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Removal of VOCs from their aqueous solution by pervaporation with PDMS-zeolite composite membrane

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ABSTRACT

VOCs were separated from water– volatile organic compound (VOC) mixtures by pervaporation using poly(dimethylsiloxane) (PDMS)–zeolite composite membranes prepared in our laboratory. Silicalite-1 particles were hydrothermally synthesized for preparation of a composite membrane. PDMS–zeolite composite membranes were prepared with a mixture of synthesized silicalite-1 particles and PDMS–polymer dissolved in a solvent. The effects of a concentration of VOCs and a weight % of zeolite particles in a membrane are presented on the VOCs/water separation. Either a dichloromethane aqueous solution or a 1,2-dichloroethane aqueous solution was used as a feed solution. The fluxes of VOCs increased significantly from 2.8 to 271.8 $g/m^2/h$ as the concentration of VOCs increased from 0.00005 to 0.001 mole fraction of VOCs. As the weight % of zeolite particles was changed from 0% to 8%, the fluxes of VOCs increased almost two times at the typical mole fraction of VOCs such as 0.0001 for dichloromethane and 0.0005 for 1,2-dichloroethane. It was also found that the separation factor of VOCs increased pretty much by adding the zeolite particles in the composite membrane.

Keywords: VOCs; Pervaporation; Zeolite; Composite membrane

1. Introduction

The volatile organic compounds (VOCs) contained in both a wastewater and a ground water may cause the environmental pollution. Even if the concentration of VOCs in such a solution is very low, VOCs are very harmful to either the environment or the human. The various removal methods of VOCs are currently available: condensation, oxidation, adsorption, air stripping, aeration, etc. These removal technologies consume a high energy. Recently, a membrane separation process has been widely used in an environmental industry. The membrane pervaporation is known to be a low energy consumption process since it needs only an electric power to maintain the permeate side in vacuum. Also, the pervaporation is an environmentally clean technology because it does not use the third material such as an entrainer for either an azeotropic distillation or an extractive distillation. This process involves a series of the adsorption, the diffusion and the desorption in the membrane in order to separate the organic compounds from their aqueous solutions [1–3]. A hydrophobic membrane could be one of the good candidates utilized in a pervaporation process to remove organic compounds. A poly(dimethylsiloxane) (PDMS) membrane has been widely used for separation of VOCs. Yeom et al. [4] reported the removal of trace VOCs from water through PDMS membranes. When the organic compound dissolved in aqueous solution has a higher affinity towards the

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PDMS membrane, the effect of water clustering in the membrane is of more significance, resulting in an increase in the enrichment factor for VOCs.

Zeolites have been widely used as separation media in a chemical process since they showed a good ability of separation. Some researchers investigated the effects of zeolite particles added to the polymer membrane for gas separation [5–9] and pervaporation [10–14].

Hennepe et al. [10] prepared a zeolite-filled silicone membrane. Their membrane was used for pervaporation of ethanol from its water mixture. It was shown that the performance of a silicone membrane was enhanced by adding an alcohol-selective molecular sieve such as silicalite-1 to the polymer membrane.

Kittur et al. [11] reported the separation of isopropyl alcohol from water using a hydrophobic zeolite-incorporated PDMS membrane. The zeolite-incorporated membranes showed much better separation of isopropyl alcohol than the original polymer membrane due to their molecular sieving action, which was attributed to the presence of straight and sinusoidal channels in the framework of the zeolite. An increase in the zeolite content in the membrane resulted in a simultaneous increase in both the permeation flux and the selectivity. They thought that a significant enhancement of the hydrophobicity and the selective adsorption of a molecular sieve might attribute the good performance.

Liu et al. [12] separated chloroform from water using a silicalite-filled poly(siloxane imide) membrane. It was shown that the silicalite content has a slight impact on the membrane performance. They observed both the chloroform separation factor and the permeation flux increased with the increase in the silicalite content.

Since there are well developed numerous microspores in a zeolite, VOCs are expected to be selectively adsorbed and diffused through the pores, leading to the increment of the VOCs' fluxes. Also, the particles may play a role of providing a large free volume between the polymer chains in the PDMS membrane. As shown in Fig. 1, the organic molecules may diffuse through both the enlarged free volume and the pores of zeolite particles, simultaneously, resulting in a high flux and a high separation factor.

