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ZIF-67 filled PDMS mixed matrix membranes for recovery of ethanol via pervaporation

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ABSTRACT

Zeolitic imidazole frameworks (ZIFs), a subclass of metal organic frameworks (MOFs), are composed of metal ions linked by organic ligands which offer an exceptionally high surface area and appealing separation potential. In this study, mixed matrix membranes (MMMs) were prepared using polydimethylsiloxane (PDMS) as a hydrophobic polymer and ZIF-67 as inorganic filler particle. ZIF-67 particles and MMMs were characterized by XRD, SEM, FTIR, BET and contact angle measurements. The prepared membranes were tested for the separation of ethanol/water mixtures via pervaporation. Compared to unfilled PDMS membranes, MMMs loaded with 20 wt % ZIF-67 showed an increase in flux and a doubled separation factor. The easy synthesis of ZIF-67 and its enhanced separation performance make ZIF-67 an attractive candidate to prepare MMMs for a variety of membrane applications.

1. Introduction

The excessive use of fossil fuels has caused serious environmental problems. Clean and renewable bio-fuels are listed as promising alternatives to fossil fuels. Bio-ethanol is currently regarded as a valuable liquid bio-fuel but the process which converts biomass to ethanol is energy intensive and involves high processing costs [1,2]. The ethanol concentration can range from 1 to 15 wt% in the fermentation broth, which usually depends on the type of biomass source, yeast and hydrolysis procedure [3]. To obtain fuel-grade ethanol, water contents should be less than 1–3 wt% [4]. Among the various purification processes, such as distillation, adsorption, membrane distillation, and liquid-liquid extraction, pervaporation is an energy-saving and cost-effective process to separate ethanol from ethanol/water mixture. Pervaporation has emerged as a promising technique holding the potential to save up to 50% energy in contrast to conventional distillation [5]. Despite its numerous advantages, pervaporation has difficulties to find its way into industrial separations due to several limitations, such as low flux, poor separation performance and stability of the membrane material.

Among the materials used for pervaporation, PDMS is the most widely used polymeric material. [6,7]. It shows very good thermal, chemical and mechanical stability along with the high hydrophobicity required for liquid separations [8–10]. The use of PDMS as a material for pervaporation is limited by its low intrinsic selectivity that does not meet the commercial demands [11]. The performance of PDMS can be further enhanced by incorporation of porous fillers to form mixed matrix membranes (MMMs) [14–19]. These membranes combine the advantageous properties of polymeric and inorganic filler materials to form a highly selective and permeable membrane. Despite their proven advantage in improving separation performance, the incompatibility of inorganic and polymeric phase, resulting into non-selective interfacial voids, often limits the true exploitation of MMMs [12–14].

Metal organic frameworks (MOFs) are a new class of porous materials that have been considered as excellent fillers for the preparation of MMMs. The presence of organic linkers coordinated to transition metal ions provides good interfacial adhesion with the polymer matrix. Recent studies showed that zeolitic imidazolate frameworks (ZIFs), a subclass of MOFs, have superior thermal and chemical stability with potential use in gas separation, catalysis, drug delivery, sensing and electronic devices [15]. Previously, a number of MOFs, such as ZIF-8, ZIF-71 and MIL-53, have been incorporated in a PDMS matrix to improve the recovery of bio-alcohols [16–23] but the major drawback of these particles were compromising either the flux or separation factor

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in terms of separation performance. An ideal pervaporation membrane should have superior flux and separation factor at the same time with good durability and mechanical stability. Many studies have been performed to minimize the tradeoff nature of pervaporation membranes. These studies explained that the separation performance of these membranes can be enhanced by increasing the hydrophobic nature of the incorporated particles. In this respect, Wang et al. tried to enhance the hydrophobicity of the used particles [24] but the obtained results were not satisfactory in terms of performance parameters (flux and separation factor). In this study, ZIF-67 was chosen as a filler material for the synthesis of MMMs to obtain satisfactory performance. Incorporation of a hydrophobic material in a hydrophobic polymer, such as PDMS, is expected to increase affinity for alcohol molecules resulting in an improved separation performance. ZIF-67 ($Co(Hmim)_2$) is synthesized by bridging cobalt cations with 2-methylimidazolate anions, resulting in a sodalite topology. It was selected due to its superior stability and high surface area (1240 m^2/g). In addition, the hydrophobicity of synthesized ZIF-67 particles would preferentially allow ethanol to diffuse through the pores [25]. ZIF-67 is iso-structural (framework structure and organic ligands) to ZIF-8, but has different metal atoms i.e. Co. Another advantage is its convenient synthesis under room temperature conditions in contrast to e.g. the hydrothermal synthesis of zeolites [26]. It is expected that by incorporating highly hydrophobic ZIF-67 particles will eventually help the easy sorption of ethanol molecules. Apart from easy sorption, the overall flux of the membrane will also be higher due to the small size and porous structure ZIF-67 particles.

In present work, hydrophobic ZIF-67 particles were incorporated as fillers in PDMS to prepare MMMs in order to improve the separation properties of these membranes. Ethanol recovery from an aqueous mixture was chosen as application to test the performance of the ZIF-67/PDMS MMM for pervaporation.

