Journal of Industrial and Engineering Chemistry 32 (2015) 305–312

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

journal homepage: www.elsevier.com/locate/jiec

Development of bacterial cellulose/alginate nanocomposite membrane for separation of ethanol–water mixtures

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ARTICLE INFO

Article history:
Received 4 July 2015
Received in revised form 24 August 2015
Accepted 13 September 2015
Available online 25 September 2015

Keywords:
Pervaporation
Bacterial cellulose
Alginate
Nanocomposite
Membrane

ABSTRACT

A bacterial cellulose (BC) hydrogel was modified via impregnation by diffusion of sodium alginate and cross-linking with calcium chloride solution. BC/alginate (BCA) membranes were configured, characterized, and used for pervaporation of mixtures of ethanol–water. BCA membranes were more hydrophilic with a more dense structure and showed improved affinity toward water and considerable enhancement of pervaporation performance. At a permeate pressure of 10 mmHg, the BCA membrane impregnated with 3% (w/v) alginate solution separated water from ethanol in the feed solution (95%, w/w) with 429.9 selectivity, and a total permeate flux of 33 g/(m^2 h).

Introduction

Ethanol is mainly produced by biomass fermentation. The obtained crude ethanol, 8–10% (w/v) [1], is then purified by distillation to produce approximately 95% (w/v) ethanol, which is a nearly azeotropic mixture of ethanol and water [2–4]. Additional separation of water from this binary mixture is required. Separation techniques such as adsorption, pressure-swing distillation, extractive distillation, azeotropic distillation and novel composites have been developed and proposed for separation and purification applications [5–13]. However, some of these techniques are complex and have high energy consumption and operating costs [5–9]. Pervaporation, a membrane-based technique, is an effective separation method, because it has high selectivity, relatively low energy consumption, mild operating conditions, low waste generation, and is environmentally friendly [2]. The selective membrane used in pervaporation is an important factor in the separation performance. Hydrophilic membranes such as poly(vinyl alcohol) [14–16], polyamide [17,18], chitosan [5,19–22], and alginate have been used to remove water from this ethanol–water azeotropic mixture. Alginate is highly hydrophilic because of its carboxyl and hydroxyl groups, but it has poor stability and mechanical strength in aqueous solutions [23–28]. On the other hand, hydrophobic polymeric membranes composed of polydimethylsiloxane (PDMS) were reported for the pervaporative separation and concentration of ethanol and butanol in fermentation broths [29,30].

The nanomaterial bacterial cellulose (BC), commonly known by the name of "Nata-de-coco" is synthesized by *Acetobacter xylinum*; it has several advantageous properties such as high chemical stability, heat resistance, and water-retention capacity, and good mechanical properties [31–33]. BC mechanical strengths and Young's moduli of 200–300 MPa and 15–35 GPa, respectively, have been reported [31]. The use of BC and composite BC membranes for dehydration of ethanol solutions has been investigated. A permeate flux greater than 100 g/m^{2}h was achieved, but the sorption selectivities at ethanol concentrations ≥90% (v/v) were quite low (<4.0) [34,35]. Alginate is also considered as a promising material for composite membrane fabrication for the separation of ethanol–water mixtures. Alginate is a highly hydrophilic polymer which possesses high affinity toward water molecules, due to the presence of carboxylic and hydroxyl groups. Alginate is not soluble in most organic solvents. It is non-toxic, inexpensive and easy to use. Alginate hydrogel matrix can be easily cross-linked by

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http://dx.doi.org/10.1016/j.jiec.2015.09.004
1226-086X/

electrostatic crosslinking with divalent ions such as calcium ions. However, typical sodium alginate membranes possess insufficient mechanical strength for pervaporation application.

The objective of this research was to develop an effective BC–alginate (BCA) nanocomposite membrane for the separation of azeotropic ethanol–water mixtures by pervaporation. The effects of the alginate concentration (1, 2, and 3%, w/v) in the BCAs on the physical, chemical, and mechanical properties of the BCA membranes were determined. The effects of the ethanol concentration in the feed solution (70–95%, w/w) and the operating temperature (30–60 °C) on the pervaporation performances of the BCA membranes were investigated. The membrane efficiency was determined in terms of permeate flux and selectivity.

Materials and methods

Materials

A. xylinum was isolated from nata de coco. The stock culture was supplied by Pramote Tammarat, the Institute of Food Research and Product Development, Kasetsart University, Bangkok, Thailand. Sucrose, ammonium sulfate, and sodium hydroxide were obtained from Ajax Finechem Pty Ltd. (Australia), sodium alginate was obtained from Acros Organics (USA), acetic acid was obtained from Mallinckrodt Chemicals (USA), and absolute ethanol was obtained from QRec (New Zealand).

Membrane preparation

A preculture was prepared by aseptically transferring *A. xylinum* stock culture (10 mL) into 200 mL sterile coconut-water-based medium. The medium was prepared from coconut water with supplements of sucrose at 5.0% (w/v), ammonium sulfate at 0.05% (w/v) and 1.0% (v/v) acetic acid. Sterilization was performed at 110 °C for 5 min. The preculture was statically incubated at 30 ± 2 °C for 7 days. A BC pellicle was prepared by adding preculture (4 mL) to the coconut-water-based medium (75 mL) in a sterile petri dish (diameter 14 cm) and statically incubating at 30 ± 2 °C for 7 days. The obtained pellicles were washed with running water for 30 min, treated with 1% (w/v) sodium hydroxide solution for 24 h, and then rinsed with deionized (DI) water until the pH was 7. The pellicles were soaked in DI water and stored at 4 °C until use.

