

Mesoporous molecular sieve (MCM-41)-filled sodium alginate hybrid nanocomposite membranes for pervaporation separation of water–isopropanol mixtures[☆]

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Abstract

Sodium alginate (NaAlg) and the mesoporous molecular sieve (MCM-41)-filled NaAlg nanocomposite membranes have been prepared by solution casting and crosslinked with glutaraldehyde. Pervaporation performance of the MCM-41-filled NaAlg membranes has been tested and compared with plain NaAlg membrane for dehydrating isopropanol at 30 °C. In the studied feed composition range of 10–50 mass% of water, 20 mass% MCM-41-loaded NaAlg membrane gave the highest selectivity ranging between 29,991 and 3332 in the range of feed water compositions of 10–50 mass%. Flux for the plain NaAlg membrane ranged between 0.067 and 0.340 kg/(m² h), while for 20 mass% MCM-41-filled NaAlg membrane, flux increased to 0.110 and 0.555 kg/(m² h). To the best of our knowledge, this is the first study reported on the membrane forming properties of an admixed hybrid composite of a mesoporous molecular sieve (MCM-41) with NaAlg used in dehydration of isopropanol, yielding high selectivity to water at higher loadings of the molecular sieve as a filler.

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1. Introduction

Zeolites are hydrated aluminosilicates composed of crystalline structures that exhibit molecular sieving effect and possess good thermal, chemical as well as mechanical stability. Zeolite membranes have several advantages over the conventional plain polymer membranes and are suitable for molecular sieving-based separations when used in the pervaporation (PV) separation of aqueous–organic mixtures [1–4]. On the other hand, the polymer hybrid-type nanocomposites prepared in this study are composed of an organic polymer matrix in which inorganic nanosized material is dispersed in order to enhance the membrane performance in selectively separating water from isopropanol. A number of studies have been devoted to molecular-based separations using zeolite-filled polymer membranes for

gas [5–7] and liquid separations [8–10]. There have been earlier reports by Koros and co-workers [11–14] on mixed matrix membranes used in membrane applications. In PV, the liquid feed from the upstream side will transport on the permeate side of the membrane by applying vacuum on the permeate side at room temperature. The PV process is therefore, more energy-intensive than distillation. PV is also environmentally cleaner, since unlike in distillation, no third component (entrainer, such as benzene, a deadly carcinogen) is added. Moreover, with liquid feed streams, the total area coverage on the feed side is quite close to saturation, so that sorptive transport takes place through the membranes. Recent studies [15–17] on PV separations have dealt with development of different types of zeolite-filled membranes, since these are known to achieve high selectivity and flux over those of pristine polymer membranes. However, majority of unfilled membranes did not give the required performance to a broad spectrum of solvents and concentration ranges in terms of flux and selectivity, particularly when used in separating aqueous–organic mixtures.

Zeolites have uniform and molecular-sized pores and hence, separation through such materials, particularly when these are incorporated in polymeric matrices, can be achieved by a com-

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bination of several effects, such as molecular sieving, selective adsorption and differences in diffusion rates between the feed liquid molecules to be separated. Majority of zeolites used in the literature are crystalline aluminosilicates and these, when dispersed uniformly in membrane matrices, could increase membrane properties over those of the virgin membranes. Literature cites many examples of such membranes used in PV separation of aqueous–organic mixtures [15–17]. In this work, it is demonstrated that when a natural polymer like sodium alginate (NaAlg) is incorporated with nanosized Mobil Composition of Matter-41 (MCM-41) particles, one could increase the water separation properties greatly over that of the membrane prepared from pristine NaAlg. Earlier, Reid et al. [18] have developed MCM-41 incorporated polysulfone membranes for gas separation studies. He et al. [19] also prepared the nanocomposite membranes consisting of silylated MCM-48 and poly(vinyl acetate) for gas separation. MCM-41 has the unique compositional and morphological flexibility with a pore size around 2–3 nm and surface area of $>1000 \text{ m}^2/\text{g}$ [20]. It is formed by the condensation of silica around the self-assembled arrays of surfactant molecules in an aqueous gel. MCM-41 is hydrophilic, which has not been used by the previous researchers in liquid separation problems. In this research, MCM-41 nanoparticles have been incorporated for the first time into the NaAlg matrix, a natural polymer derived from brown seaweeds, to develop hybrid nanocomposite membranes for the PV separation of water–isopropanol mixtures. Our earlier efforts to increase water selectivity of the pristine NaAlg membrane have not been very successful while dehydrating isopropanol [21–25].

Isopropanol forms an azeotrope at 12.5 mass% of water and hence, its separation by PV would be more advantageous than the conventional distillation. Previous reports on PV separation of water–isopropanol mixture through the modified NaAlg membranes did not offer high selectivity to water [26,27]. The highest water selectivity achieved so far in the published literature for pristine NaAlg membrane is 653. However, in this investigation, it is demonstrated that by incorporating MCM-41 into NaAlg membrane, one could achieve water selectivity as high as 29,991, a much higher value than previously reported in the literature. In this paper, PV performance of the NaAlg membranes loaded with 5, 10 and 20 mass% of MCM-41 is compared here with the pristine NaAlg membrane in separating water–isopropanol mixtures. PV results are discussed in terms of the extent of molecular sieve loading and matrix swelling.

