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Preparation of zein-based membranes and their pervaporation for ethanol aqueous solution

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ABSTRACT

Zein-based microspheres and membranes were prepared by phase separation. Increasing the concentration of zein in the stock solution resulted in the formation of three different kinds of zein microstructures i.e. discrete microspheres, sponge-like microsphere membranes and continuous membranes. Zein single (ZS) membrane and zein composite (ZC) membrane were developed by spin coating zein solutions onto porous asymmetric alumina tablets. Both the ZS and ZC membranes effectively removed ethanol from dilute ethanol aqueous solutions via pervaporation. The pervaporation performances of the two membranes were evaluated using different process parameters, such as operating time, ethanol feed concentration and temperature. The separation factors for the ZS and ZC membranes were 3.2 and 3.4 respectively and the permeation fluxes were 0.62 and 0.73 kg/m^2 hr respectively for a feed solution with 3 wt % ethanol–97 wt % water at 25 °C. In a ternary feed solution with 1 wt % acetic acid–3 wt % ethanol–96 wt % water, the pervaporation performances were slightly lower compared with those for the binary feed system. Single gas permeation of N_2 confirmed that the membranes were free of defects before and after pervaporation. The ZS and ZC membranes showed good hydrophobic properties and ethanol permselectivity, which can be explained by the Switch Effect.

1. Introduction

Zein is the major storage protein of corn and comprises ca. 45–50% of the protein in corn. It was first identified based on its solubility in aqueous alcohol solutions. It has nonpolar and relatively hydrophobic amino acid residues which form a structure with an α-helix conformation which is stabilized by hydrogen and disulfide bonds [1]. Its relatively high hydrophobicity, good elasticity, excellent film-forming abilities, biodegradability and anti-oxidative capabilities make zein a preferred protein source for several applications [2] and it has been studied as a novel bio-based polymeric material. For example, it has been extensively used in pharmaceuticals as an encapsulation material and as a controlled-release delivery material for drugs and vaccines [3,4]; it has also been used in the food industry for edible coatings and packing materials [5,6].

Because of its potential applications, zein's various morphologies, such as microspheres, sponge transitional states and membranes, have been studies extensively. Wang and Padua[7] investigated the effect of the concentration of zein and the ethanol–water ratio of the solvent on the morphology of evaporation-induced self-assembled microstructures. It has been proposed that zein microspheres prepared by phase separation methods could be used as drug vehicles for ivermectin, gitoxin or antigens of ovalbumin [8–10]. The scaffold structure of zein contains sponge-like pores which have been used to repair periodontal tissue defects [11]. Zein membranes which are composed of microspheres have been loaded with heparin and used to suppress platelet adhesion for cardiovascular devices [12]. Zein membranes have also been loaded with ciprofloxacin for the prevention of bacterial infection from implanted devices [13]. Incorporating phenolic compounds into zein membranes eliminated the classical problem of the membrane's brittleness and considerably increased the membranes flexibility and this improved the properties of zein membranes so they make better bioactive packaging materials [14].

Ethanol is an attractive alternative fuel because it is a bio-based resource. The fermentation of sugar, starch or cellulose to produce bioethanol is a widely used industrial process in many countries [15]. However, the resultant azeotropic mixtures, such as ethanol and water, have to be separated which is most commonly done by a conventional distillation process. However, with the advent of the necessity of reducing the energy consumption of such operations, pervaporation, a membrane separation technique, has been developed as an alternative to conventional methods, especially for the separation of azeotropic liquid mixtures [16,17]. Various hydrophobic membranes, such as polymeric membranes, zeolite membranes, zeolite-filled polymer composite membranes and organic–inorganic hybrid membranes have been investigated to extract ethanol from ethanol aqueous solutions of 3–5 wt % to 30 wt % or more by

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pervaporation [18–20]. An ethanol concentration of 3–5 wt % represents a typical ethanol concentration that is derived from a biomass fermentation process [21]. In production, a fermentation process can be coupled with a hydrophobic membrane pervaporation process. To the best of our knowledge, there have been no research projects focused on using membranes based on zein protein for the separation of ethanol from aqueous solutions.

Zein is a main and valuable co-product of the bio-ethanol industry [22], and approximately 13,000 tons of zein can be recovered when 50 million gallons of ethanol are produced [23]. As a result of its generally hydrophobic nature, zein is insoluble in water or anhydrous ethanol and is only soluble in ethanol aqueous solution in the range of 50–90%. This special solubility behavior is attributed to a high proportion of nonpolar amino acid residues and a deficiency in basic and acidic amino acids [24].

Two kinds of hydrophobic zein-based membranes, zein single (ZS) membranes and zein composite (ZC) membranes, were prepared on porous asymmetric alumina supports by a spin coating process, and their separation performances for extracting ethanol from a model biomass fermentation by pervaporation was investigated. The effect of the zein concentration in 70% (v/v) ethanol water mixtures on the structure and morphology of the membranes was also investigated.

