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High performance ceramic hollow fiber supported PDMS composite pervaporation membrane for bio-butanol recovery

Ziye Dong, Gongping Liu, Sainan Liu, Zhengkun Liu, Wanqin Jin*

State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemistry and Chemical Engineering, Nanjing University of Technology, 5 Xinmofan Road, Nanjing 210009, PR China

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ABSTRACT

In this work, ceramic hollow fiber supported polydimethylsiloxane (PDMS) composite membranes were developed by dip-coating PDMS layer on the surface of macroporous ceramic hollow fiber support. By controlling the properties of polymer solution and ceramic hollow fiber, high-quality ceramic hollow fiber supported PDMS composite membranes were fabricated for pervaporation (PV) recovery of bio-butanol. It was found both the viscosity of PDMS dip-coating solution and pore size and structure of ceramic support played critical roles in determining the microstructures, the mass transport and the PV performance of PDMS composite membrane. The optimized composite membrane with defect-free PDMS layer and low transport resistance of support showed a total flux of 1282 g/m^2 h and separation factor of 42.9 for 1 wt% *n*-butanol–water mixtures at temperature of 40 °C during 200 h continuous operation. In addition, the membrane PV performance and stability in acetone–butanol–ethanol (ABE) fermentation broth were investigated. The results showed the PDMS composite membrane exhibited high and stable performance for butanol recovery from ABE systems. Compared with literatures, our work demonstrated that the ceramic hollow fiber supported PDMS composite membrane could be a competitive PV membrane for recovering organic compounds from fermentation broth to produce renewable biofuels.

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1. Introduction

Pervaporation (PV) is a novel molecular separation process based on the selective permeation of membranes [1]. Compared with the traditional separation method for liquid mixtures, PV has many outstanding advantages, such as high selectivity, low energy consumption and flexible operation condition. This process is particularly appropriate for solvents dehydration, separation of organic–organic mixtures and organic recovery or removal from dilute aqueous solution [2,3].

As a main part of pervaporation membranes, the organophilic (hydrophobic) pervaporation membranes were attracted increasing attention recently. Polydimethylsiloxane (PDMS), which has been known as the most commonly used hydrophobic membrane material, was studied extensively in several areas including volatile organic compounds (VOCs) removal [4], gasoline desulphurization [5] and especially in the recovery of biofuel (ethanol or butanol) [6–11] from aqueous solution or fermentation broth. In order to meet the requirement of practical application, most PDMS membranes were made as composite membranes, which consist of a dense separation layer and a porous support. So far, the widely used supports are the polymeric flat-sheet porous membranes, such as cellulose acetate (CA) [12], polyethylene (PE) [13], polysulfone (PS) [14], polyethersulfone (PES) [15], polyetherimide (PEI) [16], poly(vinylidene fluoride) [17] and polyacrylonitrile (PAN) [18].

Our group has developed a series of tubular ceramic-supported polymer composite membranes by depositing various polymeric separation layers such as PDMS or PVA on the macroporous ceramic support [19]. This kind of membranes exhibits high pervaporation performance in the application of biofuels production [6,8,20], solvent dehydration [21], gasoline desulphurization [5] and coupling process [11]. Besides, many other works [4,22–24] also exhibited excellent performance of porous ceramic supports compared with polymer substrates. Organic/inorganic composite membranes have been shown to be a promising type of composite membranes for pervaporation application, owing to the chemical, mechanical and thermal stabilities and low transport resistance of ceramic support.

Ideally, the support for pervaporation composite membrane should only enhance the membrane mechanical strength without adding transport resistance. However, recent studies have illustrated the non-ignorable effects of support on microstructures and performance of composite membrane [13,25,26]. Bruijn et al. [25] reported that the transport resistance of support might strongly

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* Corresponding autor. Tel.: +86 25 83172266; fax: +86 25 83172292.
E-mail address: wqjin@njut.edu.cn (W. Jin).

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Table 1
Preparation conditions of hollow fiber supports.

No.	Al_2O_3 powders 0.7/1/2 (μm)	Dope composition (wt%)				Sintering temperature (°C)
		Al_2O_3	NMP	PVP	PES	
S1	100/0/0	60	28	2	10	1400
S2	10/50/40	60	28	2	10	1450
S3	10/20/70	60	28	2	10	1450

determine the permeation flux PV composite membranes by analyzing the pervaporation data in literatures. Moreover, the selectivity could also be affected by the supports, which was demonstrated by Li et al. [13]. They designed a tri-layer PDMS composite membrane and found that both the separation factor and total flux can be enhanced by the addition of a porous hydrophobic PE layer between the PDMS and rigid substrate.

