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Roll-coating of defect-free membranes with thin selective layer for alcohol permselective pervaporation: From laboratory scale to pilot scale

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HIGHLIGHTS

- PDMS/PSf composite membranes were scaled up using a roll-coating method.
- The thickness of the selective layer was successfully controlled by roll-coating.
- The membrane shows robust PV performance during the pilot-scale evaluations.

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ABSTRACT

Pervaporation offers advantages over traditional separation processes, but there is still lack of scale-up methods and manufacturing systems to easily and controllably obtain the defect-free membranes. In this work, poly(dimethylsiloxane)/polysulfone composite membranes were scaled up using a roll-coating method. The thickness of the poly(dimethylsiloxane) separation layer was successfully controlled on polysulfone substrate by roll-coating different layers. The membranes are used for separating ethanol/water mixtures. The pervaporation experiments were performed (i) in the laboratory using a radial cell with a membrane area of 0.0028 m^2; (ii) in a large cell using a plate-and-frame module with membrane area of 0.36 m^2; and (iii) in a pilot plant located at an industrial site, with a plate-and-frame module and total membrane area of 2.16 m^2. On-site operations showed that the flux of 1000–1200 g m^{-2} h^{-1} with 60–65 wt% ethanol in permeate was achieved by the pilot-scale pervaporation facility, which demonstrated technical feasibility for industrial application.

1. Introduction

In recent years, biofuel produced by biological fermentation has been prompted as a green alternative to fossil fuels [1,2]. However, due to the inhibition of high bio-alcohol concentration in the fermentation broth, the preparation of biofuel is impeded. Therefore, in situ removal and enrichment of bio-alcohol from the fermentation broth is a key issue to improve the process efficiency [3]. In order to achieve this goal, pervaporation (PV) has been widely studied, because of its energy efficiency and harmless to microorganisms [4]. However, efficient stripping of volatile organic compounds (VOC) from aqueous is more challenging than dehydration [5–6]. Previous studies by various authors have identified poly(dimethylsiloxane) (PDMS) with high separation factors for alcohol–water separations. Despite offering advantages in selectivity, dense PDMS membranes show limitations in flux and mechanical strength that limit their application. Over the past decades, the coating of a very thin top layer on a porous substrate has been applied to increase PV flux. Four main multilayer strategies have been explored: (i) dip coating [1,2], (ii) spin coating [3,4], (iii) spray coating [7,8] and (iv) doctor blading [9] at a lab scale. For example, Osorio-Galindo et al. [10] prepared PDMS-PMHS/PEI composite membranes by doctor blading. The membrane area is 78.54 cm^2 and the selective thickness is 50 μm. This composite membrane performed a separation factor of 3.7 and a flux of 270 g m^{-2} h^{-1} at 5 wt% ethanol feed concentration (40 °C). Lee et al. [11] fabricated PDMS/PEI hollow fiber composite membranes by spinning. The membrane area is 903 cm^2 and the selective thickness is 0.07 μm. The composite hollow fiber membrane was stable over the long-term (about 160 days) with an ethanol permeation flux of a total flux of 231–252 g m^{-2} h^{-1} and a separation factor of 7–9. More recently, we also prepared PDMS/PSf membranes by dip-coating with the area of 28 cm^2 and the selective-layer thickness of 1 μm [1]. The PDMS/PSf composite membrane performed a separation factor of 8.5 and a flux of 828.6 g m^{-2} h^{-1} at

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5 wt% ethanol feed concentration (60 °C). However, the manual operation involved in dip-coating brings about many uncontrollable human factors, leading to instability and low productivity of the membrane performance. For such dense composite membranes, the mass transport across the membranes is governed by a solution-diffusion mechanism. Therefore, the thickness of selective layer is one of the most important controllable factors to achieve high permeate production (flux). However, it is relatively difficult to obtain thin defect-free selective layer. Therefore, it is necessary to seek for a facile low-cost scale up fabrication approach to meet industrial requirements.

Besides membrane fabrication, it is also challenging thing to move from laboratory to pilot plant operations, since increased membrane area requirement, quantity of feedstocks, time for execution, analytical facilities, technical issues, and operating personnel are associated with such scale up. Key steps in the development of a membrane process for a separation of interest to move from lab scale to pilot plant include: (i) setting membrane performance targets; (ii) perform a proof-of-concept test with a small scale test; (iii) testing the membrane in a pilot-plant module; (iv) showing stable long-term operations [12]. These arguments in favor of plat-form composite membranes as their modules have been scaled up industrially.

