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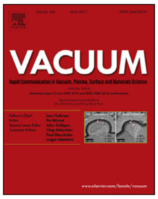

Pervaporation characteristics of a PDMS/PMHS membrane for removal of dimethyl sulfoxide from aqueous solutions

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ABSTRACT

In this study, pollution control and solvent recovery of dimethylsulfoxide (DMSO) were simultaneously attained by using pervaporation (PV) process, for the first time. In order to use PV process a hydrophobic composite membrane of poly(dimethyl siloxane)–poly(methyl hydrogen siloxane) (PDMS/PMHS) was synthesized. The synthesized membrane was characterized by Fourier transform infrared spectroscopy (FTIR), scanning electronic microscopy (SEM), and thermal gravimetric analysis (TGA). The pervaporation separation of different dimethyl sulfoxide/water mixtures with various low percentages of the organic specie was carried out. The fluxes and separation factors of the membrane were examined for the separation of dimethyl sulfoxide from their aqueous solutions, and results showed that the flux and separation factor were varied depending on the temperature of the feed solution and feed initial concentration. The operating conditions were optimized as the DMSO initial concentration of 20 wt.% and temperature of 70 °C.

1. Introduction

Wastewaters originated from different industries contain various pollutants including organic and inorganic materials which should be removed from their discharges [1–4]. On this point, removal of solvents is of importance in a variety of industries ranging from chemical to food and pharmaceutical. In this regards, dimethylsulfoxide (DMSO) as a solvent for both organic and inorganic materials in semiconductor manufacturing processes has been recently enhanced [1]. Moreover, DMSO is extensively used in preclinical and clinical research, as it increases the entrance of water-insoluble drug candidates into the central nervous system [5]. While a consensus exists that DMSO concentration of 10% are toxic in vivo [6], the effects of low DMSO concentration both in vitro [6,7] and in vivo are still judged [8]. However, the use of DMSO as a solvent has also been growing and the biological treatment of wastewater containing DMSO seems to be challenging. This is due to aerobic biological processes which cannot attain an effective level of DMSO decomposition, and anaerobic biological processes that form volatile and noxious compounds, such as $(CH_3)_2S$ or H_2S, which makes it difficult to control the treatment process [9,10].

A review of the literature reveals that researchers combined advanced oxidation processes with biological processes, to offer an effective treatment solution for wastewater containing DMSO [11]. In view of the concerns surrounding the treatment of theses wastewater and the limited information available about the degradation pathways involved in the complete mineralization of DMSO by $OH^\bullet$, we investigated the pervaporation (PV) process to recover DMSO molecules from aqueous solutions, for the first time.

PV is one of the most active areas in membrane research, and the pervaporation process has been presented to be a crucial technology for chemical separations. In pervaporation, the liquid mixture is placed in contact with a membrane and the permeated phase is removed as a low pressure vapor from the other side. PV has been commercialized for two applications: one is the dehydration of solvents, and the other is the removal or recovery of small amounts of organic compounds from their aqueous solutions. Most of the PV membranes are found to be selective for water permeation [12–15], and only a few are selective to the permeation of organic compounds [16]. In PV processes, due to stricter environmental legislation on the discharging of aqueous effluents contaminated with organic materials the evolution of organophilic membrane has been promoted [9]. As a general rule, the membranes employed for removing organic compounds from dilute solutions are mostly hydrophobic materials. Hydrophobic materials

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are preferred in this application because removing a small amount of organic compounds from their aqueous solutions is easier and consumes much less energy than dehydration of the mixtures. The most commonly used hydrophobic membrane for removal of organic compounds is polydimethylsiloxane (PDMS), also known as silicone rubber, which has an alternating–O–Si–O– unit structure and has great stability in operation [17]. Silicone including polymers show good organophilicity and silicone rubber (mainly polydimethylsiloxane) based membranes were generally used for separation of organic aqueous mixtures such as alcohols, ketones, phenols and aromatics [18–20]. Moreover, it is an extensively used membrane material that has a hydrophobic surface and resists the penetration of water molecules, while it consents organic molecules to transfer through the membrane [21–27]. In addition to PDMS, there are other materials that can be used for the membrane preparation to remove organic materials from aqueous solutions. For example, polyether-block-polyamide (PEBA) was used in the separation of toluene, dichloromethane, etc. from aqueous solutions [28–30]. The PEBA membrane showed a 40% lower organic flux than that was obtained with a PDMS membrane [29]. In addition, a polyurethane (PUR) membrane was utilized for 1,1,1-trichloroethane (TCA), toluene and dichloromethane removal from water [29,31]. Besides, polyvinylidene fluoride (PVDF) is a crystalline polymer that was tested for benzene separation from water [32]. Ethylene propylene diene monomer rubber (EPDM) has been used for the removal of toluene from aqueous solution [33]. Among the reported membranes in these literature, the selectivity of PDMS for organic materials relative to water is great [17]. Even in cases where PDMS shows limited selectivity, it can still meet the requirements of most applications [17]. Reviewing researches show that the PDMS has been used for the removal of an extensive variety of organic materials from their aqueous solutions, and while PDMS membranes are already available, applying them in a PV process will increase the economic attractiveness of this technology [10]. Therefore, in this study different dimethyl sulfoxide/water mixtures with various percentages of the organic specie were separated by PV using poly(dimethyl siloxane)–poly(methyl hydrogen siloxane) (PDMS/PMHS) membrane, for the first time. The membrane was synthesized and applied as a separation element in a membrane module. The properties of the membrane were investigated by Fourier transform infrared spectroscopy (FTIR), scanning electronic microscopy (SEM), and thermal gravimetric analysis (TGA). In order to optimize the operating temperature, pervaporation experiments were carried out in a selected initial feed concentration in the temperature range of 25–70 °C.

