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Hybrid composite membranes of sodium alginate for pervaporation dehydration of 1,4-dioxane and tetrahydrofuran*

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ABSTRACT

The study reports on the development of hybrid composite membranes of sodium alginate loaded with hydrophilic alumina-containing Mobile Composition Matter-41 i.e., Al-MCM-41 in different compositions from 3 to 10 wt.% that are used for pervaporation (PV) dehydration of 1,4-dioxane and tetrahydrofuran (THF) from aqueous mixtures in compositions of 10–40 wt.% at 30°C. The PV performance of the hybrid composite membranes was much superior to that of plain NaAlg membrane in terms of selectivity and flux due to increased hydrophilicity of NaAlg membrane in the presence of Al-MCM-41 mesoporous zeolite particles that are also hydrophilic. Membranes crosslinked with glutaraldehyde were characterised by ion exchange capacity, Fourier Transform spectroscopy and X-ray diffraction. Morphology of the membranes was assessed by scanning electron microscopy. Sorption studies have been performed to evaluate the extent of interaction and degree of swelling of the membranes with pure and mixed feed aqueous mixtures of 1,4-dioxane and THF. It is observed that flux and selectivity increased systematically with increasing amount of Al-MCM-41 particles in the NaAlg matrix. In case of hybrid composite membrane containing 10 wt.% Al-MCM-41, selectivity for water was infinity, which was attributed to the combined effects of molecular adhesion between particle surfaces and NaAlg matrix as well as higher selectivity of the composite membrane when compared to plain NaAlg membrane.

Keywords: Pervaporation; Dehydration; Sodium alginate; Al-MCM-41; Hybrid membranes

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1. Introduction

Pervaporation (PV) separation has been the widely used method for separating aqueous-organic azeotropes [1–4]. In this method, chemical structure and physical nature of dense membranes have an effect on membrane performance and recent research efforts are moving towards developing mixed composite membranes to obtain better mechanical strength and separation performance over plain membranes. In previous literature, several hybrid composite membranes loaded with inorganic zeolite particles have been developed and used for dehydrating organics [5–14]. Separation using zeolite-filled PV membranes occurs by adsorption–desorption and molecular sieving effects due to the presence of small particles [15]. Aminabhavi et al. [16–22] used different fillers to develop mixed matrix membranes of sodium alginate (NaAlg) for PV dehydration of organic liquids. Particularly, MCM-41 have periodic mesostructures with pore sizes ranging from 2 to 10 nm and attempts were made to incorporate these as fillers into polymeric matrices to derive improved membrane performance over plain polymeric membranes [23].

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As a part of our ongoing program of research on developing PV membranes, we report here the preparation of hybrid composite NaAlg membranes by incorporating with Al-MCM-41 zeolite particles to boost membrane performance over that of plain NaAlg membranes. Earlier to this report, MCM-41 incorporated polysulfone membranes [23] and nanocomposite membranes of silylated MCM-48 filled poly(vinyl acetate) [24] were used in gas separation. MCM-41 has the unique compositional and morphological flexibility with a pore diameter of around 2–3 nm and surface area of >1000 m^2/g [25] formed by the condensation of silica around self-assembled arrays of surfactant molecules in aqueous gel. MCM-41 is a hydrophilic zeolite, used rarely in developing PV membranes for the separation of water-organic mixtures. In our previous study, Al-MCM-41-loaded NaAlg membranes were developed for the first time in PV separation of water-isopropanol and water-ethanol mixtures [26]. We now extend these studies for the PV dehydration of 1,4-dioxane and THF, since these are widely encountered solvents in chemical and pharmaceutical industries and can form azeotropes at 18.1 and 6.7 wt% of water, respectively. By incorporating Al-CM-41 particles into NaAlg resulted in hybrid composite membranes that are quite efficient to selectively remove water from feeds containing 1,4-dioxane or tetrahydrofuran (THF). Effect of feed water composition and extent of filler loadings have been investigated in relation to PV separation of the aqueous mixtures of 1,4-dioxane and THF.

2. Experimental

2.1. Materials and methods

Sodium alginate, 1,4-dioxane, THF, glutaraldehyde (GA) and hydrochloric acid (HCl) of reagent grade samples were all purchased from S.D. Fine Chemicals (Mumbai, India). Deionized water, having a conductivity of 20 μS/cm, was produced in the laboratory itself from the Permeonics pilot plant (Vadodara, India) using the nanofiltration membrane module.

2.2. Particle size measurement of Al-MCM-41

Particle size was measured by a Zetasizer (Model 3000HS, Malvern, UK). The sizes of the completely dried Al-MCM-41 particles were measured by the wet sample technique using a wet sample adapter. Particles were dispersed in water and placed on a sample couvette and zeta average diameter was recorded. After measurement of particle size, the sample couvette was cleaned thoroughly to avoid cross contamination. Particle size was measured in triplicate, but average value was considered in data analysis.

