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Separation of aqueous salt solution by pervaporation through hybrid organic–inorganic membrane: Effect of operating conditions

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ABSTRACT

Hybrid polymer-inorganic membranes were prepared by crosslinking poly(vinyl alcohol) (PVA), maleic acid (MA) and silica via an aqueous sol–gel route. Membrane characterisation results revealed silica nanoparticles (<10 nm) were well dispersed in the polymer matrix and significantly reduced swelling of the membrane. The membranes were tested for pervaporation separation of aqueous salt solution with NaCl concentrations of 0.2–5.0 wt% at temperatures 20–65 °C, feed flowrates 30–150 mL/min and permeate pressures 2–40 Torr. The salt rejection remained high (up to 99.9%) under all operating conditions. A high water flux of 11.7 kg/m^2 h could be achieved at a feed temperature of 65 °C and a vacuum of 6 Torr. The effect of operating conditions on water flux is discussed in relation to diffusion coefficients of water and fundamental transport mechanism through the membrane. The activation energy for water permeation was found to vary from 23.8 to 20.1 kJ/kmol when the salt concentration in the feed was increased from 0.2 to 5.0 wt%.

1. Introduction

Pervaporation processes are able to separate mixtures in contact with a membrane via preferentially removing one component from the mixture due to its higher affinity with, and/or faster diffusion through the membrane. In order to ensure continuous mass transport, very low absolute pressures are usually maintained on the downstream side of the membrane, removing all molecules migrating to the surface, and thus rendering a concentration difference across the membrane [1]. The mechanism of mass transfer of liquids across non-porous polymeric membranes includes successive stages of sorption of a liquid and its diffusion through the free volume of the polymeric material [2].

Pervaporation has been extensively used for separation or concentration of mixtures of aqueous-organic or organic liquids. However, there are only limited studies on the application of this technology for water desalination [2,3]. In desalination applications, pervaporation has the advantage of near 100% of salt rejection and potential low energy consumption. The pervaporation of an aqueous salt solution can be regarded as separation of a pseudo-liquid mixture containing free water molecules and bulkier hydrated ions formed in solution upon dissociation of the salt in water [2]. A summary of previously reported open literature on desalination by pervaporation is presented in Table 1 [4]. The water flux in systems reported so far is generally low, at <6 kg/m^2 hr. The feed temperature was found to be a crucial parameter due to the increase in diffusivity and reduction in viscosity that occurs on heating. In addition, the vacuum, the membrane thickness and the inherent permeability of the membrane polymer are also important.

Poly(vinyl alcohol) (PVA) membranes have been studied extensively as pervaporation materials in various applications due to its excellent film-forming and highly hydrophilic properties. PVA membranes are known to exhibit high degrees of swelling in aqueous solutions due to the presence of hydroxyl groups [8–10]. To improve the performance and stability of PVA membranes in the aqueous solution, it is necessary to insolublise or modify the membrane by crosslinking or addition of hydrophobic groups to achieve a stable membrane with good mechanical properties and selective permeability to water. Incorporation of inorganic particles in PVA membranes to form hybrid organic–inorganic membranes has been one such technique to improve the stability and separation performance of PVA membranes [11,12].

In our recent work, the pervaporation separation of aqueous salt solution was carried out to evaluate the pervaporation performance of hybrid organic–inorganic membranes based on PVA, maleic acid (MA) and silica [13]. We found that the hybrid PVA/MA/silica membrane showed superior performance with a high water flux (up to 5.5 kg/m^2 hr) and a very high salt rejection (up to 99.9%). Chemical crosslinking among PVA, MA and silica inhibited the swelling of PVA and led to a compact and stable structure. The introduction of silica nanoparticles in the polymer matrix enhanced both the water flux and salt rejection due to increased diffusion coefficients of water through the membrane.

It is well known that the pervaporation performance is not only dependent on the properties of membranes, but also the operation

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Table 1
Summary of previous studies on pervaporation desalination (adapted from ref. [4]).

Membrane polymer	Feed conc., g/L	Temp., °C	Membrane thickness, μm	Flux, kg/m^{2}h	Reference
Cotton cellulose	40	40	30	6.1	[2]
Cellulose diacetate on MD membrane	40	40	0.5–1.5	4.1–5.1	
Sulphonated PE, cation exchanger	0–176	25–65	100	0.8–3.3	[5]
Quaternised PE, anion exchanger	0–176	45–65	50–180	1.5–3.0	[6]
	35	60	70	2.3	
	35	60	170	0.5	
Polyether amide	35	Solar, 46–82	40	0.2	[3]
Polyether ester	3.2–5.2	Solar, 22–29	160	0.15	[7]
	9.9–18			0.13	
	20–30			0.12	

conditions such as feed concentration, temperature, permeate pressure and feed flowrate [14]. For scale up, it is important to design and operate the system under optimum operating conditions to make the process more efficient and also economically viable. The objective of this work is to study the effect of operating conditions on pervaporation separation performance of aqueous salt solutions. A synthesised hybrid PVA/MA/silica membrane was tested for separation of aqueous salt solution by the pervaporation process at various salt concentrations and operating conditions. The activation energy of permeation was calculated from the Arrhenius relationship. The performance was discussed in relation to the diffusion coefficient of water to understand the fundamental transport mechanism within the membrane.