2. Experimental

2.1. Materials

PDMS and its curing agent; PMHS; under the trade name Sylgard® 184 Silicone Elastomer, were purchased from Dow Corning company (USA). DMSO was supplied by Merck (Darmstadt, Germany). Deionized water was produced in the laboratory from an automatic water still (Fineteck, Korea).

2.2. Membrane preparation

At first, PDMS was heated in an oven at 100 °C to reduce its viscosity and consequently to facilitate it's mixing with the curing agent. After that, it was mixed with PHMS as the crosslinker agent according to a 10:1 wt ratio to prepare casting mixture. Afterward, the prepared mixture was casted on a Teflon flat base petridish. It was then placed in an oven at 80 °C for 1 h to fully crosslink the polymer. After, it was cooled at −30 °C, and the transparent PDMS membrane was prepared with a thickness of about 75 μm.

2.3. Pervaporation experiments

All experiments in this study were performed using the same PDMS/PMHS membrane with a thickness of 75 μm. The PV setup is shown in Fig. S1 (It was presented in supplementary Figs.). It was made of a stirred stainless steel cell displayed in Fig. S1.

The effective mass transfer area of the membrane placed between two chambers was 21.23 cm^2. To avoid any leakage, a rubber O-ring was located between the membrane and the lower support plate. A disk turbine powered by a DC motor was used to stir the feed solution in the upper chamber. The temperature of the feed mixture was controlled by means of a temperature controller and an electrical heating coil. To evaluate the performance of the membrane through the PV separation process, feed mixtures were provided with three initial percentages of 10, 15 and 20 wt.%, for DMSO.

The permeate effluent was continuously vacuumed with a low pressure vacuum pump (Vacuubrand, RZ 2.5, GMBH, Germany) placed after two cold traps set in parallel. Two cold traps were placed into an ultra-low temperature freezer (PLATILAB 340 SV-3-STD- Italy) to condense permeate phase, completely. Moreover, third cold trap was also used after these two parallel cold traps to avoid any liquid output transferred from the traps into the vacuum pump. The weight of the condensed permeate phase in the cold trap was measured with a balance (Kern, model ABS 120-4) with the accuracy of 0.0001 g.

The flux of J (kg/m^{2}h) was evaluated from the permeate weight by using the following Eq. (1):

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

where M (g) and A (m^2) represent the amount of permeate mass through the experimental time interval t (h), and the effective area of the membrane, respectively.

From the composition of the feed and the permeate phases, the separation factor (α_{ij}) was determined using Eq. (2):

$$\alpha_{ij} = \frac{y_j x_i}{y_i x_j} \tag{2}$$

where y and x present the weight fraction of i and j components in the permeate phase and the feed mixture, respectively.

A Karl Fischer automatic titrator (787 KF Titrino, Metrohm, Germany) was employed to determine the water content of the feed and the permeated phases.

2.4. Sorption measurements

Sorption of both pure liquids and binary mixtures with varies DMSO content (5, 10, 15 and 20 wt.%) in the membranes was examined on 2 × 2 cm^2 membrane samples at different temperatures. The samples were immersed in the mixtures for at least 8 h. The membranes surface was wiped dry, and then the amount of solution sorbed was measured by weighting using a laboratory balance (Kern, model ABS 120-4) with an accuracy of 0.0001 g. The sorption percentage of the membrane in the solutions was evaluated by:

$$S(\%) = \frac{w_s - w_d}{w_d} \tag{3}$$

where, W_d and W_s present the weights of the dried and swollen membranes, respectively.