The BCA nanocomposite membranes were prepared by immersing BC pellicles in sodium alginate solutions of concentration 1, 2, or 3% (w/v) at 50 ± 2 °C for 5 days. The BCA pellicles were rinsed with DI water, cross-linked with 5% (v/v) calcium chloride ($CaCl_2$) for 3 h, rinsed again with DI water, and dried in ambient air for 3 days. The obtained BCA membranes are denoted by BCA1, BCA2, and BCA3.

Characterization

The BC and BCA thicknesses were measured using a thickness gauge (Mitutoyo 7301, Japan). The cross-sectional and surface morphologies of BC and BCA were examined using scanning electron microscopy (SEM; JSM-7610F, JEOL, USA) at 15 kV and magnifications of 20,000 and 10,000. Membrane samples were prepared by immersion in liquid nitrogen, immediately followed by cutting and coating with a thin layer of gold. The surface areas and average pore sizes of the membranes were determined using a Brunauer–Emmett–Teller (BET) surface area analyzer (Autosorb-1, USA). Physical adsorption of nitrogen gas was measured at 77.35 K.

The absorption capacities or swelling degrees of the BC and BCA membranes in distilled water, absolute ethanol, and ethanol–water mixtures were determined by immersing the dried membranes (dry weight W_d) in the appropriate liquid until equilibration. The liquid-hydrated membranes were weighed (W_w). The absorption capacity was calculated as

$$\text{Absorption capacity}\,(\%) = \frac{W_w - W_d}{W_d} \times 100$$

The contact angles were measured using a CAM-PLUS (USA) contact angle meter equipped with a charge-coupled device camera. A droplet (5 μL) of DI water was randomly dropped onto the dry membrane. The contact angles against five different spots were averaged.

The tensile strengths, Young's moduli, and percentage elongations at break of the membranes were determined using a Universal testing machine (Hounsfield H 10 KM, Redhill, UK). Membrane samples of area 1 × 10 cm^2 were installed; the test area was 1 × 6 cm^2. The test conditions were those described in ASTM D882. The tensile strength and break strain were reported as average values determined from at least five specimens.

The chemical properties of the composite membranes were determined using Fourier-transform infrared (FTIR) spectroscopy (Perkin Elmer Spectrum One, USA), over the wavenumber range 2000–800 cm^{-1}. Crystallinity was measured with an X-ray diffractometer (Model D8 Discover, Bruker AXS, Karlsruhe, Germany). X-ray diffraction patterns were recorded with CuKa radiation (k = 1.54 Å). The operating voltage and current were 40 kV and 40 mA, respectively. Samples were scanned from 10–40° 2θ at a scan speed of 3° min^{-1}. Profile fitting and crystallinity (%) calculations were performed with Topas version 3.0 (Bruker, AXS) software. Differential scanning calorimeter (DSC) thermograms of the membranes were performed using DSC (204 F1 Phoenix, Germany) measurements using about 10 mg of the samples over the temperature range of 25–400 °C at the heating rate of 5 °C min^{-1} under nitrogen atmosphere (30 mL min^{-1}).

Pervaporation experiments

The pervaporation set-up, which is shown schematically in Fig. 1, consisted of feed, separation, and permeate compartments. The feed compartment contained a 900 mL feed vessel equipped with a heating bar, temperature sensor, and four flat-blade disk-turbine impellers. Ethanol–water mixture feeds with ethanol concentrations of 70%, 80%, 90%, and 95% (w/w) were used. The liquid mixture in the vessel was circulated at 150 rpm and the operating temperature was controlled at 30, 40, 50, and 60 °C throughout the experiments. In the separation compartment, a prepared BC or BCA membrane of effective area 19.625 cm^2 was mounted at the bottom of the feed vessel. The permeate compartment was evacuated to various pressures, i.e., 2, 4, 6, 8, and 10 mmHg, using a high-vacuum pump (Model RV5, Edwards,

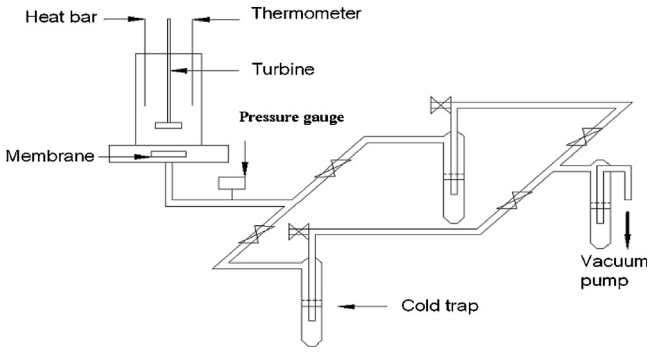

Fig. 1. Schematic diagram of pervaporation experiment set-up.