2. Experimental

2.1. Hybrid membrane synthesis and characterisation

The hybrid PVA/MA/silica membrane containing 5 wt% MA and 10 wt% SiO_2 with respect to PVA was synthesised via an aqueous sol–gel route. Reagent grade chemicals including PVA (98–99% hydrolysed, average MW 160,000), tetraethyl orthosilicate (TEOS, 98%), maleic acid (MA), *p*-toluene sulfonic acid (98.5%, monohydrate) were obtained from Sigma-Aldrich and used without further purification.

PVA polymer powder (8.0 g) was first dissolved in 100 mL Milli-Q deionised water (18.1 MΩ cm at 25 °C) at 95 °C. The obtained 8 wt% PVA solution was left to cool to room temperature, followed by the addition of 0.4 g of MA and 0.08 g of *p*-toluene sulfonic acid into the solution (pH 1.9 ± 0.1). A premixed 2.78 g TEOS and 25.0 g ethanol mixture (weight ratio of TEOS:ethanol = 1:9) was added drop wise to the above PVA solution under steady stirring and continuously stirred for another 2 h. The resulting homogeneous mixture was cast on Perspex Petri dishes to the desired thickness and dried in air followed by heat treatment in a fan forced oven at 140 °C for 2 h. A pure PVA membrane sample was also prepared as a reference for comparison. The thickness of membranes was measured at different points across the membrane using a Fowler electronic digital micrometer (accuracy ± 1 μm) and the membranes used in this study had an average thickness of 20 μm.

Energy dispersive X-ray spectrometry (EDS) of the hybrid membrane was performed by an EDAX detector on a Philips XL30 scanning electronic microscope (SEM) with a voltage of 15 kV and a working distance of 15 mm. Samples were coated by sputtering with carbon. The morphology of the hybrid membrane sample was imaged using a TECNAI F30 Transmission electron microscope (TEM) with an accelerating voltage of 200 kV. TEM samples were prepared by a focused ion beam (FIB) technique. The hydrophilic properties of membrane samples were assessed by a KSV contact angle meter (CAM200) equipped with a video capturing system. Static contact angles were measured by the sessile drop method. A 6 μL water drop was formed on the levelled surface of the membrane for contact angle measurements.

The water uptake of PVA and PVA/MA/silica hybrid membrane was measured by the following procedures: (1) immersing the dried membrane in deionised water at room temperature for 48 h to reach the absorption equilibrium. (2) blotting surface of wet membrane with the cleansing tissue to remove surface water and quickly weighing the wet membrane within 10 s (W_s). (3) drying the membrane in a vacuum oven at 50 °C for overnight and then weighing again to obtain the mass of the dried membrane (W_d). The water uptake of membrane was then calculated according to:

$$\text{Water uptake} = (W_s - W_d) / W_d \times 100\% \qquad (1)$$

2.2. Pervaporation testing

The pervaporation experiments were carried out on a laboratory scale pervaporation unit as shown in Fig. 1. The membrane was placed in the middle of a pervaporation cell with an effective surface area of the membrane of 12.6 cm^2. During the experiment, the feed solution

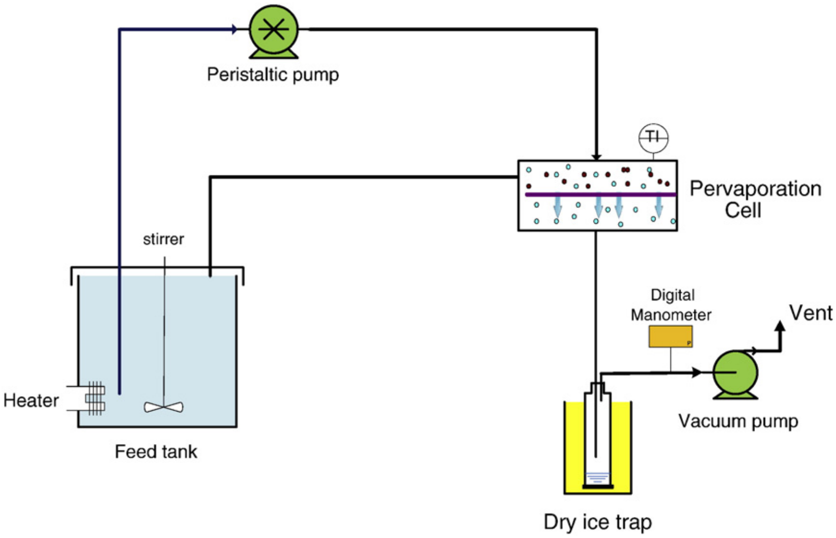

Fig. 1. Schematic drawing of the pervaporation unit.