In the present work, we firstly designed a facile roll-coating system in pilot scale and prepared poly(dimethylsiloxane)/polysulfone (PDMS/PSf) membranes by a roll-coating method (Fig. 1) which has great potential for economical scale up. The thickness and optimized operation parameters of the membranes were investigated for improving separation performance and obtaining a stable pervaporation process. Scanning electron microscopy (SEM) was used to understand the microtopographical changes the membrane surfaces as a function of processing changes to correlate with the PV performance. The effect of feed composition, permeate pressure and feed temperature on transmembrane flux and separation characteristics has been investigated to optimize the performance. The stability of the membranes was monitored for 1000 h. To the best of our knowledge, such a detailed insight in up-scaling of PDMS membranes for pervaporation has not been reported yet.

2. Experimental

2.1. Materials

PDMS with a viscosity of 2550 mPa s was purchased from China Bluestar Chengrand Chemical Co. Ltd. (China). Tetraethyl silicate (TEOS) and ethanol were obtained from Beijing Chemical Company (China). Dibutyltin dilaurate, *n*-heptane and *n*-butanol were supplied by Tianjin Fuchen Chemical Reagents Company (China). In our experiments, all reagents were of analytical grade and were used without further purification.

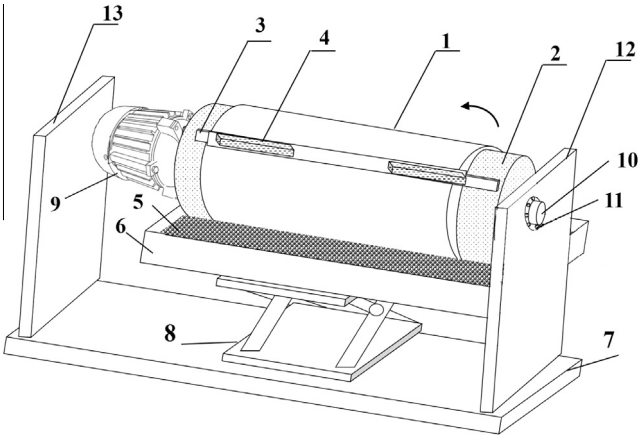

Fig. 1. The apparatus of roll-coating system for the preparation of composite membranes. 1 – PSf substrate, 2 – roller, 3 – slot, 4 – snaps, 5 – polymer solution, 6 – polymer solution tank, 7 – base, 8 – lifts, 9 – motor, 10 – shaft, 11 – gear, 12 – support plate (a), 13 – support plate (b).

2.2. Preparation of lab scale and pilot-scale PDMS/PSf composite membrane

The PSf substrate was soaked for 24 h using pure water. The pores of the supports were filled with water to minimize penetration of the coating polymer solution into the pores; and allowed to dry for 30 min to remove excess water on the support surface before roll-coating the polymer solution [2]. PDMS was dissolved in *n*-heptane to form a 10 wt% PDMS solution. After the polymer solutions were stirred at room temperature for 1 h, the cross-linking agent TEOS and the catalyst dibutyltin dilaurate were added into the polymer solution (W_{PDMS}:$W_{n\text{-heptane}}$:W_{TEOS}:$W_{dibutyltin\ dilaurate}$ = 1:10:0.1:0.005), and the resulting mixture was continuously stirred for 3 h [2]. Air bubbles trapped in the polymer solution were removed by degassing at 100 Pa for 10 min. The polymer solution was poured into a feed tank, which was placed under a roller, and roll-coated on the surface of the PSf support with lab scale or pilot-scale roll-coating system (Fig. S1). To produce defect-free membranes, removal of the solvent at room temperature for 12 h and subsequent curing in the oven at 80 °C for 12 h was used to fabricate the PDMS/PSf composite membranes in a low humidity enclosure.

2.3. Membrane characterization

SEM photographs of PDMS/PSf membranes were taken using a scanning electron microscope (Hitachi-4300, Japan). The membranes were fractured in liquid nitrogen. Membrane surfaces and liquid nitrogen fractured cross section were coated with a conductive layer of sputtered gold to make it conductive. X-ray diffraction (XRD) experiments were conducted on an X-ray diffractometer (D8 ADVANCE, Bruker/AXS, Germany).

2.4. Pervaporation experiments

The specification of the composite PDMS/PSf membrane module is given in Table 1.

2.4.1. Laboratory test

The pervaporation performance of the membrane was evaluated using a pervaporation apparatus fabricated in our laboratory [13,14]. The selected ethanol concentration in the feed solution was ~10 wt% and the experiments were conducted at 60 °C. The

Table 1
Specification of the PDMS/PSf composite pervaporation membranes.

Membrane	Specification	Dimension
Laboratory cell	Coating layer	1–60
	Thickness of selective layer	1–5 μm
	Number of sheets	1
	Effective area of module	0.0028 m^2
Pilot plant in lab	Coating layer	30
	Thickness of selective layer	~4 μm
	Number of sheets	6
	Effective area of module	0.36 m^2
Pilot plant in factory	Coating layer	30
	Thickness of selective layer	~4 μm
	Number of sheets	36
	Effective area of module	2.16 m^2