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Mixed matrix membrane of ZSM-5/poly (ether-block-amide)/polyethersulfone for pervaporation separation of ethyl acetate from aqueous solution

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ABSTRACT

The ZSM-5/poly (ether-block-amide) (PEBA)/polyethersulfone (PES) dual layer mixed matrix membranes (MMMs) were prepared for pervaporation (PV) separation of ethyl acetate (EAc) from aqueous solutions. The ZSM-5 zeolite nanoparticles were synthesized by the conventional hydrothermal method and characterized using the XRD, XRF and FESEM analysis. The effect of top layer thickness, PEBA concentration, zeolite loading concentration, feed concentration and temperature on the separation performance of the prepared membranes was investigated. The FTIR, SEM, contact angle and swelling tests were used to characterize the fabricated MMMs. The results indicated that loading ZSM-5 zeolite nanoparticles into the PEBA matrix had a significant influence on the separation performance of the prepared membranes. The ZSM-5/PEBA/PES membrane containing 7.5 wt% ZSM-5 with a top layer thickness of 20 μm, showed the highest separation factor. The total flux was decreased by loading ZSM-5 into the membranes up to 7.5 wt% and further enhancement in the zeolite loading content resulted in increasing the total permeation flux. The best separation factor and total flux of the ZSM-5/PEBA/PES-07.5 membrane were found to be 108.52 and 1895 $g\,m^{-2}h^{-1}$, respectively for a feed concentration of 5 wt% EAc and temperature of 50 °C.

1. Introduction

Ethyl acetate (EAc) is widely used as a solvent in various industries for the production of adhesive agents, drugs, perfumes, plasticizers, thinners and varnishes [1]. EAc is commonly synthesized by esterification reaction of acetic acid with ethanol [2,3]. Thus, the separation of EAc with a low concentration from water and ethanol is inevitable. The main drawbacks of conventional separation technologies like the distillation process are low separation efficiency, high energy consumption and large equipment investment [4]. Furthermore, the volatile organic compounds such as EAc have been lost during the productions of beverages and foods by conventional processes such as distillation [5]. In this consent, pervaporation (PV), as an energy saving membrane separation process, has a high potential for the recovery of EAc from aqueous solution [5]. In the PV process, the development of membranes with high flux and separation factor, high mechanical stability, and economic viability should be considered. The hydrophobic membranes fabricated from poly(vinylidene-fluorideco-hexafluoropropene (P(VDF-co-HFP)) [5], polydimethylsiloxane (PDMS) [6,7], poly(dimethylsiloxane)-poly(methyl hydrogen siloxane) (PDMS/PMHS) [8], polyurethaneurea (PU) [9], polyoctylmethylsiloxane (POMS) [10] and poly (ether-block-amide) (PEBA) [11–13] have been used for the separation of low concentrations of organic compounds from water. In comparison to flexible polyether and rigid polyamide, PEBA due to its excellent chemical and mechanical properties as well as high thermal stability, has been recently studied for the PV process with high efficiency [11]. However, the use of pure polymeric membranes is limited due to the trade-off relationship between the selectivity and permeability [6,14]. The development of mixed matrix membranes (MMMs) can improve the trade-off problem of the polymeric membrane by incorporating inorganic fillers such as zeolites [15,16], functionalized carbon nanotubes [17], clay [18], and mesoporous materials [19].

Zeolites such as ZSM-5 due to their high hydrophobicity, high surface area and uniform pore size distribution have been extensively used to improve the performance of pure polymeric membranes for the recovery of organic compounds from water compared with other inorganic fillers. Kittur et al. [20] synthesized the PDMS/ZSM-5 composite membranes for the recovery of isopropanol from water. The highest separation factor was obtained by loading 30 wt% ZSM-5 into the PDMS membrane. Vane et al. [21] also prepared ZSM-5 filled PDMS

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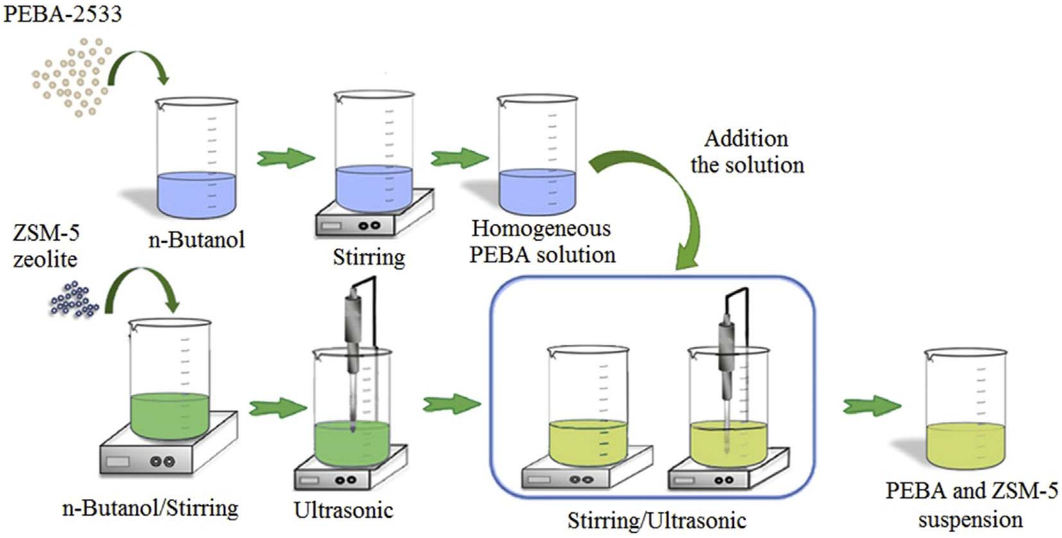

