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Synthesis and characterization of biopolymer based mixed matrix membranes for pervaporative dehydration

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ABSTRACT

Several blend membranes were prepared from different weight ratios of polyvinyl alcohol (PVA) and hydroxyethyl cellulose (HEC) and these unfilled membranes were crosslinked with maleic acid. In a similar way mixed matrix blend membranes were also prepared by varying weight ratio of PVA and HEC with micro and nano bentonite filler in each of these blends. These membranes were used for pervaporative dehydration of 89 wt% tetrahydrofuran (THF). Three membranes designated as UF (unfilled), MF2 (containing 2 wt% micro filler) and NF2 (containing 2 wt% nano filler) showing the best results for flux and selectivity were identified. These membranes were characterized by FTIR, UV, XRD and DTA-TG and used for separation of 80–99 wt% THF from water by pervaporation. The NF2 membrane was found to show the best results in terms of flux and separation factor.

1. Introduction

Pervaporation (PV) membranes of high separation potentials may be obtained by blending natural and synthetic polymers. Natural polymers are biocompatible and abundant in nature. Hence, these polymers are not expensive. However, it is difficult to make membrane from a pure natural polymer since most of these polymers are not soluble in common solvents and melt processing of natural polymers is also difficult because of degradation of its native structure on application of heat. On the other hand synthetic polymers possess better mechanical and thermal properties than natural polymers and these polymers can be processed to a wide range of products by melt processing or solution casting (Sionkowska, 2011). However, synthetic or man made polymers are expensive and the residual monomer, crosslinker or initiator of a synthetic polymer may also affect the separation performance of a PV membrane (Suh & Matthew, 2000). Blending of these two kinds of polymers may eliminate their respective shortcomings. Presently, PV membranes made by blending a synthetic polymer with a natural or semi synthetic polymers have been attempted by many researchers.

Cellulose or polysaccharide is natural polymer but not soluble in any solvent. Several semi synthetic polymers such as chitosan, sodium alginate, carboxymethyl cellulose, hydroxyethyl cellulose, etc., are made by chemical modification of polysaccharide or cellulose. These semi synthetic polymers may be processed to a suitable product. Blend and filled membranes of chitosan (Chanachai et al., 2000; Smitha, Dhanuja, & Sridhar, 2006; Sun, Lu, Chen, & Jiang, 2008), sodium alginate (Gao et al., 2014; Kalyani, Smitha, Sridhar, & Krishnaiah, 2006; Kuila & Ray, 2014), carboxymethyl cellulose (Chapman, Tan, Livingston, Li, & Oliveira, 2006; Wang et al., 2014; Das & Ray, 2013) hydroxyethyl cellulose (Chanachai et al., 2000; Kalyani et al., 2006; Naidu & Aminabhavi, 2005; Naidu, Sairam, Raju, & Aminabahvi, 2005) with different synthetic polymers have been reported for pervaporative separation. Thus, in the present work several membranes have been synthesized by blending polyvinyl alcohol (PVA) and hydroxyethyl cellulose (HEC). PVA has already been commercialized as hydrophilic membrane. HEC is cellulose ether soluble in water. It is compatible with wide range of water soluble polymers (Naidu, Sairam, et al., 2005; Rao et al., 2006). HEC with several hydroxy groups (—OH) in its structure is expected to improve hydrophilicity of PVA. Further, hydrophilic bentonite filler of micro and nano size was incorporated in the blend membrane. The inorganic filler not only improves the mechanical strength of the membranes but it also improves its separation potential. The incorporation of adsorptive fillers improves separation performance due to synergestic effects of molecular sieving effects, preferential adsorption and difference in rate of diffusion through organic polymer and inorganic filler (Bastani, Esmaeili, & Asadollahi, 2013). The objective of the present work was to improve hydrophilicity and mechanical strength of the PVA membrane by blending it with a hydrophilic polymer and incorporating

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inorganic fillers. In our previous works (Kuila & Ray, 2014; Das & Ray, 2013) several blend membranes were prepared and the unfilled blend showing the best results for flux and selectivity was filled with varied concentrations of micro or nano fillers. In these works composition of the polymer blends were not varied in presence of filler. However, blend composition showing the optimum results may also vary in presence of a fixed amount of filler because of polymer–filler interaction. Thus, in the present work several unfilled membranes were prepared by blending different concentrations of PVA and HEC. Similarly, several filled blend membranes with varied amounts of PVA and HEC were also prepared in presence of 2 wt% micro and 2 wt% nano fillers. The concentration of filler was kept constant at 2 wt% since in one of our previous works blend membranes containing 2 wt% filler showed the best results for flux and selectivity. In the present work these unfilled and filled blend membranes were used for pervaporative separation of THF–water mixtures. THF is an important and expensive organic solvent. It is frequently utilized in many pharmaceutical synthetic procedures because of its broad solvency for polar and nonpolar compounds. However, it is miscible with water in all proportion and it also forms an azeotrope with water. Thus, pervaporative separation of THF–water would be a better candidate since PV may be carried out at low temperature and unlike distillation no azeotrope is formed during PV separation of aqueous THF. In the present work a systematic method has been employed to find out optimum blend compositions for maleic acid crosslinked unfilled and filled blend membranes and these membranes were used for dehydration of 80–99 wt% THF.