Recent works indicated that the configurations of the support could also play an important role in improving the PV performance of composite membrane. The hollow fiber-supported NaA or MFI zeolite membranes showed much higher flux than the conventional tubular zeolite membranes [27,28]. In addition, the low transport resistance hollow fiber membranes have many other advantages such as high-packing density, cost-effective and a self-support structure compared with other configuration of supports. So far, only PS [29] and PEI [30] hollow fiber supports were used to prepare PDMS composite membranes for pervaporation of alcohols aqueous mixture. Unfortunately, both of these PDMS composite hollow fiber membranes did not exhibit expected higher performance than that of the reported PDMS composite flat or tubular membranes for separation of ethanol–water mixture. Furthermore, to ensure the formation of defect-free polymer separation layer, the pretreatment of ceramic support or the repetition of coating process is also critical for preparing polymer/ceramic hollow fiber composite membranes, even though some of the treatment processes is relatively complex [4,22]. For preparing PV composite hollow fiber membranes, it is still a challenge to directly form a thin and defect-free polymer separation layer on hollow fiber support.

In this work, therefore, we developed a type of ceramic hollow fiber supported PDMS composite membrane by dip-coating PDMS polymer solution on macroporous ceramic hollow fiber supports. The membrane microstructures and PV performance were optimized by varying the pore size and structure of the support and meanwhile controlling the viscosity of polymer casting solution. The separation performances of ceramic hollow fiber supported PDMS composite membranes were systematically evaluated by pervaporation separation of *n*-butanol from *n*-butanol/water mixtures under various feed temperature and concentration. Furthermore, the prepared PDMS composite membrane was applied for PV of acetone–butanol–ethanol (ABE) model solution, fermentation broth and a long stability experience.

2. Experiment

2.1. Materials

α,*ω*-Dihydroxypolydimethylsiloxane (PDMS), with average molecular weight of 5600, was purchased from Sigma-Aldrich. Tetraethylorthosilicate (TEOS), *n*-heptane, dibutyltin dilaurate, polyvinyl pyrrolidone (PVP), N-methyl-2-pyrrolidone (NMP) and *n*-butanol were obtained as analytical reagents from Sinopharm Chemical Reagent Co., Ltd, China. Polyethersulfone (PES) was purchased from Radel A-300, Ameco Performance, USA. Al_2O_3 powders, with three different particle diameters of 0.7, 1.0 and 2.0 μm, were supplied by Shandong Xinfumeng chemical Company, China.

2.2. Preparation of membrane

2.2.1. Ceramic hollow fiber support

According to reported literature [31], ceramic hollow fibers were fabricated by phase-inversion and sintering method. Some quantity of aluminum powder, PVP and NMP were taken in a stainless steel bottle, being stirred by a stirring paddle. After the uniform suspended solution was formed, the required quantity of PES was added into the suspension solution slowly. The result polymer solution was degassed for 5 h. Then the spinning dope was extruded by variable flow pump through a spinneret into tap water with 150 mm air distance. Finally, the prepared precursor was dried at 100 °C for 12 h and sintered at high temperature to form ceramic hollow fiber, whose pore-size was determined by the bubble–pore method. By changing preparation conditions, three different kinds of ceramic hollow fibers abbreviated as S1, S2 and S3 were fabricated, respectively. The preparation conditions are given in Table 1.

2.2.2. Composite membrane

The dip-coating method introduced in our previous work [6] was employed in preparing ceramic hollow fiber supported PDMS composite membranes. The required quantity PDMS polymer and *n*-heptane were mixed uniformly in a Teflon bottle, and then TEOS and dibutyltin dilaurate were added into the solution. *n*-Heptane, TEOS and dibutyltin dilaurate were used as a solvent, a crosslinking agent and a catalyst, respectively. Polymer solution viscosity was controlled with different prepolymerization times and the details of conditions have been described in our previous work [32]. Then ceramic hollow fibers which were filled pure water immersed in the coating precursor for 60 s. After drying at room temperature for 24 h, the composite membranes were heat treated at 120 °C for 12 h. The composite membranes with supports of S1, S2 and S3 were labeled as M1, M2 and M3, respectively.

2.3. Characterization

The mean pore size and gas permeability of the hollow fiber supports were determined by the bubble–pore method. Gravimetric analysis of water entrapped in the pores of the hollow fiber walls were used to determine the volumetric porosities of the membranes. The details of the procedure have been described by reported literature [31].

The viscosities of polymer coating solution were determined by using Brookfield viscometer (DV-II+ pro, Brookfield Engineering Laboratories, USA). The determination of viscosity was worked out at 30 °C.

Attenuated total reflection Fourier transform infrared spectrum (ATR-FT-IR) spectra of pure PDMS and composite membrane were recorded in an ATR-FT-IR spectrophotometer (AVATAR-FT-IR-360, Thermo Nicolet, USA) with the range of 4000–600 cm^{-1}. Thirty-two scans were accumulated with a resolution of 4 cm^{-1} for each spectrum. The surface and cross-section morphology of composite membranes and the thickness of PDMS layer were characterized by field emission scanning electron microscopy (FE-SEM, Hitachi-4800, Japan) which contained with Energy Dispersive X-Ray Spectroscopy (EDX) equipment. The FE-SEM was operated at 5 kV and 10 μA. Fouled membrane samples after the PV experiment for spent fermentation broth were fixed and dried procedure following previous work [11]. All the membrane samples (fresh and fouled) were gold-coated by a sputter and scanned under FE-SEM at 50, 200, 5000 magnification times.

2.4. Pervaporation experiment

A pervaporation experiment was carried out by using a home-made apparatus, which is introduced in our previous work [5].

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