2. Experimental

2.1. Materials

Sodium alginate (NaAlg), isopropanol, cetyltrimethyl ammonium bromide, sodium silicate, glutaraldehyde, acetone, hydrochloric acid and sulfuric acid were purchased from S.D. Fine Chemicals, Mumbai, India. Deionized double distilled water having a conductivity of $20 \mu\text{S}/\text{cm}$ was produced in the laboratory using the Permionics Pilot Plant (Vadodara, India) by nanofiltration membrane module.

2.2. Preparation of MCM-molecular sieve

Pure siliceous MCM-41 was synthesized using the gel compositions: $10 \text{ SiO}_2:5.4 \text{ C}_n\text{H}_{2n+1}(\text{CH}_3)_3\text{NBr}:4.25 \text{ Na}_2\text{O}:1.3 \text{ H}_2\text{SO}_4:480 \text{ H}_2\text{O}$. Typical synthetic procedure used for C_{16} -MCM-41 using cetyltrimethylammonium bromide as a template is described here briefly. Cetyltrimethylammonium bromide (34.66 g) was mixed with 115 g of water and stirred for 30 min. Sodium silicate solution (37.4 g) was added drop-wise to the surfactant solution with vigorous stirring for another 30 min. Then, 2.4 g of H_2SO_4 in 10 g of water were added to the above mixture and stirred for additional 30 min. The resulting gel was transferred to a polypropylene bottle and kept in an oven at 100°C for 24 h. After cooling to room temperature, the resultant solid was recovered by filtration, washed with distilled water and dried in an oven at 100°C for 6 h. Finally, the materials were calcined in a muffle furnace at 540°C for 10 h.

2.3. Membrane preparation

NaAlg (4 g) was dissolved in 80 mL of water with constant stirring. Then, 0.4 and 0.8 g of MCM-41 were weighed with respect to weight of NaAlg separately and dispersed in 20 mL of water, sonicated for 30 min and added to NaAlg solution (already prepared) with further stirring for 24 h. The solution was poured on a glass plate to cast the membranes. Dried membranes were peeled off from the glass plate and immersed in a crosslinking bath containing (30:70) water:acetone mixture along with 2.5 mL of glutaraldehyde and 2.5 mL of conc. HCl. After keeping the membranes in a crosslinking bath for about 12–14 h, membranes were removed, washed repeatedly with deionized water and dried in oven at 40°C . The plain NaAlg membrane was also prepared in the same manner. Membrane thickness as measured by a micrometer screw gauge were around $50 \pm 1.0 \mu\text{m}$.

2.4. Particle size measurement of MCM-41

Zeta average diameter of MCM-41 particles dispersed in water was measured using a Zetasizer, Model 3000HS, Malvern, U.K.

2.5. Characterization of membranes

2.5.1. Scanning electron microscopic (SEM) studies

SEM micrographs of the MCM-41-filled hybrid nanocomposite membranes and pristine NaAlg membrane were obtained under similar resolutions (Mag. $2\text{K}\times$) using Leica Stereoscan-440 scanning electron microscope equipped with Phoenix energy dispersive analysis of X-rays (EDAX). Since these films were nonconductive, gold coating (15 nm thickness) was done on samples and measurements were done at National Chemical Laboratory, Pune (courtesy of Dr. S.R. Sainkar, Center for Materials Characterization Division).

2.5.2. Differential scanning calorimetric (DSC) studies

DSC thermograms of the MCM-41-filled nanocomposite membranes and pristine NaAlg membrane were recorded using

Rheometric Scientific, UK (Model DSC SP) instrument. Thermograms were recorded between 25 and 400 °C at the heating rate of 10 °C/min under nitrogen atmosphere.

2.5.3. Swelling experiments

Swelling experiments were performed by gravimetrically on all the membranes in 10, 20 and 50 mass% water-containing feed mixtures at 30 °C. The % error while preparing these mixture compositions was less than 3%. Initial mass of the circularly cut (diameter = 2.5 cm) nanocomposite and NaAlg membranes was taken on a single-pan digital microbalance (Model AE 240, Mettler) sensitive to ±0.01 mg. The samples were placed inside the specially designed airtight test bottles containing 20 cm³ of the test solvent. Test bottles were transferred to the oven maintained at a constant desired temperature. Mass of the samples was measured at the selected time intervals by removing the test samples from the bottles and wiping the surface-adhered liquid droplets by gently pressing between the filter paper wraps; samples were again placed back into the oven. In order to minimize the solvent evaporation losses, this step was completed within 15–20 s. All samples reached equilibrium sorption within 25 min, which remained constant over an extended period of time up to 75 h. After the completion of equilibrium swelling, degree of swelling, DS, was calculated as,

$$DS = \frac{W_{\infty} - W_0}{W_0} \quad (1)$$

where W_0 is initial dry mass of the sample and W_{∞} is equilibrium mass of the membrane.

