anti-washing in the filtration process.

Comparing with above-mentioned heterogeneous-reinforced (HTR) hollow fiber membranes, homogeneous-reinforced (HMR) hollow fiber membrane that contained the same materials in the surface layer and the reinforced layer had good interfacial bonding

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state. Zhang et al. [12,15] prepared the HMR polyvinylidene fluoride (PVDF) hollow fiber membranes through a concentric circles coating process, where the porous PVDF hollow fiber membrane prepared by melt spinning and stretching process was used as the matrix membrane. Similarly, the HMR polyvinyl chloride (PVC) hollow fiber membranes were fabricated by Liu et al. [16,17]. During the preparation of HMR membranes, the coating solutions would infiltrate into the porous matrix membrane, which induced some negative effects, such as swelling and dissolving. The swelling and dissolving of the matrix membrane could provide the excellent interfacial bonding strength after the solidification of the HMR membranes. However, these effects would also reduce the permeability of the HMR membranes; Therefore, the pre-wetting process was helpful but complicated [17].

Based on the good interfacial bonding state of HMR hollow fiber membranes, homogeneous braid reinforced CA hollow fiber membrane was prepared using an HMR method, which CA solution was coated on the outer surface of the CA braid and the membrane was formed through a non-solvent induced phase separation (NIPS) process [18]. However, the CA fibers in the braid were likely to be swollen and adhered together, which would reduce the membrane permeability. Inspiration by advantage and disadvantage of the HMR method mentioned above, the idea of combining the HMR method and an HTR method with a 'hybrid' braid was formulated. The hybrid effect was most often found in the organic–inorganic hybrid membranes and the hybrid fiber reinforced composites. In the hybrid membranes, the unique hybrid features had been developed to change porous structure and enhance the properties of membrane [19]. Unlike the hybrid membrane, a better positive hybrid effect of fibers was found on the composite materials reinforced by carbon fiber and glass fiber [20]. In this study, the HMR method and the HTR method were combined together to reduce the weaknesses of each of them and to achieve the best result.

The BR CA hollow fiber membrane was fabricated by coating CA solution on the 'hybrid' braid in the present study. The 'hybrid' braid was prepared by the two-dimensional braided technique using CA filaments as the homogeneous fiber and PAN filaments as the heterogeneous fiber. The mechanical property and permeation performance of the BR CA hollow fiber membranes with various fiber ratios in the braid and various CA concentrations in the coating solution were investigated, which gave a new approach to obtain BR CA membrane with desirable performance. Finally, a BR CA hollow fiber membrane module was applied in the filtration of skim milk solution comparing with a hydrophilic PVDF hollow fiber membrane module produced by the NIPS method. The effluent characteristics, the flux, membrane fouling and cleaning processes were studied respectively.

2. Experimental

2.1. Materials

Cellulose acetate (CA, Mw=60,000) was purchased from Wuxi Chemical Industry Research & Design Institute Co., Ltd. (China). N, N-dimethylacetimide (DMAc, 98%), poly (ethylene glycol) (PEG, Mw=2000) and sodium hypochlorite (NaClO) solution were obtained from Tianjin Kermel Chemical Reagent Co., Ltd. (China). Bovine serum albumin (BSA, Mw=68,000) was provided by Beijing Solarbio Science & Technology Co., Ltd. (China). Cellulose acetate filament (CA fiber) was provided by SVACO (H.K.) Ltd. (China). Polyacrylonitrile filament (PAN fiber) was supplied by Changshu Xiangying Special Fiber Co., Ltd. (China). The specification and performance of CA and PAN fiber were shown in Table 1. Skim milk was provided by Inner Mongolia Yili Industrial Group Co., Ltd. (China). The hydrophilic PVDF hollow fiber membrane (d_p=0.20 μm, prepared by NIPS method) was supplied by Tianjin Motimo Membrane Engineering & Technology Co., Ltd. (China).

Table 1
Performance comparison of CA fiber and PAN fiber.

Fiber	Specification (denier/filament)	Density (g/cm^3)	Breaking strength (MPa)	Breaking elongation (%)
CA	150D/30F	1.32	153	23.7
PAN	150D/60F	1.20	303	16.9

2.2. Membrane fabrication

The preparation process of the BR CA membranes is schemed in Fig. 1. First of all, three bundles of filament tows were combined into one filament tow (3 × 150D) with various CA/PAN ratios, and then the hollow tubular braids were prepared by the two-dimensional braiding machine using the combined tows. The BR CA hollow fiber membranes were fabricated via dry–wet spinning process. Fig. 2 shows the spinning setup [18]. In this process, the hollow tubular braids were coated with the CA solutions (70 °C) and guided through a water coagulation bath (25 °C), where the BR CA hollow fiber membranes were formed. The air-gap distance and take-up speed were set at 10 cm and 100 cm/min, respectively. The CA solutions were prepared by the blending of different compositions consisting of CA, DMAc and PEG, under constant mechanical stirring in a flask for 4 h at 70 °C. After the formation of the BR CA hollow fiber membranes, the prepared membranes were stored in water for at least 48 h to remove the residual solvents and wash out the water-soluble additive. The recipe of the coating solutions and the braids are shown in Table 2. During the following discussion about the effect of CA concentration on membrane performance, the CA12 membrane referred only to the same membrane as the M1 membrane.

2.3. Morphology observation

The morphologies of the membranes were observed using a scanning electron microscope (SEM, TM3030, HITACHI, Japan). The water contained in the samples was substituted by ethyl alcohol, t-butanol/ethyl alcohol (50/50 vol%) and t-butanol for 12 h successively. After the freeze drying, the samples were cut off by a razor blade.

2.4. Mechanical characterization

The tensile properties of the hollow fiber membranes were determined at room temperature by an Electromechanical Testing Machine (JBDL-200N, Yangzhou Jingbo, China). The gripping range and tensile rate was set at 100 mm and 100 mm/min, respectively.

The bursting strength of the hollow fiber membranes were measured by using an apparatus with nitrogen cylinder and pressure gauge.

2.5. Permeation characterization

The pore size and distribution of the freeze dried membranes were determined by using an Automatic Mercury Porosimeter (AutoPore IV-9500, Tektronix, USA).

The pure water flux (PWF) of the membranes was determined by a cross-flow batch (Fig. 3). The pressure difference across the membrane was 0.1 MPa under the condition of outside feeding.