2. Experimental

2.1. Materials and chemicals

Zein with a minimum protein content of 97% was purchased from Wako Pure Chemical Industries Limited (Japan, biochemical reagent). Commercial porous asymmetric alumina tablets were supplied by NGK Insulators Limited (Japan). All other chemicals and reagents such as anhydrous ethanol, hydrochloric acid, sodium hydroxide and acetic acid were analytical grade and were purchased from Alfa Aesar Company (Tianjin, China). Double-distilled water was used throughout the study.

2.2. Preparation of zein-based membranes

Commercially available porous asymmetric alumina tablets with a mean pore diameter of 0.1 μm were used as the membrane supports. A series of stock solutions was prepared by dispersing different amounts of zein in 50 mL of 70% (v/v) ethanol–water. After being dispersed by an ultrasonic processer (KQ-250B) for 3 min, the zein alcoholic solutions were transferred to flasks coupled with a high-speed homogenizer (HENC, C20), then vigorously sheared (10,000 rpm) for 10 min, and 50 mL of distilled water was added dropwise to the flasks during the shearing process (rate flow: 5 mL). Subsequently, the casting solvents were coated on porous asymmetric alumina tablets by spin coating. The spin coating was performed in a class 1000 clean room at 25 °C and 50% R.H. to prevent contamination by dust, which causes pinholes in the membranes. After the spin coating procedure was repeated six times, the membranes were dried at 25 °C for 12 h.

Two different kinds of zein membranes were prepared. One, labeled zein single (ZS) membrane, was cast with a solution of 100 mg zein/mL 70% (v/v) ethanol. The other, the zein composite (ZC) membrane, consisted of two layers, where the inner layer was a sponge-like film cast from a solution of 30 mg zein/mL 70% ethanol, and the outer layer was a continuous zein film cast from a solution of 100 mg zein/mL 70% ethanol.

2.3. Scanning electron microscope images

The morphology of the zein microspheres and the surfaces and cross-sections of the zein-based membranes were observed using a scanning electron microscope (SEM, XL-30 TMP). The samples were sputter-coated with a thin layer of gold to improve the electrical conductivity of the surfaces.

2.4. Sorption and diffusion of pure solvents in the membranes

The sorption levels of ethanol and water in the membranes were determined using a gravimetric method [25]. The dried membranes were cut into pieces and the dry weight and thickness of the membranes were recorded. The dry films were immersed in pure ethanol or water at 25 °C. After each time interval, the membrane was removed and blotted with tissue paper to remove the liquid remaining on the surface of the film. Next, the membrane was weighed using an electronic balance (Model JP_2-160, Chyo Balance Corporation, Japan). The sorption capacity (SC) was calculated using the weights of the swollen and the dry membrane samples and is expressed in units of grams of absorbed mixture per gram of dry membrane using the expression.

$$SC = (m_M - m_D)/m_D \quad (1)$$

where m_M and m_D are the masses of the swollen and dry membranes, both in grams, respectively.

The SC was measured until no significant weight increase was observed for the swollen membrane and this value was used as the maximum sorption capacity (SC_∞) which describes the solvent solubility in the membrane.

The diffusion coefficients of the water and ethanol in the membranes were calculated from the transient regimes of the solvent uptake history. The relative weight increase was calculated as the ratio of SC_t/SC_∞ for the period of time prior to sorption saturation. The diffusion coefficients were calculated from the Balik method using SC_t/SC_∞ versus time (t) data [26,27] and the equation:

$$t_{0.5} = 0.04919h^2/D \quad (2)$$

where $t_{0.5}$ (min) is the time at which $SC_t/SC_\infty = 0.5$, h (μm) is the thickness of the membrane and D (m^2/s) is the diffusion coefficient of solvents.

2.5. Swelling measurements in dilute ethanol aqueous solution

The swelling measurements of the two kinds of membranes were carried out by immersing the dried membranes in 0.3–5 wt % ethanol aqueous solution at 25 °C. The maximum sorption capacity of the membranes was determined by a gravimetric method by varying the concentration of the ethanol aqueous solutions [25]. In addition, the sorption of the membranes in a ternary system of 1 wt % acetic acid–3 wt % ethanol–96 wt % water was carried out following the same procedure described for the binary system.

2.6. Pervaporation measurements

Pervaporation measurements using diluted aqueous ethanol solutions of 0.3–5 wt % as the feed were carried out under various operating conditions using an apparatus described in detail in our previous work [28]. The effective membrane area was about 7–8 cm^2 and the pressure on the permeate side of the membrane was 0.1 kPa. Composition analyses of the feed and permeate were performed on a gas chromatograph (Shimadzu GC-2010). During the pervaporation measurement, the permeate solution was removed from the collection tube and analyzed every 4 h. For each feed concentration, at least 5 permeate samples were collected to ensure steady-state operation. Feed samples were also taken from the feed tank as the permeate samples were collected. The separation ability of a membrane can