2.3. Membrane fabrication

Al-containing mesoporous silica viz., Al-MCM-41 was synthesized by the hydrothermal treatment of aluminosilicate precursor and mixed with a surfactant, cetyltrimethylammonium bromide, following the procedure described previously [26]. NaAlg of high viscosity grade was dissolved in distilled water to prepare 4 wt.% solution at 30°C by stirring for 24 h to obtain homogeneity. After the removal of insoluble impurities using a glass filter, it was stirred for another 1 h at 30°. The NaAlg membrane was prepared by pouring the casting solution onto a glass plate. The solvent was allowed to evaporate completely at 50°C for 24 h; after complete drying, the membrane was peeled off.

Sodium alginate (4 g) taken in 80 mL of water was stirred vigorously until the solution became homogeneous. Known weights of Al-MCM-41 particles (i.e., 3, 6 and 10 wt.% with respect to weight of NaAlg) were dispersed in 20 mL of water, sonicated for 120 min and added to the above prepared NaAlg solution. The whole mixture was stirred for about 24 h to obtain a homogeneous solution, which was poured on a completely cleaned dry glass plate with the help of doctor's knife to form membranes of uniform thickness. The caste membranes were kept at ambient temperature for drying; the dried membranes were peeled off from the glass plate and immersed in a crosslinking bath containing (30:70) water: methanol mixture along with the solution of 2.5 mL of GA and 2.5 mL of conc. HCl as an acid catalyst. After allowing for 6 h, the crosslinked membranes were removed from the bath, washed repeatedly with deionized water and dried in an oven at 40°C. The hybrid composite membranes are designated as NaAlg/Al-MCM-41 (3 wt.%), NaAlg/Al-MCM-41 (6 wt.%) and NaAlg/Al-MCM-41 (10 wt.%), respectively that contained 3, 6 and 10 wt.% of Al-MCM-41.

Plain NaAlg membrane was also prepared by crosslinking with a solution of 2.5 mL GA and 2.5 mL of conc. HCl for about 6 h. Membrane thickness as measured by the thickness dial gauge is around 60±1.0 μm. It was found that zeolite loading had a significant influence on the uniformity of membranes. The hybrid composite membranes formed were homogeneous at 3, 6 and 10 wt.% loadings of the filler. The plain NaAlg (crosslinked) membrane is designated as NaAlg. It is important to note that for mixed matrix membranes with the incorporation of more than 10 wt.% of Al-MCM-41, phase segregation was observed and membranes were brittle, which could not be employed in PV experiments.

2.4. Scanning electron microscopy

SEM micrographs of the plain NaAlg and NaAlg/Al-MCM-41 hybrid composite membranes containing

3 wt.% of Al-MCM-41 particles were taken to see the distribution of Al-MCM-41 particles in the NaAlg matrix. Membranes were sputtered with gold coating to make them conducting and placed on a copper stub. Scanning was done using a JEOL model JSM-840A (Japan), available at UT Southwestern Medical Center, Dallas, TX, USA. (courtesy of Dr. N.N. Mallikarjuna and Professor P.V. Kulkarni). The thickness of the gold layer accomplished by gold sputtering was about 15 nm.

2.5. FTIR

Membrane samples were ground well with KBr to make pellets using a hydraulic pressure of 400–450 kg/cm^2. FTIR spectra were taken for NaAlg, before and after crosslinking, using a Nicolet-740 and Perkins-Elmer-283B (Milawaukee, WI, USA) FTIR spectrophotometers. Membranes were scanned to confirm the crosslinking of NaAlg with GA.

2.6. X-ray diffraction (XRD)

A siemens D 5000 (Germany) powder X-ray diffractometer was used to study the solid-state morphology of the membrane with and without Al-MCM-41 loading. X-ray diffractograms were recorded for Al-MCM-41 particles, Al-MCM-41loaded NaAlg hybrid composite membrane and plain NaAlg. The X-ray of 1.5406 Å wavelength was generated by a CuK$_\alpha$ source. The angle of diffraction, 2θ, was varied from 0° to 50° to identify any changes in the crystalline domains.