In this study, it was investigated how silicalite-1 particles in the PDMS membrane and the concentration of VOC in a feed affect the pervaporative separation of VOCs from their water mixtures. Silicalite-1 particles are hydrothermally synthesized and PDMS–zeolite composite membranes are prepared with a mixture of synthesized silicalite-1 particles and PDMS–polymer. They are used to separate VOCs from the aqueous solution. Pervaporation characteristics such as a permeation flux and a separation factor are investigated in terms of the feed concentration and the weight % of zeolite particles in the membrane. Since the solubility of either dichloromethane or dichloroethane in water is quite low such as an order of 10^{-3} in a mole fraction, it was not sure that they could be effectively separated with a silicalite-1-filled PDMS membrane. However, it turned out that those VOCs could be relatively well separated. Also, it was found that the fluxes and the separation factors through PDMS–zeolite composite membranes were affected by both the feed concentration and the added zeolite particles in the membrane.

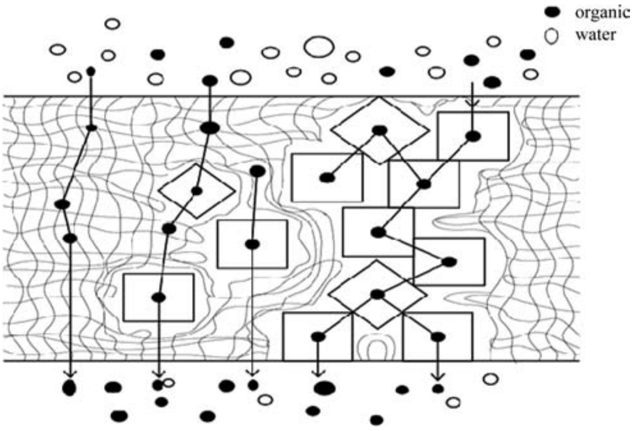


Fig. 1. Possible paths of organic molecules through zeolite pores and free volume of polymer.

2. Experimental

2.1. Synthesis of silicalite-1 zeolite

Silicalite-1 particles were synthesized from the liquid mixture in which the chemical compositions were 1 TPABr: 21 SiO_2: 3 NaOH: 788 H_2O. Ludox AS-40 (Dupont, U.S.A.) was used as a source material for Si; tetrapropylammonium bromide (Aldrich, U.S.A.) was used as a template; sodium hydroxide (Samchun, Korea) was used as a source chemical for Na. After preparing a Si solution and a template solution, the template solution was added to the Si solution [15]; the mixed solution was agitated and aged for 24 h. It was poured in the teflon bomb. The reaction was carried out at 170°C for 8 h. After synthesis, the silicalite-1 particles were washed, dried and calcined at 480°C.

2.2. Preparation of composite membrane

A PDMS polymer was prepared by adding two parts: Sylgard 184A and B(Dow Corning). A casting solution was prepared by dissolving A and B with a

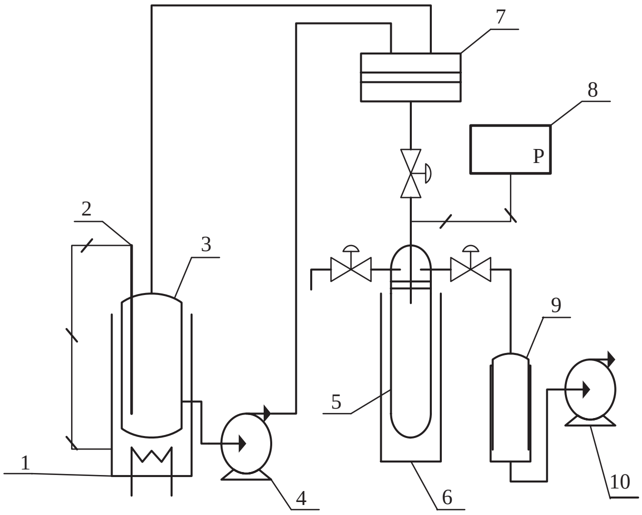


Fig. 2. A schematic flow diagram of pervaporation experimental apparatus. (1) thermostat; (2) thermocouple; (3) feed tank; (4) volumetric pump; (5) cold trap; (6) liquid nitrogen; (7) membrane cell; (8) pressure gauge; (9) desiccators and (10) vacuum pump.

