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Enhancing the separation performance by introducing bioadhesive bonding layer in composite pervaporation membranes for ethanol dehydration[☆]



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ABSTRACT

A high performance composite membrane was prepared under the inspiration of bioadhesion principles for pervaporative dehydration of ethanol. Chitosan (CS) and polyacrylonitrile (PAN) ultrafiltration membranes were used as the active layer and the support layer, respectively. Guar gum (GG), a natural bioadhesive, was introduced as the intermediate bonding layer to improve the separation performance and stability of the fabricated CS/GG/PAN composite membranes. The contact angle of the GG layer was just between those of the CS layer and the PAN layer, minimizing the difference of hydrophilicity between the active layer and the support layer. The peeling strength of the composite membrane was significantly enhanced after the introduction of the GG layer. The effects of preparation conditions and operation conditions including GG concentration, operating temperature and ethanol concentration in feed on the pervaporation performance were investigated. The as-fabricated CS/GG/PAN composite membrane showed the optimum performance with a permeation flux of up to $804 \text{ g} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ and a separation factor higher than 1900. Besides, the composite membranes exhibited a desirable long-term operational stability.

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1. Introduction

Pervaporation is an efficient membrane process for liquid separation [1]. With great potential to solve separation problems related to various industrial processes, pervaporation is cost effective in the field of separating azeotropic and close boiling mixtures as well as being safe for handling heat-sensitive and hazardous compounds [2]. Pervaporative ethanol dehydration is the best-developed domain of the pervaporation application processes [3]. The core of pervaporation processes is the pervaporation separation membrane, which requires high permeability, good selectivity and sufficient mechanical strength. Composite membranes composed of a thin active layer formed usually on a chemically different asymmetrical porous support layer have been intensively investigated and utilized in practical applications to improve pervaporation performance especially to increase the permeation flux. The structural integrity is always the key problem to be overcome before the commercialization of composite membranes. The difference

of the surface hydrophilicity between the active layer and the support layer leads to an uncoordinated swelling behavior, which occurs inevitably during the pervaporation process. Segregation of the neighboring layers would be caused when interfacial stress exceeds their maximum interfacial adhesion [4]. Binding the active layer with the support layer via covalent bonds can solve this problem [5,6], but chemical specificity is inevitably required, thus limiting its wide application [7]. Constructing a bonding layer is an effective alternative approach to improve interfacial compatibility by anchoring the active layer onto the support layer [8].

Adhesives are prime choices for the fabrication of bonding layer. Adhesives can be classified [9] into natural bioadhesives [10,11] and artificial synthetic adhesives [12,13] according to their origins [9]. Natural adhesives show advantages over the synthesized adhesives in cost, availability, adhesion strength and durability [14]. Recently, inspired by bioadhesive mechanism, employing natural adhesives into composite materials preparation has become an innovative method. 3, 4-l-Dihydroxyphenylalanine (DOPA) is the key compound in the formation of marine adhesive proteins found in many marine organisms such as mussels [15]. It is a good representative of bioadhesives with unique adhesion ability via self-polymerization and has been used in preparing composite materials. Xu *et al.* [16] prepares a DOPA-coating composite membrane to immobilize heparin where DOPA strongly adhere to the wet surfaces it resides. Yang and co-workers [17] exploit the application

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of DOPA-incorporated ceramic and polymer scaffold in bone regeneration to achieve biocompatibility and bioactivity simultaneously. Derivatives of DOPA such as dopamine have also been utilized as adhesives. Jiang's group [7,10,18,19] fabricate composite membranes with preferable separation performance by using dopamine to form adherent coatings through spontaneous self-polymerization.

Exploitation of bioadhesives extracted from plants is now burgeoning [20–22]. Guar gum (GG), a non-ionic, biodegradable and biocompatible polymer [23] derived from the seeds of guar plant *Cyanopsis tetragonolbus* [24], has been employed as viscosity builder and water binder in many commercial applications such as pharmaceutical, food, textile, explosive and petroleum. GG is constituted by β -D (1 \rightarrow 4)-mannopyranose backbones linked with α -D-galactopyranose units via (1 \rightarrow 6) linkages [25]. It is a neutral polysaccharide with sufficient adhesivity and forms viscous colloidal dispersions in cold water [26]. A novel bone adhesive composed of sodium alginate and GG has been used in comminuted fracture cure [27]. To our best knowledge, such plant-extracted bioadhesives have not been applied in the fabrication of composite separation membranes yet.

Chitosan (CS) is a well-known membrane material in pervaporative dehydration of alcohols for its high water-permselective performance [28]. CS-based composite membranes are of great potential for industrial practice. In this study, CS and porous polyacrylonitrile (PAN) substrate are used as the active layer and the support layer, respectively. Composite membranes bearing a three-layer structure are fabricated by inserting GG bonding layer between the CS layer and the PAN layer to strengthen the interfacial stability. The pervaporation performance of the as-fabricated composite membranes is investigated.