2.6. Pervaporation experiments

Pervaporation experiments were performed in an apparatus indigenously designed earlier [28]. The instrument consists of a stirred stainless steel cell with an effective membrane area of 28.27 cm² and a diameter of 6.0 cm. Volume capacity of the cell is about 250 mL. At the downstream side of the PV apparatus, 10 Torr vacuum was applied using a vacuum pump (Toshniwal, Mumbai, India). Test membrane was equilibrated for 2 h with the feed mixture before the start of the experiment. After establishment of a steady state, liquid permeate was collected in traps immersed in liquid nitrogen. Permeate was condensed in traps using liquid nitrogen. Experiments were performed with the feed mixtures ranging from 10 to 50 mass% of water. The % error values in computing different mixture compositions were less than 3%, since all the weight measurements were done within ±0.01 mg. Depleted water and make-up water for the next composition was enriched by adding the required amount of fresh water and further equilibrated for 1 h. Mass of permeate in the trap was collected and its composition was determined by measuring refractive index using the Abbe refractometer (Atago, Model 3T, Tokyo, Japan). From the PV data, we have computed the permeation flux, J , and selectivity, α , as,

$$J = \frac{W_p}{At} \quad (2)$$

Table 1

Pervaporation results of water + isopropanol mixtures for different membranes at 30 °C

Mass% of water in the feed	Water flux (kg/(m ² h))	Selectivity (α)	Mass% of water in the permeate
Pristine NaAlg membrane			
10	0.067	653	98.64
20	0.122	223	98.24
30	0.167	127	98.20
40	0.232	38	96.24
50	0.340	25	96.16
MCM-41 (5 mass%)-filled NaAlg membrane			
10	0.083	689	98.71
20	0.198	236	98.33
30	0.291	130	98.23
40	0.354	40	96.35
50	0.442	26	96.22
MCM-41 (10 mass%)-filled NaAlg membrane			
10	0.106	29991	99.97
20	0.324	13329	99.97
30	0.404	7775	99.97
40	0.501	62	97.62
50	0.522	41	97.62
MCM-41 (20 mass%)-filled NaAlg membrane			
10	0.110	29991	99.97
20	0.349	13329	99.97
30	0.421	7775	99.97
40	0.526	4999	99.97
50	0.555	3332	99.97

$$\alpha = \left(\frac{P_W}{P_{IPA}} \right) \left(\frac{F_{IPA}}{F_W} \right) \quad (3)$$

Here, W_p is mass of permeate, A the effective area of the membrane and t is time; P_W and P_{IPA} are mass% of water and isopropanol, respectively, in permeate; F_W and F_{IPA} are mass% of water and isopropanol, respectively, in feed. Triplicate measurements of flux and selectivity were reproducible within 3% standard errors, but the average values are presented in Table 1.

3. Results and discussion

3.1. Particle size analysis

The number average size distribution histogram of MCM-41 particles dispersed in water displayed in Fig. 1 suggests that nearly all particles have the diameter <100 nm.

3.2. SEM analysis

Fig. 2 compares the SEM surface images of the 10 mass% MCM-41-filled nanocomposite membrane with that of plain NaAlg membrane under similar resolutions. Fig. 3 shows the cross-sectional view of MCM-41-filled NaAlg nanocomposite membrane. It can be seen that MCM-41-filled NaAlg membrane exhibited molecular level distribution of MCM-41 particles in NaAlg matrix. However, surface SEM micrographs showed better distribution of particles than the cross-sectional picture, since particles are dispersed uniformly in the polymer matrix

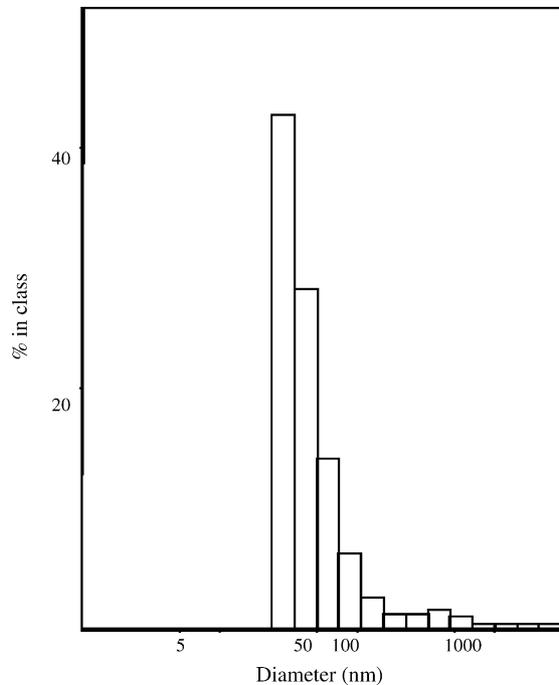


Fig. 1. Number average particle size distribution histogram of MCM-41 molecular sieve.

that can be observed through the cross-sectional picture of SEM.

