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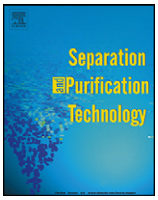

Short communication

Preparation of dual-layer cellulose/polysulfone hollow fiber membrane and its performance for isopropanol dehydration and CO_2 separation

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ABSTRACT

Dual-layer cellulose/polysulfone (PSf) hollow fiber membrane used for isopropanol (IPA) dehydration and CO_2 separation was prepared by using co-extrusion technique with a triple-orifice spinneret. N-methylmorpholine-N-oxide monohydrate (NMMO·H_2O) was selected as the cellulose solvent since it can dissolve cellulose through a purely physical process. Scanning electron microscopy (SEM) images show that there is no obvious delamination between the inner and outer layer and no obvious defect can be seen in the outer skin of the fiber. In order to find out the advantage of novel prepared dual-layer membrane over homogeneous cellulose membrane, tests including isopropanol dehydration by pervaporation and CO_2 separation were carried out. For pervaporation experiments, the effects of operation conditions including feed concentration and operation temperature on pervaporation (PV) performance were investigated systemically. The results showed that similar with the flat cellulose membrane, the permeation flux increased obviously with the increase of both water concentration in feed and operation temperature. Under all tested conditions, water contents in permeate maintained higher than 99.90 wt.%, and it reached a maximum value of 99.98 wt.% with a water content of 5 wt.% in feed at 25 °C. Moreover, the water-swollen dual-layer cellulose/PSf hollow fiber membrane showed much higher gas permeation rate and comparable selectivities of CO_2/H_2, CO_2/N_2 and CO_2/CH_4. The CO_2 permeance of dual layer cellulose/PSf hollow fiber membrane was ∼3 GPU, which was five times higher than that of single-layer cellulose hollow fiber membrane. In a word, the performance, especially the permeation rate of new developed dual layer cellulose/PSf hollow fiber membrane was greatly improved by its reduced separation layer, and this could definitely increase its potential for later practical application.

1. Introduction

As a linear polysaccharide cellulose is the most abundant regenerating organic material with outstanding properties and a variety of useful applications [1]. However, strong hydrogen bonding between the hydroxyl groups makes cellulose a highly crystalline, insoluble polymer that degrades before melting. Thus, traditionally, cellulose membrane is made by converting purified cellulose to a soluble derivative, such as xanthate or cuprammonium cellulose complex, and then precipitating from its coagulation bath. Cellulose derivatives such as cellulose acetate (CA), cellulose triacetate (CTA), and cellulose nitrate (CN) are routinely and extensively used as membrane materials [2,3]. However, chemical treatments always cause serious environmental problems as well as irreversible damages to cellulose structure and deteriorate its excellent resistant properties to acid, alkali and organic solvents [4–7]. N-methylmorpholine-N-oxide (NMMO) can dissolve cellulose directly without the formation of the cellulose complex or its derivatives. The use of NMMO as the new solvent for cellulose opens up new perspectives for cellulose membrane development. Using this new dissolving process, creative researches have been carried out and interesting results were reported in recent years including both gas separation and liquid separation [8–14].

Membrane-based pervaporation (PV) is a promising process in the separation of liquid mixtures because of their economic advantage, ability to separate isomeric and azeotropic mixtures and being safe for handling heat-sensitive and hazardous compounds. As one of the important solvents and cleansers, isopropanol (IPA) is widely used in petroleum industry, semi-conductor industry, liquid crystal display industry and medicine. Recycling of IPA from IPA/water mixtures is necessary for both environmental and economical consideration. Otherwise, IPA and water can form an azeotropic mixture at 87.4 wt.% of IPA concentration and the separation of these mixtures by conventional methods such as distillation is difficult and uneconomical. PV process is a good option for dehydration of IPA aqueous solution and was studied widely. In a recent article [15], we have developed this novel cellulose membrane for pervaporation dehydration of isopropanol and it exhibited very high

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selective performance. However, it is challenging to fabricate asymmetric cellulose membranes for pervaporation and gas separation because cellulose membranes will shrink seriously during naturally drying process [15].

At the same time the gas separation, especially CO_2 separation performance of cellulose hollow fiber membranes were carried out, and interesting results were obtained [10]. It was reported that under fully "water-swollen" state, cellulose membrane shows very high separation of CO_2 over nitrogen, methane and even hydrogen. While unfortunately caused by its dense membrane structure, the gas permeation rates of cellulose hollow fiber membranes are very limited, thus in order to improve the gas permeation performance of cellulose membrane, researchers must find a way to effectively reduce the its separation layer. Usually asymmetric structure would be the first choice for separation layer reducing, while restricted by its low dissolving ability in NMMO and severe structure shrinkage in drying process, it looks like impossible for us to fabricate an asymmetric cellulose hollow fiber membrane. In this case composite membrane with cellulose as the separation layer will inevitably be the only one and best choice. Investigations on co-extrusion dual-layer hollow fiber membranes offered a new method to fabricate asymmetric membrane for those materials that cannot be prepared to asymmetric membranes by traditional technologies [16–26]. The dual-layer hollow fiber membranes prepared by co-extrusion method remain all the advantages of single-layer hollow fiber membranes: high active surface area to volume ratio, low resistance, self-supporting structure, facility for fabrication and the ability to be operated at high pressure. In this study, simultaneous co-extrusion through a triple-orifice spinneret was employed to fabricate the dual-layer cellulose/polysulfone hollow fiber membranes. Both its pervaporation dehydration of isopropanol and CO_2 separation properties were investigated.

