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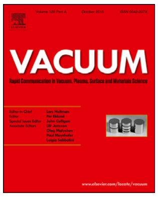

Synthesis of magnetite in poly(vinyl alcohol) matrix and its use in separation of acetone/water mixtures via pervaporation, vapor permeation with and without temperature difference methods

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ABSTRACT

In this paper, poly (vinyl alcohol) (PVA) magnetite (Fe_3O_4) nanocomposite membranes were prepared and used for the separation of acetone/water mixtures via pervaporation (PV), vapor permeation (VP) with and without temperature difference (TDVP) methods. Various PVA membranes having 10–25 wt.% in situ synthesized magnetite nanoparticles were prepared and the resultant nanocomposite membranes characterized by differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). Contact angles were measured for the description of the surface hydrophilicity of the membranes. Detailed studies were carried out for the investigation of the effects of membrane thickness (20–40 μm), operating temperature (30–50 °C), feed composition (0–100 wt.%) and magnetite content (10–25 wt.%) on the separation performance. The optimum membrane thickness, magnetite percentage, operating temperature and feed composition were determined as 35 μm, 20 wt.%, 40 °C and 20 wt.%, respectively, for PV. Permeation fluxes in VP and TDVP were found to be lower than that of PV, however, the highest separation factors were obtained in TDVP method. Fe containing PVA polymer matrix showed high separation factors but slightly decreased permeation flux, compared to pristine PVA polymer membranes. Depending on the operation conditions and the method the permeation fluxes and separation factors were found to be in the range of 0.015–0.091 kg/m^2 h and 29.1–14,000, respectively. In addition sorption and diffusion properties of the magnetite containing PVA membranes were investigated at different operating temperatures. It was observed that the sorption selectivity was dominant factor in the separation of acetone/water mixtures.

1. Introduction

Pervaporation and vapor permeation are two special membrane separation processes for the separation of the mixtures. These processes have some important advantages since the feed mixture can be either in liquid (pervaporation) or in vapor (vapor permeation) form and need low energy consumption. In the pervaporation (PV) process, as shown in Fig. 1a, liquid feed mixture is in direct contact with the membrane material which forms a barrier between the feed mixture and the permeate in vapor phase. However, in the vapor permeation (VP) process, (Fig. 1b), the membrane is in contact with the saturated vapor of the feed instead of the liquid feed solution. For this reason, this process exhibits some advantages over the pervaporation. Additionally, in case of vapor permeation with temperature difference (TDVP) process a temperature difference between the membrane surrounding and the feed mixture was set up (Fig. 1c). However, the success of all these methods depends on utilization of a suitable membrane. For this purpose different polymeric materials have been used in these techniques [1–5].

PVA is a suitable polymeric material for the membrane separation of organic-water mixtures since it has an excellent film forming property, good chemical resistance and biodegradable nature. Even though PVA membranes has good mechanical strength in dry state, they have poor stability in aqueous solutions [6,7] which were overcome by chemical methods such as blending, crosslinking, grafting, chemical modification etc. [8,9]. Due to high demanding nature of chemical methods, recently the trend has

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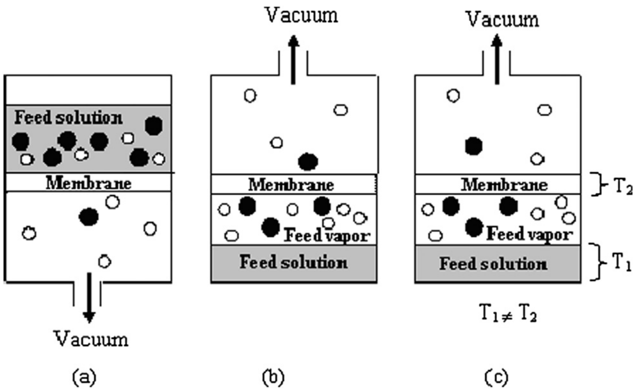

Fig. 1. Schematic diagram of (a) the PV method, (b) the VP method and (c) the TDVP method.

shifted towards developing filler reinforced membranes. Polymeric materials were filled with micro and nanosized fillers to selectively separate water from organic/water mixtures [10–13]. Adoor et al. [10] reported the use of mixed matrix membranes of PVA with sodium montmorillonite clay for PV separation of aqueous-organic mixtures. Veerapur et al. [11] investigated pervaporation separation of 1, 4-dioxane/water mixtures by PVA and Zeolite T matrix composite membranes. A novel PVA-TiO_2 mixed matrix membranes were prepared for pervaporation separation of water-isopropanol mixtures by Sairam and coworkers [12]. Likewise, PVA nanocomposite membranes were also prepared by using different amounts of Fe^{2+} and Fe^{3+} (in an alkaline medium) while synthesizing in situ nanoparticles of metal oxides [12]. Mandal and co-workers [7] have studied the dehydration of aqueous acetonitrile solutions by pervaporation using PVA-iron oxide nanocomposite membranes.