3.3. DSC analysis

DSC curves of the crosslinked NaAlg (curve a) and crosslinked NaAlg membranes containing 5, 10 and 20 mass% of MCM-41 are displayed in Fig. 4(b–d). Broad endotherms are observed in the region of 30–100 °C for all the membranes due to release of moisture from the membranes. Crosslinked NaAlg membrane has an endotherm with the onset temperature at 170 °C and the peak position at 187 °C, which is shifted to higher temperature region in the MCM-41-filled NaAlg nanocomposite membranes.

3.4. Degree of swelling

Equilibrium degree of swelling, DS data obtained from sorption experiments at 30 °C for the three membranes as a function of mass% of water in the feed are displayed in Fig. 5. Note that to calculate DS, the equilibrium weight gain data were obtained from the dynamic sorption results (not displayed to minimize the number of plots) performed in different media (10, 20 and 50 mass% of water in the feeds). Swelling kinetics depends on the mutual diffusion of solvent molecules in response to polymer chain relaxation [29]. During swelling, mass uptake increased initially, rather rapidly, due to quick absorption of water molecules from the feed mixture, thereby filling microvoids of the membranes; the sorption curves later reached equilibrium (until no more weight gain was observed). However, the time required to reach equilibrium swelling depends upon the type of the membrane as well as migrating liquid molecules.

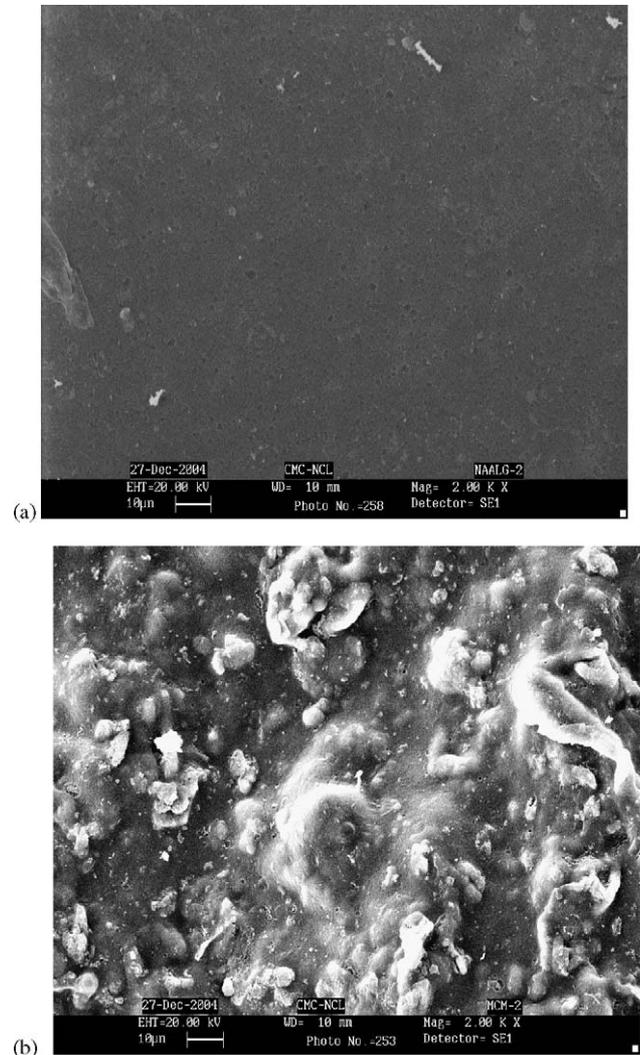


Fig. 2. Surface scanning electron micrographs of (a) pristine NaAlg membrane and (b) MCM-41 (10 mass%)-filled NaAlg nanocomposite membrane.

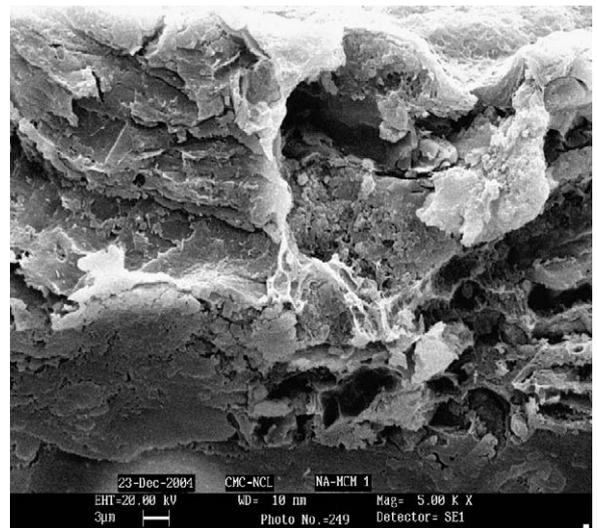


Fig. 3. Cross-sectional scanning electron micrograph of MCM-41 (10 mass%)-filled NaAlg membrane.