ratio of 10 to 1 in *n*-hexane. Synthesized zeolite particles were added in the solution. The weight fraction of zeolite particles was controlled up to 8 wt% based on the composite membrane only. In order for the particles to be homogenously dispersed, the solution was sonicated for 1 h [16]. That solution was cast on the porous polysulfone (PSF) support. Evaporation was carried out at 40°C in a vacuum oven for 24 h to remove the solvent. After evaporation of *n*-hexane, a crosslinking was completed at 110°C in the oven.

2.3. Pervaporation

The pervaporation experiments were carried out using a pervaporation apparatus as schematically shown in Fig. 2. The membrane was installed in a membrane test cell. The effective membrane area in contact with a feed was 11.3 cm^2.

The aqueous feed solution was fed at 25°C and circulated with a diaphragm pump (DMA-05, Daekyung, Korea). The feed concentration was regulated up to the solubility of each VOCs in water as shown in Table 1. The permeate was collected in a liquid nitrogen trap and the permeate side is maintained in vacuum of 5 torr.

Both the feed and the permeate concentrations were analyzed with a Gas Chromatograph (M600D, Younglin Co., Korea) where Porapak Q (Supelco, U.S.A.) column was equipped. A flame ionization detector (FID) was used to determine the concentration of organic.

Table 1
Physical properties of VOCs

Organics	CH_2Cl_2	$C_2H_4Cl_2$
Molecular weight	84.92	98.95
Boiling point (°C)	39.8	83.7
Solubility[a] (g/L)	13.0	8.1
Molar volume (10^6 m^3/mol)	64.5	78.8
Vapor pressure (kPa)	57.72	5.23

[a] VOCs in water at 25°C

Pervaporation characteristics might be presented in terms of a flux and a separation factor defined as follows:

$$\text{Flux} = P/(A \cdot t), \tag{1}$$

$$\text{Separation factor} = (Y_\text{O}/Y_\text{W})/(X_\text{O}/X_\text{W}), \tag{2}$$

where P represents a weight of permeate (g), A denotes a membrane area (m^2) and t is a permeation time (h). Y_O and Y_W refer to the mole fractions of VOCs and water at the permeate side, respectively. X_O and X_W represent the mole fractions of VOCs and water at the feed side, respectively.

2.4. Characterization

The crystal structure of the zeolite was confirmed by X-ray diffraction (D/Max-2200 Ultima/PC, Rigaku Co., Japan, 30 kV, 15 mA). The particle size of the synthesized silicalite-1 was measured with a particle size analyzer (HELOS/RODOS, Sympatec GmbH, Germany). The morphology of the composite membrane was analyzed by scanning electron microscopy (SEM, JSM-840A, Jeo Ltd., Japan, 10 kV).

3. Results and discussion

3.1. Synthesis of silicalite-1

Fig. 3 shows XRD patterns of the synthesized silicalite-1 particles. The synthesized particles were confirmed as a silicalite-1 since the XRD pattern was the same as that of the standard silicalite-1 zeolite [17].

Fig. 4 shows that the average particle size is 1.44 μm. This particle size is thought to be small enough for preparation of the composite membrane since the thickness of the membrane active layer is about 5 μm.

3.2. Membrane characterization

Fig. 5 show SEM images of surface and cross-sectional views of the PDMS–zeolite composite