Acetone is a readily available chemical which is commonly used in the production of chemicals and plastics as well as a solvent in pharmaceutical industry. Although it does not form an azeotrope with water, a large reflux is required for its distillation, necessitating a large column and high-energy costs. Hence, membrane processes are good alternative methods to be used for the concentration of the acetone solutions. Several articles are present in the literature on the separation of acetone/water mixtures [14–24] related to PV method. We have also studied the separation of acetone water mixtures by using sodium alginate-poly (vinyl pyrrolidone) membranes by pervaporation and evapomeation with and without temperature difference [25,26]. As a continuation of our work in the current study, we have aimed to design iron oxide containing PVA nanocomposite membranes to separate acetone/water mixtures. For this purpose nanosized magnetite particles were synthesized in PVA matrix by blending Fe^{2+} and Fe^{3+} solutions and the resultant membranes were utilized in separation of acetone-water mixtures. Various operational parameters such as; membrane thickness, magnetite percentage, operating temperature and feed composition were optimized. The results were compared with the pristine PVA and the other PVA based membranes.

2. Experimental

2.1. Materials

PVA (average molecular weight; 72,000) with degree of saponification 98%, anhydrous $FeCl_2$ and $FeCl_3$ and potassium hydroxide were purchased from Merck (Darmstadt, Germany). Acetone was obtained from Carlo Erba.

2.2. Membrane preparation

Nanocomposite PVA-Fe membranes with different magnetite contents based on pristine PVA were aimed (10–25 wt.%). For this purpose known amount of Fe^{2+} and Fe^{3+} solution with a ratio of 1/1 (wt.%) were added into 8 wt.% PVA aqueous solution, stirred and then poured onto round glass dishes. The resulting solution was evaporated at 50 °C to form the membrane. The dried membrane was immersed in a bath containing 4 M KOH solution for 24 h to synthesize the magnetite in the membrane matrix. Membrane was removed from KOH solution bath and washed repeatedly with distilled water until neutrality was obtained. Prepared four nanocomposite membranes were designed as PVA-Fe10, PVA-Fe15, PVA-Fe20 and PVA-Fe25, respectively. Pristine PVA membrane designed in similar way without the addition of Fe^{2+} and Fe^{3+} solutions, dried and heat treated at 130 °C for the crosslinking purpose.

2.3. Membrane characterization

FTIR spectra of pristine PVA and PVA-Fe20 nanocomposite membranes were recorded on a Mattson 1000 FTIR spectrophotometer. Morphology of the PVA-Fe20 nanocomposite membrane was observed using Scanning Electron Microscopy (SEM, JEOL JSM-6400). For this purpose membrane was deposited on a brass holder and sputtered with a thin coat of gold under vacuum. DSC thermograms of PVA and PVA-Fe20 nanocomposite membranes were recorded by using differential scanning calorimeter (DSC, Shimadzu, Japan). Measurements were performed over the temperature range of 0–300 °C at a heating rate of 10 °C/min. Contact angles of the dry membranes were measured using PHX 160 Surface Electro Optics (SEO).

2.4. Swelling studies

A preweighed portion of the unused dry membrane was immersed in different concentrations of acetone solutions for 48 h at 40 °C. The swollen membrane was wiped with a cleansing tissue to remove the excess solvent and weighted. When the swollen membrane reached a constant mass, the swelling degrees (SD) of the membrane was calculated using the following equation;

$$SD = \frac{(W_S - W_D)}{W_D} \times 100 \qquad (1)$$

where W_S, W_D were the mass of the swollen membrane in the feed solution and dry the membrane, respectively.

2.5. Pervaporation experiments

In this study; separation of acetone-water mixtures was carried out in the range of 0–100 wt% compositions at temperatures varying from 30 °C to 50 °C through nanocomposite PVA-Fe membranes by using the PV, VP and TDVP apparatus (Fig. 1a–c). The membrane surface area was 19 cm^2 and pressure was kept at 0.7 mbar with a vacuum pump (Edwards). Feed mixture was circulated between PV cell and feed tank at constant temperature and permeate was collected in liquid nitrogen traps. Composition of permeate, which was collected after steady state conditions attained, was analyzed with Atago DD-5 type digital refractometer.

VP and TDVP experiments were performed similar to PV experiments. Temperature of the membrane surroundings was controlled by a cold medium in a permeation cell of a jacket type.