Fig. 1. The schematic for the preparation of the PEBA and ZSM-5 suspension in n-butanol.

membranes for the separation of ethanol from water by the PV process. Zhang et al. [9] prepared the hydroxyl terminated polybutadiene (HTPB)-based PU/ZSM-5 membrane for pervaporation separation of isopropyl acetate from aqueous solution. Gu et al. [22] fabricated the single layer PEBA/ZSM-5 membrane for the separation of EAc from aqueous solution. They found that the PEBA/ZSM-5 membranes containing 10 wt% ZSM-5 had the highest separation factor. Although the incorporation of inorganic fillers such as hydrophobic zeolites into the polymeric membranes can improve the PV separation of organic compounds from water, the main drawback of MMMs is the incompatibility between the inorganic and polymeric phases. Recently, multi-layer MMMs, which have a thin active dense layer containing inorganic fillers on a porous sub-layer as a mechanical support, have been employed for the dehydration of alcohols by the PV process [23,24]. However, there are few studies about the recovery of organic compounds from water by the multi-layer PV MMMs.

In the present study, the ZSM-5 filled PEBA/polyethersulfone (PES) dual layer MMMs were prepared for the separation of EAc from aqueous solutions by the PV process. For this purpose, the ZSM-5 zeolite nanoparticles were synthesized and characterized using the XRD, XRF and FESEM analysis. The prepared membranes were also characterized by the FTIR, SEM, swelling tests and water contact angle analysis. The effects of membrane preparation variables like PEBA concentration, PEBA thickness and ZSM-5 loading content as well as the effects of PV operating parameters including feed concentration and temperature on the performance of the prepared membranes toward the recovery of EAc from its aqueous solutions were investigated.

2. Experimental

2.1. Materials

The PEBA with the trade name of Pebax-2533 (80 wt%. PEO and 20 wt%. PA) and PES with a molecular weight of 58000 g mol^{-1} (Ultrason E6020P) were supplied from Arkema Inc. (Paris, France) and BASF (Ludwigshafen, Germany), respectively. Tetrapropyl ammonium hydroxide (TPAOH, $C_{16}H_{37}NO$), N,N-dimethylformamide (DMF), n-butanol, sodium hydroxide, aluminum isopropoxide, and ethyl acetate were purchased from Merck Co. Ltd. (Darmstadt, Germany). Tetraethyl orthosilicate (TEOS) was supplied from Sigma Inc. (Sigma Aldrich, MO, USA).

2.2. Synthesis of ZSM-5 zeolite

To synthesize ZSM-5 zeolite nanoparticles, 4.22 g TPAOH was initially dissolved in 20 g de-ionized water followed by the addition of 8 g TEOS under stirring for 2 h and named solution A. Solution B was prepared by dissolving 1.8 g TPAOH, 0.48 g NAOH and 0.3 aluminum isopropoxide in 20 g de-ionized water. Solution B was then added to solution A under stirring for a further 4 h to obtain a homogeneous gel. The prepared gel was then undergoes to crystallization in a teflon lined steel autoclave at 200 °C for 2 days. The synthesized zeolite was centrifuged and washed with de-ionized water three times. After that, the obtained solid product was dried at 110 °C for 12 h. Finally, the synthesized zeolite was calcined at 550 °C for 5 h.

2.3. Membrane preparation

The ZSM-5 filled PEBA/PES dual layer MMMs were prepared by the phase inversion technique. At first, the PES ultrafiltration membrane was prepared as a support layer by the non-solvent induced phase inversion method as previously described [25]. Briefly, 16 wt% PES was dissolved into the DMF to obtain a homogenous solution. Then, the prepared bubble-free homogeneous PES solution was casted on a glass plate using a casting machine. The casted polymer film was then immersed into the de-ionized water bath at room temperature. The separated PES membrane was stored into another de-ionized water bath for 24 h to remove the residual DMF solvent. Finally, the PES membrane was dried at room temperature for 24 h.

The ZSM-5 filled PEBA was prepared as a selective top layer on the surface of the PES sub-layer by the solvent evaporation induced phase inversion method [26]. Fig. 1 shows the schematic for the preparation of the PEBA and ZSM-5 suspension in n-butanol. Briefly, 10 wt% PEBA solution was prepared by dissolving the PEBA granules in n-butanol under stirring for 5 h at 70 °C to obtain a PEBA homogenous solution. Suspensions of ZSM-5 zeolite were prepared by adding a specific amount of ZSM-5 nanoparticles to n-butanol under stirring and sonication for 30 min in an ultrasonic (UP200S (200W, 24 kHz), Hielscher Ultrasonics GmbH, Germany). Then, one sixth of the PEBA solution was added to the zeolite suspension under stirring for 30 min and then sonicated for 15 min. This procedure was continued until all of the polymer solution was added to the zeolite suspension. Afterwards, the PEBA/ZSM-5 suspension was vacuumed to remove the dissolved air bubbles. The bubble-free PEBA/zeolite suspension was casted over the porous PES support membrane using a casting machine. The prepared film was dried at room temperature for 24 h, and then the residual