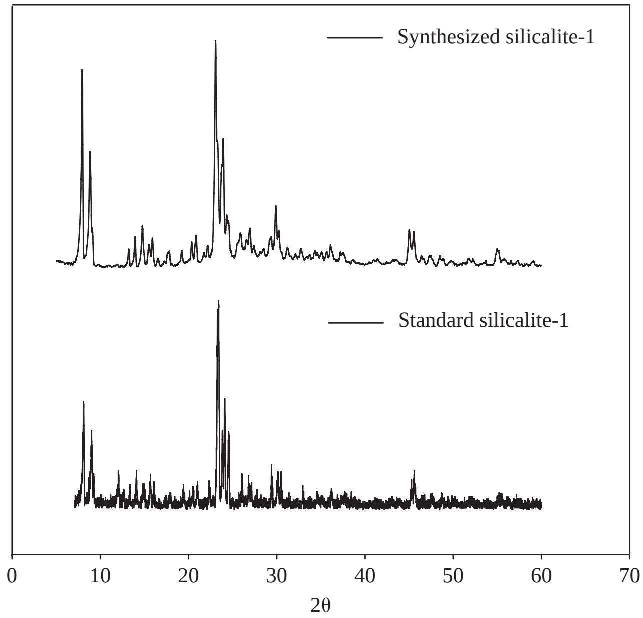
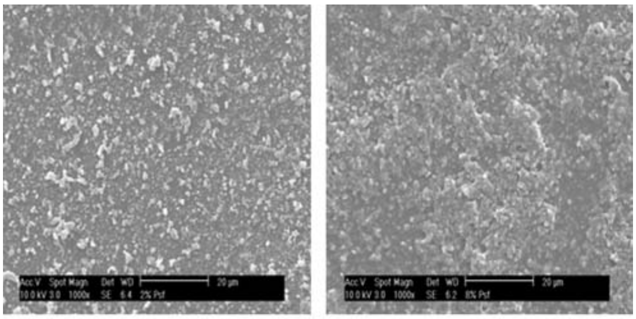
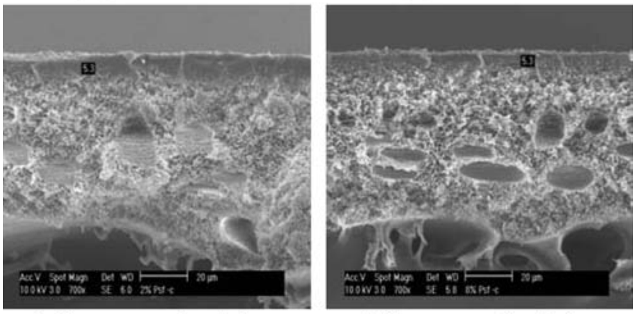


Fig. 3. XRD pattern of silicalite-1 particles.

membrane prepared with two different weight % of silicalite-1 in the membrane. In both SEM images, it can be seen that the silicalite-1 particles are relatively well dispersed. As the weight % of silicalite-1 particles increases, the number of particles shown on the surface composite membrane increases. It was observed that the thickness of the PDMS-zeolite composite membrane active layer was 5.3 μm as shown in Fig. 5.



(a.1) a surface view (b.1) a surface view



(a.2) a cross-sectional view (b.2) a cross-sectional view

Fig. 5. SEM images of composite membranes prepared with (a) 2 wt% silicalite-1 particles and (b) 8 wt% silicalite-1 particles.

3.3. Organic fluxes

Fig. 6 shows the fluxes of dichloromethane and 1,2-dichloroethane through the composite membrane. Regardless of the kind of VOCs, the flux of VOCs increases as the concentration of VOCs in the feed solution increases. Also the flux was observed to increase as the weight % of silicalite-1 in the membrane increases. The driving force of the flux is known to be the difference of the fugacity of VOCs between the feed side and the permeate side. As it can be seen in Table 2, the fugacity of VOCs increases as the concentration of VOCs increases, leading to the increase of the difference of the fugacity across the membrane. As a result, it is expected that the flux increases, indicating that the increase in flux is clearly caused by the increase in the VOC concentration in the feed side. When the silicalite-1 particles are added, VOCs can easily diffuse through both the micropores of silicalite-1 and the enlarged free volume, resulting in the increase of the flux. Hennepe et al. [10] reported the preparation of the zeolite-filled silicone rubber membranes and the pervaporation results on bioreactor alcohols. The increase in flux depended on the silicalite content of the membrane, and their experiments indicated that at least part of the transport took place through the zeolite pores. The increase in selectivity with increasing a zeolite content of the membrane was explained by the increase in the selective sorption of organic. Kittur et al. [11] also reported the pervaporation separation of isopropyl alcohol through the ZSM-5 zeolite-incorporated PDMS membrane. The permeation flux increased systematically with respect to the zeolite loading because the addition of an adsorptive filler to a polymer matrix was known to improve the selective property of a membrane in addition to the creation of a smooth path for the diffusion of selective molecules. It was found that