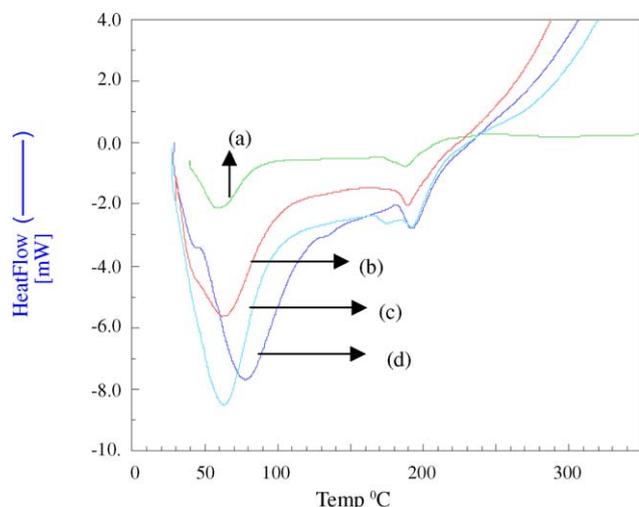


Fig. 4. DSC curves for (a) crosslinked NaAlg membrane, (b) MCM-41 (5 wt%)-filled crosslinked NaAlg membrane, (c) MCM-41 (10 wt%)-filled crosslinked NaAlg membrane and (d) MCM-41 (20 wt%)-filled crosslinked NaAlg membrane.

For instance, pristine NaAlg membrane reached equilibrium swelling within 25 min, while the MCM-41-filled NaAlg membranes took <20 min. This could be due to the combined sorption-swelling effect of the molecular sieves as well as the NaAlg matrix. To ensure complete equilibration, swelling experiments were continued for longer times, i.e., until no more weight gain occurred. Polymer swelling showed a clear-cut dependence on permeation flux and selectivity data. For instance, swelling is higher for MCM-41 (20 mass%)-NaAlg membrane than observed for MCM-41 (10 mass%)-NaAlg, which in turn, is higher than that of the pristine NaAlg membrane.

3.5. Membrane performance

In pervaporation, molecular transport occurs due to a concentration gradient existing between the feed and permeate mixtures

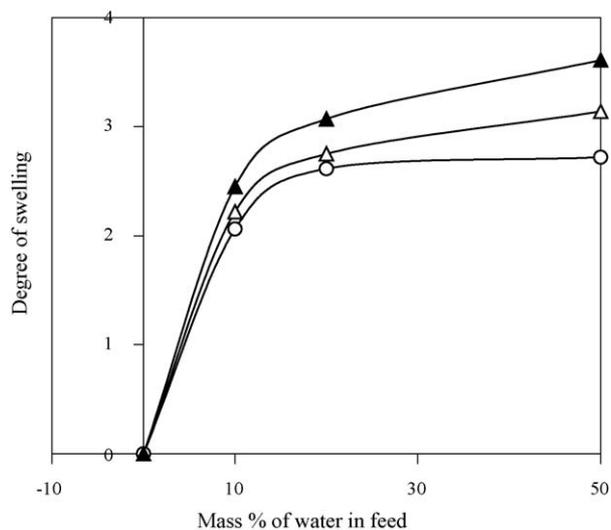


Fig. 5. Swelling curves for MCM-41-filled NaAlg. (○) Pristine NaAlg, (△) MCM-41 (10 mass%) and (▲) MCM-41 (20 mass%)-filled NaAlg membranes.

as envisioned by the solution–diffusion principles [30,31]. Permeating molecules first dissolve into the membrane and diffuse out on the product side as a result of concentration gradient. In case of nanocomposite membranes of the present study, overall separation can be explained as due to the delicate balance of solvent properties, viz., its nature and affinity towards membrane, size and vapor pressure in addition to morphological set up of the membrane. Considering the PV separation of aqueous–isopropanol mixtures, the relative affinity of either isopropanol or water molecules towards membrane could be assessed from the sorption (swelling) measurements. When the hydrophilic MCM-41 filler is mixed with a hydrophilic NaAlg polymer, the permeation flux of such membranes would be enhanced in proportion to the amount of filler added (see Table 1). Equilibrium swelling and/or dynamic sorption data described before corroborate this observation. For instance, when higher amount of molecular sieve (20 mass%) is present, greater would be the degree of swelling and as well as permeation flux. On the other hand, when 10 mass% of MCM-41 is added, membrane swelling would be higher than plain NaAlg membrane, but lower than observed for 20 mass% loaded membrane, while flux values vary accordingly.

At low level of MCM-41 loading, presumably the molecular sieves spread around considerably within the NaAlg bulk matrix, which would form the isolated islands within the matrix environment. Such a matrix is likely to absorb more of water molecules as compared to unfilled NaAlg matrix. However, at higher filling (20 mass%), the degree of swelling would be higher because the filler particles will help the hybrid matrix to absorb more of water molecules. At any rate, the pore size of MCM-41, being in the range of 2–3 nm, would favor the preferential permeation of smaller size (0.28 nm) water molecules than isopropanol (0.42 nm). Moreover, the hydrogen-bond type interactions between water and hydrophilic MCM-41 particles as well as NaAlg polymer are responsible for higher values of flux and selectivity as compared to the pristine NaAlg membrane. A substantial increase in selectivity and a moderate increase in permeation flux rate over that of pristine NaAlg membrane for both 10 and 20 mass% MCM-41 loaded hybrid nanocomposite membranes is due to the fact that in the swollen state, hydrophilic nanoporous molecular sieves would preferentially allow the water molecules to be sorbed faster than isopropanol, and this would increase the selectivity and flux values even at higher amounts of water in the feed.