2. Experimental

2.1. Materials

P-84 polyimide (PI) powder was purchased from HP polymer (Austria), toluene and methanol from VWR international (UK), methyl isobutyl ketone and isopropanol (IPA) from BDH laboratory supplies (England) and Sigma-Aldrich respectively, N-methyl pyrrolidinone (NMP) and tetrahydrofuran (THF) from Merck (Germany), PDMS pre-polymer and cross-linker (RTV 615 A and B) from Techsil (UK), 2-methylimidazole (99.0%) and cobalt nitrate hexahydrate Co $(NO_3)_2{\cdot}6H_2O$ from Acros Organics and Fischer Chemicals respectively.

2.2. Synthesis of ZIF-67 nanoparticles

ZIF-67 crystals were prepared in accordance with the literature [26]. In a typical synthesis, 0.35 g of cobalt nitrate hexahydrate Co $(NO_3)_2{\cdot}6H_2O$ was dissolved in 11.3 g of methanol. 2-methylimidazole (0.66 g) was dissolved in 11.3 g of methanol separately. The prepared solutions were mixed and stirred continuously for 2 h at room temperature to yield purple crystals. The mother liquid was centrifuged at 3500 rpm for 20 min, decanted and several times washed with methanol. The obtained crystals were dried overnight at 85 °C.

2.3. Preparation of composite MMMs

The phase inversion technique was used to prepare a porous support layer from a polymer dope solution. PI dope solution (15 wt% PI, 2 wt% H_2O, 62.25 wt% NMP and 20.75 wt% THF) was prepared and casted on a non-woven polypropylene/polyethylene fabric (Novatex-2471) using an automatic film applicator (HTML, Belgium) [19]. After an evaporation time of 30 s, the cast film was immersed in deionized water for 10 min at room temperature. The membrane formed by this process was post-treated by a sequential solvent exchange. This was done by immersing the support in IPA (3 h) and then in a mixture of MIBK, toluene and oil in a 40:40:20 (v/v) composition for 3 days. The support was subsequently dried at 65 °C for 1 h.

The composition of the solvent mixture was found to be critical in obtaining a homogenous dispersion of filler particles in the membrane matrix. Different ratios of both solvents were screened to evaluate the effect on filler dispersion. An 80:20 composition of toluene-hexane resulted in an optimum dispersion, even at the highest filler loading. The selective layer of PDMS was coated on the support using a dip-coating technique. A 15 wt% PDMS solution in toluene and hexane (80:20) comprising of RTV 615 A and 615B in a 10:1 ratio was pre-crosslinked for 2 h at 60 °C. To prepare MMMs, coating solutions were loaded with different filler concentrations (5 wt%, 10 wt%, 15 wt% and 20 wt%), stirred and sonicated for 15 min each (3 times). This sonication of ZIF-67 filled PDMS mixtures is very important as this will hinder the aggregation of ZIF-67 particle in the polymer matrix.

In order to coat a PDMS layer, the support plate was kept at an angle of 60° and PDMS solution was poured on the support. This step was repeated at least three times allowing solvents to evaporate for 5 min in between. The cross-linking was completed in an oven at 110 °C for 24 h.

2.4. Pervaporation experiments

The separation performance of the synthesized membranes was measured using a custom-built pervaporation unit. A schematic diagram of the set-up is shown in Fig. 1. The experiments were conducted with a 6 wt% aqueous ethanol solution at the selected temperature range of 40–70 °C using a thermo-stated water bath. A cross-flow pervaporation module (CF016, Sterlitech) was used. The effective membrane area was 16 cm^2. Before running the experiments, the membranes were kept in contact with feed solution for 10 h to reach steady state. The feed was pumped by a peristaltic pump at a continuous volumetric flow rate of 1 L/min at atmospheric pressure. The retentate was sent back to the feed tank for recycling purpose. A vacuum pump was used at the permeate side to maintain the vacuum. The permeate vapors were condensed in a cold trap to obtain a liquid permeate samples which were analyzed by a gas chromatograph (7890A, Agilent, USA) equipped with a thermal conductivity detector. The permeate flux was calculated by using Eq. (1)

$$J = \frac{Q}{At} \tag{1}$$

where J is the flux in kg/m^2 h, Q is the permeate flow rate and t is the time in h. Membrane separation factor ($\beta_{i/j}$) was calculated by the ratio of mole fractions of two components in the upstream (y) and downstream (x) as shown in Eq. (2):

$$\beta_{i/j} = \frac{y_{i/y_j}}{x_{i/xj}} \tag{2}$$

2.5. Membrane uptake

The membrane uptakes of the free-standing MMMs were measured by immersing them in particular solvent. The free-standing films were prepared by pouring a dispersion of PDMS/ZIF-67 into a flat bottom glass petri-dish. The solution was placed in the oven at 70 °C for 12 h. The dried pieces of PDMS films with different filler loadings were immersed in the solvent for 48 h. The excess solution was quickly wiped off using filter paper. After the equilibrium was established, films were weighed on the electronic balance to calculate the difference between weight before and after immersion in solvents. The uptake was calculated using the following equation:

$$\text{Membrane uptake} = \frac{W_s - W_d}{W_d} \tag{3}$$