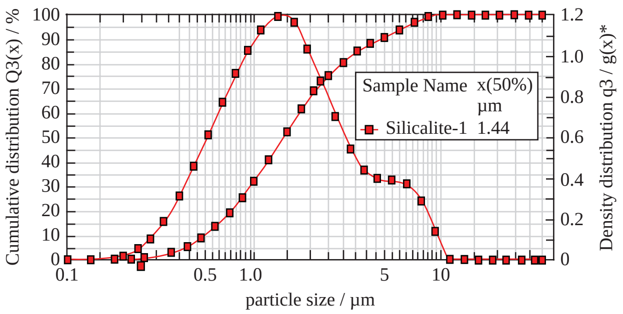
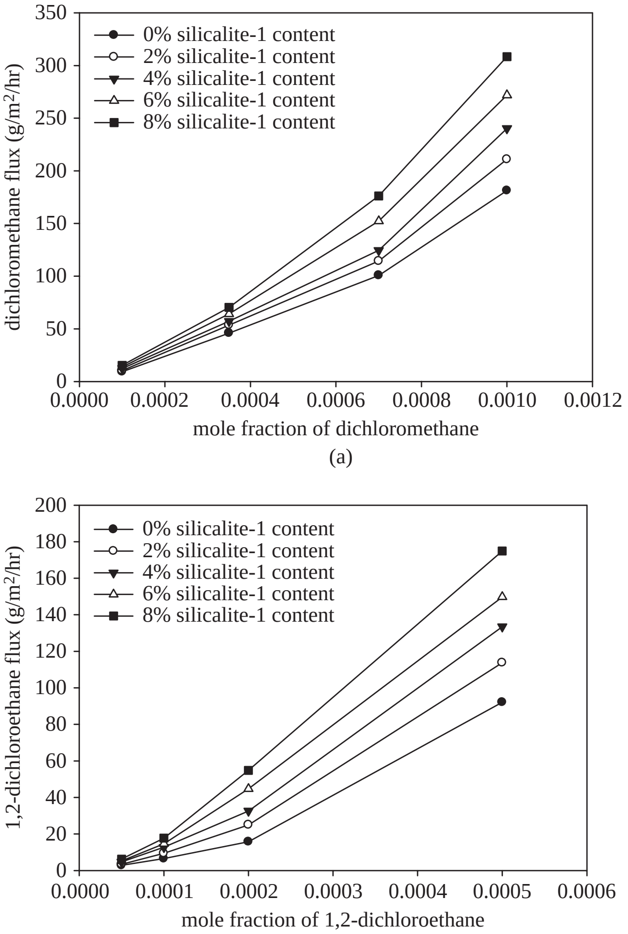


Fig. 4. Particle size distribution of synthesized silicalite-1.



(a)

(b)

Fig. 6. Organic flux through PDMS-zeolite composite membrane. (a) dichloromethane and(b) 1,2-dichloroethane.

the flux of 1,2-dichloroethane was higher than that of dichloromethane at the same concentration as shown in Table 3, even if the fugacity of 1,2-dichloroethane is smaller than that of dichloromethane. The solubility of 1,2-dichloroethane in the membrane was reported to be much larger than that of dichloromethane since the interaction of 1,2-dichloroethane with the membrane is stronger due to its higher hydrophobicity [4]. It is thought that in this case such a solubility plays a more important role on the flux than the fugacity difference.