The importance of using zeolite-filled membranes in PV separation has been well documented in the earlier literature for a variety of polymer-zeolite combinations [32,33]. The crystalline ordered structure of hydrophilic MCM-41 with a narrow size distribution has a higher resistivity to organic liquids than water. Thus, by dispersing MCM-41 particles into NaAlg polymer matrix, the increase in permeation flux of the hybrid nanocomposite membranes could be the result of preferential interaction of water molecules, which would accommodate higher amount of water than isopropanol. This could be possibly due to: (i) strong adsorptive hydrophilic interaction of water molecules onto MCM-41 particles, (ii) surface diffusion from cage to cage and (iii) vaporization on the permeate side. Physical adsorp-

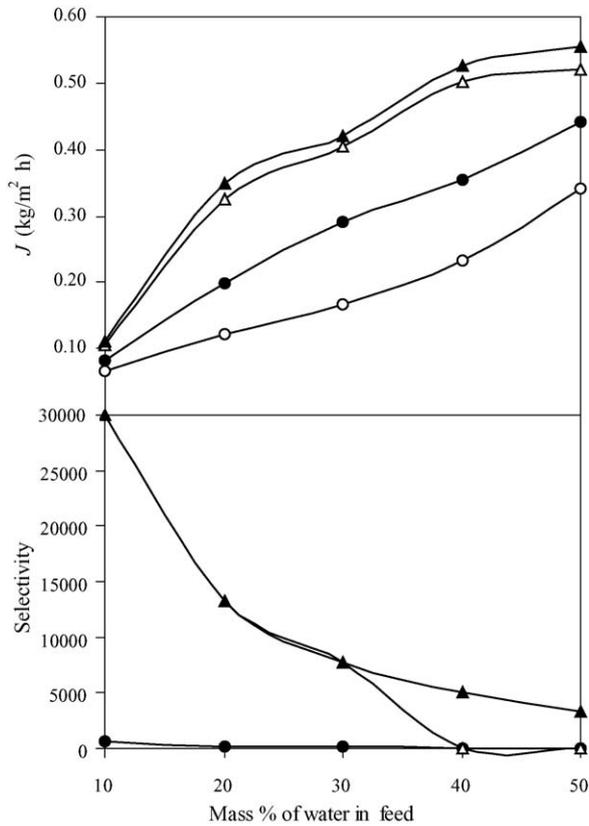


Fig. 6. Water flux and selectivity vs. mass% of water in the feed at 30 °C. (○) Pristine NaAlg, (●) MCM-41 (5 mass%), (△) MCM-41 (10 mass%) and (▲) MCM-41 (20 mass%)-filled NaAlg membranes.

tion involves both van der Waals type dispersion-repulsive and electrostatic interactions due to polarization, as well as dipole and quadrupole type interactions. The complimentary effects of molecular sieve on water transport would thus improve the membrane performance. It is worth mentioning that the varying effects of flux and selectivity are attributed to the amount of MCM-41 filler present in the NaAlg matrix.

Flux and selectivity results are displayed in Fig. 6. The flux of pristine NaAlg membrane has increased from 0.067 to 0.340 kg/(m² h) for feeds containing 10 mass% of water to 50 mass% of water. However, selectivity of the pristine NaAlg decreased from 653 to a considerably smaller value of 25 when water in the feed mixture water increased from 10 to 50 mass%. Parallel to this effect, mass% of water in permeate also decreased from 98.64 to 96.16. However, increase in flux with increasing amount of water in the feed could be attributed to plasticization effect of the membrane as a result of membrane swelling, thus permitting more of water molecules from the feed mixture to permeate side through the membranes. Note that after the addition of MCM-41, the membrane properties have changed drastically. For instance, water flux for 5 mass% MCM-41 loaded NaAlg membrane has increased from 0.083 to 0.442 kg/(m² h), while the water flux for 10 mass% MCM-41 loaded NaAlg membrane increased from 0.106 to 0.522 kg/(m² h). In case of 20 mass% MCM-41 loaded NaAlg membrane, water flux increased from 0.110 to 0.555 kg/(m² h) with increasing amount of water in the feed from 10 to 50 mass%. Water in permeate for 5 mass%

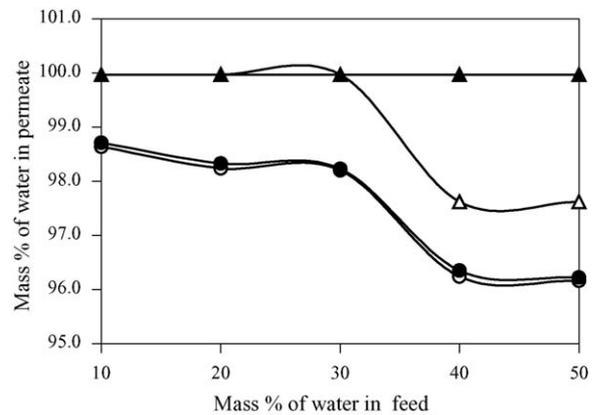


Fig. 7. Mass% of water in permeate vs. mass% of water in feed at 30 °C. (○) Pristine NaAlg, (●) MCM-41 (5 mass%), (△) MCM-41 (10 mass%) and (▲) MCM-41 (20 mass%)-filled NaAlg membranes.