2. Experimental

2.1. Materials

The flat-sheet polyacrylonitrile (PAN) ultrafiltration membranes ($M_w = 100000$) were purchased from Shanghai MegaVision Membrane Engineering & Technology Co. Ltd. (Shanghai, China). Guar gum (GG) was purchased from Hubei Longtai Bio-Pharmaceutical Co. Ltd. (Hubei, China). Chitosan (CS) with 90.2% *N*-deacetylation degree was purchased by Jinan Haidebei Marine Bioengineering Co. Ltd. (Jinan, China). Ethanol, glutaraldehyde (50%) and acetic acid were purchased from Tianjin Guangfu Science and Technology Development Co. Ltd. (Tianjin, China). All chemicals were of reagent grade or higher, and were used without further purification. The water used in all experiments was treated by the Millipore Milli-Q purification system.

2.2. Membrane preparation

Sequential casting and spin coating was performed to prepare CS/GG/PAN composite membranes. PAN ultrafiltration membranes with a size of 9 cm \times 9 cm which have been fixed on glass plate by cellulose tape, were used as the support layers after fully dried in air. The GG solutions were prepared by dissolving different amounts of GG (mass fraction of 0.05%, 0.10%, 0.50%, 1.00%, 3.00%, respectively) in demineralized water. CS was dissolved into acetic acid solution (2%, by mass) at 353 K to prepare the 2% CS aqueous solution. After cooled, 2.5% (by mass) glutaraldehyde (GA) solution was added to allow crosslinking and then conducted a 1 h stir. The GG solution was spin-coated upon the surface of the PAN support membrane, dried at room temperature and labeled as GG(X)/PAN where X indicated the concentration of GG solution. Finally, the GA precrosslinked CS solution was cast onto the GG/PAN membrane, dried at room temperature and denoted as CS/GG(X)/PAN composite membrane. For comparison, CS/PAN membranes without GG layer were also prepared by casting the GA precrosslinked CS solution directly onto the PAN membrane under the same conditions.

2.3. Pervaporation experiments

The experimental apparatus applied in all the pervaporation experiments were exhibited in our previous study [10,12,13]. The effective membrane area was about 25.6 cm². The downstream pressure was maintained at 0.3 kPa and the feed flow rate was about 60 L \cdot h⁻¹. The permeate vapor was collected in liquid nitrogen-cold traps. The concentrations of ethanol in both the feed and the permeate were estimated by HP4890 gas chromatography (GC).

The primary evaluation indices of membrane separation performance were the separation factor (α) and permeation flux (J). The separation factor was calculated by Eq. (1),

$$\alpha = \frac{P_W/P_E}{F_W/F_E} \quad (1)$$

where P_W and P_E were the mass fraction of water and ethanol in permeate, respectively; F_W and F_E were the mass fraction of water and ethanol in feed, respectively. The permeation flux (J , g \cdot m⁻² \cdot h⁻¹) was defined by Eq. (2),

$$J = \frac{M}{A \times t} \quad (2)$$

where M (g) was the mass of the permeate in operating time t (h) and A (m²) was the effective membrane area. All the experiments were conducted using a 90% (by mass) ethanol aqueous solution at 353 K except otherwise indicated.

2.4. Membrane characterization

Field emission scanning electron microscope (FESEM) (Nanosem 430) was used to observe the interfacial configuration of the composite membranes. The Fourier transform infrared (FT-IR) spectra for each layer of the CS/GG/PAN composite membrane were recorded on a Nicolet-560 spectrophotometer to identify the structural completeness. The contact angles of the PAN support membrane, the GG bonding layer and the CS active layer were measured by a contact angle goniometer (JC2000C Contact Angle Meter, Powereach Co., Shanghai, China) at room temperature. The interfacial adhesion strength of the composite membrane was acquired via T-peel adhesion strength test using a Micro-Uniaxial Fatigue Testing system (MUT-1020, CMC).

3. Results and Discussion

3.1. Membrane characterizations

3.1.1. FESEM study

The cross-section morphologies of the GG(1)/PAN and CS/GG(1)/PAN composite membranes were observed by FESEM. Fig. 1(a) and (b) showed that indistinct demarcation existed at the GG-PAN interface and the CS-GG interface. The exact thickness of GG layer could hardly be detected due to pore penetration and good compatibility of the two layers via hydrogen bonding between the hydroxyl groups ($-\text{OH}$) on GG and cyan groups ($-\text{CN}$) on PAN. It could also be measured from Fig. 1(b) that the total thickness of CS layer and GG layer was only about 220 nm. The good compatibility of the CS layer with the GG bonding layer was due to the formation of hydrogen bonds between the hydroxyl groups ($-\text{OH}$) on GG and the hydroxyls groups ($-\text{OH}$) and the amine groups ($-\text{NH}_2$) on CS. The schematic structure and the interfacial interaction of the CS/GG/PAN composite membrane were tentatively depicted in Fig. 2.

3.1.2. FT-IR analysis

The FT-IR spectra for PAN, GG(1)/PAN, CS/GG(1)/PAN membranes were presented in Fig. 3. The spectrum of PAN showed the characteristic

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