3.4. Separation factor

Fig. 7 represents the separation factor of VOCs through the composite membrane as a function of the mole fraction of VOCs in a feed solution. As the concentration of VOCs increases, the separation factor increases. When the silicalite-1 is added more, the increase of the separation factor is found to be more profound. As explained in the previous section of fluxes of VOCs, the flux of VOCs increases as the concentration of VOCs increases while the flux of water decreases. Once VOCs are dissolved in the membrane, the water molecules may have a difficulty to be dissolved in the membrane due to the existence of VOCs. Such a difficulty can become more significant as the concentration of VOCs increases, resulting in the increment of the separation factor. If the silicalite-1 particles exist in the membrane, VOCs can be more strongly adsorbed to silicalite-1 particles than to the pure PDMS polymer. This may contribute the high separation factor. As seen in Fig. 1, the dissolved VOCs can diffuse through either the silicalite-1 particle or the polymer matrix. It implies that the permeating route of VOCs can be straight.

Table 2
Fugacity of VOCs in aqueous solution [15]

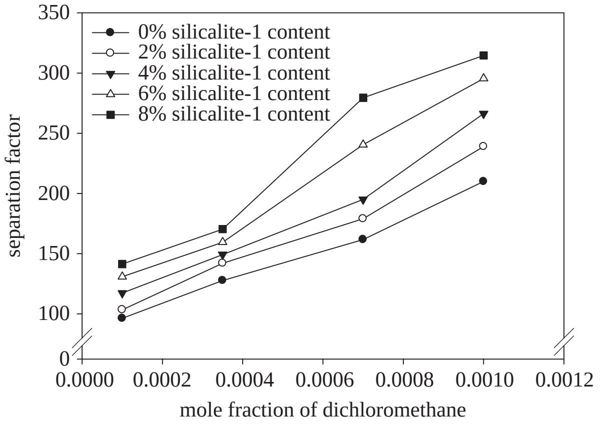
CH_2Cl_2		$C_2H_4Cl_2$	
Mole fraction	Fugacity	Mole fraction	Fugacity
0.0001	1.56	0.00005	0.17
0.00035	5.45	0.0001	0.34
0.0007	10.90	0.0002	0.68
0.001	15.58	0.0005	1.71

On the other hand, the path of water may be much longer than that of VOCs because water molecules cannot pass through the silicalite-1 particles, but they have to diffuse around the particles.

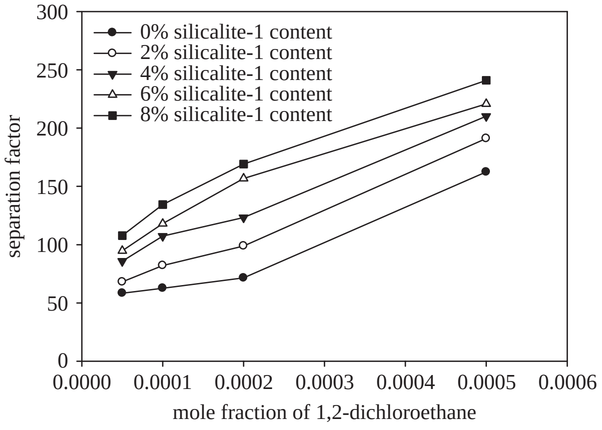
The separation factor of 1,2-dichloroethane is found to be slightly higher than that of dichloromethane. This is also expected simply because the higher flux of 1,2-dichloroethane is obtained at the same concentration. If the more hydrophobic VOCs are dissolved in the membrane, the stronger block by VOCs may be established against the passage of water molecules, leading to the higher separation factor.

Table 3
Organic fluxes at the same mole fraction of 0.0001 in feed solution

Zeolite in membrane (wt%)	Flux of CH_2Cl_2 (g/m^2 h)	Flux of $C_2H_4Cl_2$ (g/m^2 h)
0	8.62	9.49
2	9.63	10.41
4	12.38	12.72
6	13.80	14.64
8	15.38	17.67



(a)



(b)

Fig. 7. Separation factor through PDMS–zeolite composite membrane. (a) dichloromethane and (b) 1,2-dichloroethane.

4. Conclusions

PDMS–zeolite composite membranes were successfully synthesized. Synthesized PDMS–zeolite composite membranes showed a reasonable flux and a good separation factor for VOCs–water binary mixture. The flux and the separation factor through the composite PDMS membrane were strongly affected by the composition of a zeolite and the concentration of feed mixture. It can be said that the PDMS–zeolite composite membrane might be applicable for the separation of VOCs from its aqueous solution.

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