2. Experimental

2.1. Materials

The cellulose with polymerization degree of about 1000 and polysulfone with polymerization degree of 3500 were purchased from Sigma Company. They were pre-dried at 80 °C for 8 h to constant weight before use. N-methylmorpholine-N-oxide monohydrate ($NMMO{\cdot}H_2O$) was purchased from Acros Company.

All other chemical reagents in this work were analytically pure and supplied by Tianjin Kermel Chemical Reagent Development Center.

2.2. Preparation dual-layer hollow fiber membrane

Firstly, $NMMO{\cdot}H_2O$ in a 500 mL flask was heated to 100 °C with an oil bath. Then n-propyl gallate (0.5 wt.% of cellulose, as an antioxidant to avoid decomposition of cellulose) and dried cellulose with known weight were added. The mixture was stirred vigorously until a homogenous polymer solution with a cellulose concentration of 6 wt.% was obtained. Polysulfone solution was prepared by mixing polysulfone and N,N-dimethylacetamide (DMAc) in a three-neck flask and stirred at 40 °C until the polymers were dissolved completely. The homogeneous dopes were poured into doper jars and degassed for at least 24 h. Details of the spinning conditions are listed in Table 1. After the coagulation, the membrane was taken out of the coagulant and washed with running tap water for 24 h to remove the solvent and then stored in de-ionized water for 1 day to leach out the residual solvent. Then the prepared dual-layer hollow fiber membranes were natural dried for 24 h in the air. The morphology of the resulting hollow fiber membranes was observed by scanning electron microscopy (SEM) (KYKY-2800).

Table 1

Spinning conditions of dual-layer asymmetric hollow fiber membranes.

Parameters	Value
Outer dope composition	6 wt.% cellulose in $NMMO{\cdot}H_2O$
Outer dope temperature (°C)	98
Outer dope pressure (MP)	0.2
Inner dope composition	23 wt.% PSf in DMAc
Inner dope temperature (°C)	35
Inner dope pressure (MP)	0.15
Bore fluid composition	75 wt.% DMAc in de-ionized H_2O
Bore fluid flow rate (ml/min)	0.05
Spinning temperature (°C)	75
Air gap distance (mm)	20
Coagulation	H_2O
Coagulation temperature (°C)	25
Room temperature	19
Relative humidity	45
Dope flow rate ($m\,min^{-1}$)	1.88
The dimension of the spinneret	1.15 mm (o.d. of the outer orifice), 0.95 mm:0.85 mm (o.d.:i.d. of the middle tube) 0.40 mm:0.25 mm (o.d.:i.d. of the inner tube)

2.3. Pervaporation experiments

Dehydration experiments of isopropanol were carried out at temperatures between 25 and 65 °C, and a feed water concentration between 5 and 20 wt.%. At the permeate side a vacuum was maintained (less than 500 Pa) by a cascade of a liquid nitrogen cold trap and a vacuum pump. The feed mixture with a predetermined composition was circulated from a thermostated tank through the shell side of the hollow fiber and the permeate vapor came out from the lumen side. The permeation rate was determined gravimetrically by weighing the permeate sample collected over a given period of time using an analytical balance, and the permeate composition was analyzed using a gas chromatography (GC7890II, Shanghai Techcomp Instrument, China) equipped with a thermal conductivity detector. The feed circulation rate was kept substantially high to minimize the effect of concentration polarization. The permeation rate and permeate composition were tested periodically until a steady state was reached.

Membrane performance in PV experiments was studied by calculating the total flux (J) and separation factor (α) using the following equations:

$$J = \frac{W}{At} \tag{1}$$

$$\alpha = \frac{P_{\text{water}}/P_{\text{IPA}}}{F_{\text{water}}/F_{\text{IPA}}} \tag{2}$$

where W is the mass of the permeate (kg), t is the permeation time (h), A is the membrane area (m^2); where F_{water} and F_{IPA} are the weight fractions of water and iso-propanol in the feed and P_{water} and P_{IPA} are those in permeate, respectively.

2.4. Gas permeation experiments

Each test modules comprised of a bundle of ten hollow fibers. One end of the fiber bundle was sealed with epoxy resin, whereas another end was glued onto an aluminum holder with epoxy. After hydrated in water to form water-swollen cellulose layer, the prepared module was fixed into a stainless steel pressure cell for gas permeation measurement. The pure gas was fed through a humidifier. The humidifier was filled with stainless filler and the gas was saturated with water vapor after sufficiently contacting with de-ion water. Feed gas was fed at the shell side, while the permeate gas was collected at the bore side of hollow fiber membranes. The permeate side was kept at atmospheric pressure. The permeation test setup was controlled at 35 °C. The test system was running under selected conditions for at least 2 h for stabilization at beginning of