MCM-41 loaded NaAlg membrane ranged between 98.71 and 96.22 and, for 10 mass% MCM-41 loaded NaAlg membrane, it ranged between 99.97 and 97.62%, while for 20 mass% MCM-41 loaded NaAlg membrane, it was as high as 99.97% over the whole range of water compositions of the feed mixture. Since membranes of this study are highly water selective, very small differences in these compositions may cause huge differences in selectivities. Therefore, sensitivity of water measurements is plotted in Fig. 7, which shows the exact composition of water in permeate as a function of mass% of water in feed for different loadings of MCM-41 in NaAlg matrix. This could be due to hydrophilic nature of MCM-41, which might have exerted high affinity to water molecules than isopropanol, since water is more polar than isopropanol. Free channels in the structure of MCM-41 cage as well as the polymer plasticization effect could also be responsible for this effect in addition to strong molecular sieving effect induced as a result of higher amount of MCM-41 in the NaAlg matrix. Thus, the observed higher selectivity for 10 and 20 mass% MCM-41 loaded NaAlg membranes as compared to the pristine NaAlg membrane and 5 mass% MCM-41 loaded NaAlg membrane could be due to the combined effect of molecular sieving as well as the hydrophilic nature of molecular sieves incorporated into hydrophilic NaAlg matrix.

The decrease in selectivity for all the membranes with increasing water content of the feed depends upon the amount of filler added in the NaAlg matrix. For instance, with MCM-41 (5 mass%)-filled membrane, selectivity dropped from 689 for 10 mass% water to 26 for 50 mass% water, which is almost close to the value observed for pristine NaAlg membrane and by this, it is evident that with a lower amount of MCM-41 in NaAlg, very small amount of water molecules could pass through the pores of MCM-41. For MCM-41 (10 mass%)-filled membrane, selectivity improved greatly, i.e., the observed value is 29,991 for 10 mass% water in the feed, which dropped steeply to 41 for 50 mass% water in the feed. On the other hand, for the nanocomposite membrane containing 20 mass% of MCM-41, even though there was a slight improvement in flux, but selectivity values are quite higher over the entire range of feed mixture compositions. For instance, a value of $\alpha = 3332$ obtained

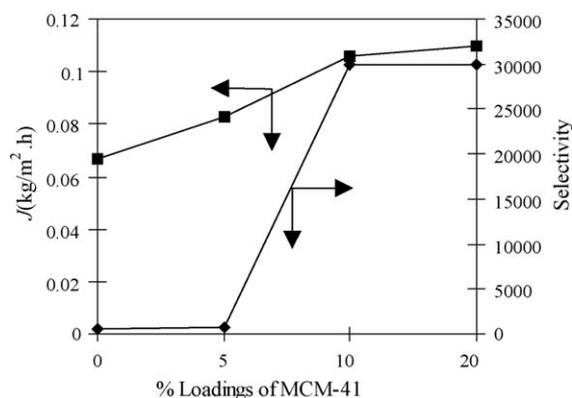


Fig. 8. Water flux and selectivity vs. %MCM-41 loadings (0, 5, 10 and 20 mass%) for 10 mass% of water in the feed.

with 20 mass% MCM-41 loaded NaAlg membrane at 50 mass% water in the feed is quite higher than that observed for 10 mass% MCM-41 loaded nanocomposite membrane for the same feed mixture composition. It is thus evident that the presence of higher amount of MCM-41 in the NaAlg membrane, higher number of water molecules would transport through the pores of MCM-41, thereby increasing its selectivity to water, but not for isopropanol.

3.6. Comparison of PV results with vapor–liquid equilibrium (VLE) data

Water/isopropanol has an azeotropic composition of 12.5 mass% of water. It is difficult to separate the mixture at this composition by the conventional distillation without using an entrainer, such as benzene, a deadly carcinogen. In contrast, PV has the advantage to separate azeotropes because vapor–liquid equilibrium is not the controlling mechanism while separating through membranes. However, in PV, a trade-off has to be achieved between flux and selectivity and balancing these factors is a challenging task. Therefore, in large-scale industrial applications of PV membranes, it is important to achieve a proper balance between flux and selectivity. In the present research, it is demonstrated that it is possible to increase simulta-