2. Experimental

2.1. Materials

Tetrahydrofuran (THF) of analytical grade used for this study was purchased from E. Merck (India) Ltd., Mumbai. Polyvinyl alcohol (PVA) of number average molecular weight 125,000 and degree of hydrolysis of 98–99% was obtained from S.D. Fine Chemicals, Mumbai. Hydroxyethyl cellulose (HEC, viscosity average molecular weight 150,000) and maleic acid were purchased from Loba Chemie Pvt. Ltd., Mumbai and E. Merck, Mumbai, respectively and were used as obtained. Hydrophilic bentonite micro filler (API grade, residue of diameter > 75 μm or 200 mesh is 3.5%) and hydrophilic bentonite nano filler (sodium montmorilonite Na + MMT, polymer grade containing 98% montmorilonite, particle size 30–90 nm, aspect ratio 300–500, mineral's thickness 1 nm, cation exchange capacity 120 mequiv./100 g) was kindly given by Amrfeo pte. Ltd., Kolkata. These fillers were used after drying in a hot oven at 110 °C for 2 h. Deionized water, having a conductivity of 20 μS/cm was produced in the laboratory from a reverse osmosis module.

2.2. Preparation, crosslinking and casting of blend membranes

2.2.1. Preparation of blend solution

At first 5 wt% PVA solutions were made in deionized water in a 250 ml glass beaker by gradual addition of required amount of PVA to boiling water in several intervals with constant stirring to obtain a viscous clear PVA solution. In a similar way 3 wt% HEC solution was made in deionized water. The clear and homogeneous HEC solution was then mixed with aqueous solution of PVA for making unfilled membranes from this mixture. For filled membranes (micro and nano), required amounts of the filler were added and stirred with magnetic stirrer for 8 h to get filler incorporated polymer dispersion.

2.2.2. Preparation of membrane

The aqueous blend solutions of PVA and HEC were mixed with required amounts of maleic acid (2 wt% of polymer blend) and stirred for 3 h at room temperature. These solutions were then cast on a clean and smooth glass plate covered with polyethylene sheet, dried at ambient temperature for 24 h and then peeled off. The membranes were then cured at 110 °C for 3 h in a hot air oven for crosslinking reaction (Singha, Parya & Ray, 2009). The thickness was measured by Test Method ASTM D 374 using a standard dead weight thickness gauge (Baker, Type J17).

2.3. Membrane characterization

2.3.1. Fourier transform infrared spectroscopy (FTIR)

The FTIR spectra of the membrane samples were recorded on a Perkin Elmer, model-Spectrum-2, (Singapore) spectrophotometer using a thin film (~10 μm) of the polymer.

2.3.2. UV spectroscopy

UV spectra of the membrane samples were recorded on a UV–vis spectrophotometer (Perkin Elmer, model lamda25, USA) by inserting the membrane samples in the cuvette to record their absorbance in the wavelength range of 190–250 nm.

2.3.3. X-ray diffraction (XRD)

Wide angle X-ray diffraction profile of unfilled and filled blend membranes were studied at room temperature with a diffractometer (model: X'Pert PRO, made by PANalytical B.V., The Netherlands) using Ni-filtered Cu K_α radiation ($\lambda = 1.5418$ Å) and a scanning rate of 2° (2θ/s).

2.3.4. Differential thermal analysis and thermogravimetric analysis (DTA–TGA)

DTA and TGA of the membrane samples were carried out in a Perkin Elmer instrument in nitrogen atmosphere at the scanning rate of 10 °C/min in the temperature range of 60–600 °C.

2.3.5. Mechanical strength

The tensile strength and elongation at fracture of the unfilled and filled blend membranes were determined in a Lloyd-Tensile tester (Lloyd instruments, England). The experiment was performed according to ASTM D 882-97.

2.4. Sorption and permeation by pervaporation (PV)

The transport of solutes through membranes is governed by preferential sorption and diffusion due to concentration gradient from bulk feed to downstream side of the membranes. The relative performances of the membranes were evaluated by pervaporation (PV) experiments. However, PV is a dynamic process combining both sorption and diffusion. The evaluation of the membranes by sorption is important to find out the operating condition for pervaporation (Xiao, Feng, & Huang, 2007).

2.4.1. Total and partial sorption

For sorption experiments the membrane samples of known weights were immersed in THF–water mixtures of known concentration (~99–80 wt% THF in water) and allowed to equilibrate for 96 h at 30 °C. Each sample was weighed periodically until no weight change was observed. These membranes were taken out from the solution and weighed after the superfluous liquid was wiped out with tissue paper. Total sorption % (S_t) of water and THF mixtures by the membranes (%) is obtained as

$$S_t = \frac{w_i - w_d}{w_d} \times 100 \tag{1}$$