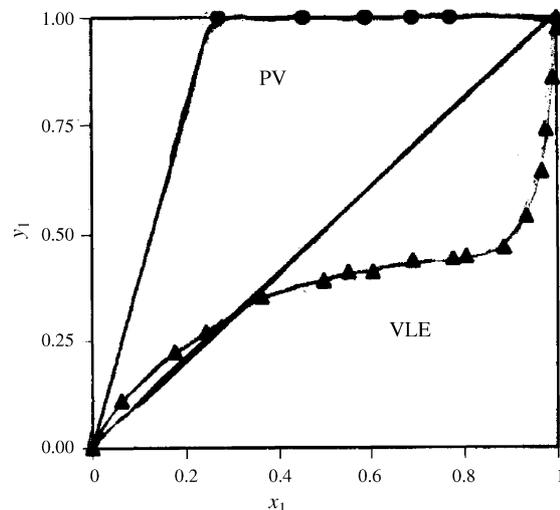


Fig. 9. Comparison of vapor–liquid equilibrium curve (▲) with PV data (●) for water + isopropanol mixture at 30 °C for MCM-41 (20 mass%)-filled NaAlg membrane.

neously both flux and selectivity to water by filling the membrane using MCM-41 nanoparticles. The results presented in Fig. 8 for 10 mass% water-containing feed display this effect. Therefore, in PV, membrane acts as a third phase to break the azeotrope and it saves the energy requirements.

Fig. 9 compares the results of water concentration obtained in permeate by PV (for 20 mass% MCM-41 loaded nanocomposite membrane) and that obtained in the vapor phase by VLE experiments for the feed mixtures of this study. Note that membrane selectivity is indeed very high, since permeate is primarily composed of water over the entire concentration range of the feed mixture [34].

3.7. Comparison of PV performance of the present membranes with the literature

Table 2 compares flux and selectivity data of the present membranes with those of the literature data. A comparison of all the membranes was made under similar feed conditions and tem-

Table 2
Comparison of PV performance of the present membranes with literature at 30 °C

Membrane	Mass% of water in feed	J (kg/(m ² h))	α	Reference
MCM-41 (10%)-filled NaAlg (40–50 μ m)	10	0.106	29991	Present work
MCM-41 (20%)-filled NaAlg (40–50 μ m)	10	0.110	29991	
NaAlg + 5% PVA + 10% PEG (40–50 μ m)	10	0.072	3591	Toti and Aminabhavi [26]
NaAlg-g-PAAm + 5% PVA + 10% PEG (at 20% water in the feed) (40–50 μ m)	10	0.091	96	
NaAlg (40–50 μ m)	10	0.058	411	Toti and Aminabhavi [21]
NaAlg/GG-g-PAAm (40–50 μ m)	10	0.062	796	
NaAlg/GG-g-PAAm (40–50 μ m)	10	0.043	891	
NaAlg/PVA (75:25) (40–50 μ m)	10	0.025	195	Kurkuri et al. [22]
NaAlg/PVA (50:50) (40–50 μ m)	10	0.034	119	
NaAlg/PVA (25:75) (40–50 μ m)	10	0.039	91	
Composite membrane of NaAlg and Chitosan (40–50 μ m)	10	0.055	2010	Moon et al. [27]

NaAlg, sodium alginate; PAAm, poly(acryl amide); PVA, poly(vinyl alcohol); PEG, poly(ethylene glycol).

perature. On comparison, we find that the present membranes offered the highest selectivity and flux values for water and hence, these could be effective in dehydrating isopropanol from aqueous streams.

4. Conclusion

Dehydration of organic solvents using hydrophilic pervaporation membranes is a well-established technology. In the present study, water permeates through both the molecular sieve and nonmolecular sieve pores because of its smaller size as indicated by its higher flux and selectivity values as compared to plain sodium alginate membrane. Compared to other studies in the literature on sodium alginate membranes to dehydrate isopropanol, flux and selectivity values of this study are much higher. The highest selectivity of water is 29,991 for both 10 and 20 mass% MCM-41 loaded sodium alginate membranes when tested for 10 mass% water in the feed. Flux of all the membranes increased with increasing water feed concentration, but selectivity decreased drastically for membranes with lower loadings of MCM-41 (<20 mass%). However, these trends are similar to those of swelling data. The precise pore structure of MCM-41 could be the possible reason (due to its molecular sieving effect) in simultaneously increasing selectivity and flux over the range of feed concentrations studied. The observed high PV performance of the MCM-41-filled membranes is due to capillary condensation of water molecules in the pores of the molecular sieves. Additionally, high selectivity could also be due to preferential sorption of water as a result of the differences in degree of swelling of the membranes. Repeated PV operations indicated that all membranes of this study are mechanically strong and chemically inert. The 20 mass% MCM-41 loaded hybrid nanocomposite membranes gave reasonably higher value of selectivity of 3332 even at 50 mass% water in the feed. MCM-41-filled membranes have distinct advantages of the uniform crystal sizes, leading to significantly higher separation efficiencies as compared to pristine sodium alginate membrane. However, detailed mechanistic interpretation of PV results requires a consideration of both true microcavity uptake as well as interstitially held water molecules between crystallites of the membrane matrix. Much research yet to be done in these areas to understand such problems, particularly choosing different molecular sieve-filled polymeric membranes.

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