2.7. Pervaporation experiments

PV experiments were performed on 100 mL batch level instrument with an indigenously constructed manifold operated at a vacuum level of 0.05 mmHg in the permeate line. The effective membrane area was 20 cm^2 and weight of the feed mixture taken in the PV cell was 70 g. Temperature of the feed mixture was maintained constant by a thermostatic water jacket. Before starting the PV experiment, test membrane was equilibrated for about 2 to 4 h with the feed mixture. After establishment of steady state, permeate vapors were collected in cold traps immersed in liquid nitrogen for up to 4–5 h. The weight of permeate collected was measured using a Mettler balance (model B 204-S, Greifensee, Switzerland: accuracy 10^{-4} g) to determine flux, J (kg.m^{-2}h^{-1}) using weight of liquids permeated, W (kg), effective membrane area, A (m^2) and measurement time, t (h) as:

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

The analysis of feed and permeate samples was done using a Nucon gas chromatograph (model 5765, Mumbai, India) equipped with a thermal conductivity detector and DEGS or Tenax packed column of 1/8" ID of 2 m in length. Oven temperature was maintained at 70°C (isothermal), while injector and detector temperatures were maintained at 150°C. The sample injection volume was 1 μL. Pure hydrogen was used as the carrier gas at 0.75 kg/cm^2 pressure. The GC response was calibrated for column and for known compositions of water with 1,4-dioxane or THF mixtures. Calibration factors were fed into GC software to obtain the analysis for unknown samples. The selectivity, α and separation index, *PSI*, were calculated as:

$$\alpha=\left(\frac{P_\mathrm{A}}{1-P_\mathrm{A}}\right)\left(\frac{1-F_\mathrm{A}}{F_\mathrm{A}}\right) \tag{2}$$

$$PSI=J(\alpha-1) \tag{3}$$

where F_A is weight % of water in feed and P_A is weight % of water in permeate. A minimum of three independent readings on flux and α were taken under similar conditions of temperature and feed compositions to confirm steady-state pervaporation.

2.8. Degree of swelling

Swelling experiments were performed gravimetrically on all membranes in 10, 20 and 30 wt.% water-containing feed mixtures at 30°C as per the procedure published before [27]. Initial weights of the circularly cut (dia = 2.5 cm) NaAlg and Al-MCM-41 incorporated NaAlg hybrid composite membranes were taken on a single-pan digital microbalance (model AE 240, Mettler, Switzerland) to an accuracy of ±0.01 mg. Samples were placed inside the specially designed airtight test bottles containing 30 cm^3 of the test media. Test bottles were transferred to an oven maintained at a constant desired temperature. Dry membranes were equilibrated by soaking in different compositions of feed mixtures in a sealed vessel at 30°C for 48 h. The swollen membranes were weighed immediately after carefully blotting them in between soft filter paper wrappings. The % degree of swelling, *DS*, was calculated as:

$$DS=\left(\frac{W_\infty-W_0}{W_0}\right)\times 100 \tag{4}$$

where W_∞ and W_0 are the weights of swollen and dry membranes, respectively.

2.9. Ion-exchange capacity (IEC)

In order to determine the effect of crosslinking, ion exchange capacity (*IEC*) of the polymer was estimated. *IEC* indicates the number of groups present before and after crosslinking. This gives an idea of the extent of crosslinking. In reality, *IEC* indicates the number of milliequivalents of ions in 1 g of dry polymer. To determine *IEC*, specimens of similar weight were soaked in 50 mL of 0.1N sodium hydroxide solution for about 12 h at the ambient temperature. Then, 10 mL of this per sample solution was titrated with 0.1 N sulfuric acid. The sample was regenerated with 1 N hydrochloric acid, washed and dried until constant weight. Then, *IEC* was calculated as [28]:

$$IEC=\left(\frac{(B-P)\times 0.1\times 5}{m}\right) \tag{5}$$

where B is sulfuric acid used to neutralize the blank sample, P is sulfuric acid used to neutralize the PV membrane, 0.1 is normality of sulfuric acid, number 5 represents the factor corresponding to the ratio of the amount of NaOH taken to dissolve the polymer to the amount used for titration and m represents the sample mass (g).

3. Results and discussion

3.1. Physical structure of the NaAlg/Al-MCM-41 hybrid membrane

XRD measurements were performed to understand the crystalline nature of Al-MCM-41 as well as the composite membranes. Fig. 1 (curve a) displays the crystalline nature of Al-MCM-41 powder, which shows a sharp peak around 2θ of 1–3°. Fig. 1 (curve b) is the X-ray diffractogram of the Al-MCM-41 (3 wt.%) loaded NaAlg hybrid composite membrane, which shows small peaks, indicating the homogeneous dispersion of Al-MCM-41 particles into the NaAlg matrix. However, in case of Fig. 1 (curve C) at 2θ= 40°, it is partly crystalline and amorphous due to pristine NaAlg matrix. These peaks are not seen when Al-MCM-41 is added to the polymeric matrix due to the increase of the amorphous nature and decrease of the crystalline nature of the polymeric matrix (Fig. 1, curve b).

Fig. 2 displays the surface SEM micrographs of both plain NaAlg membrane and NaAlg/Al-MCM-41 hybrid composite membrane containing 3 wt.% Al-MCM-41 particles. The hybrid composite membrane has shown uniform distribution of Al-MCM-41 particles on its surface, giving a contrast from SEM micrograph of the plain NaAlg membrane. The particles of Al-MCM-41 are spherical with sizes varying between 500 and 1000 nm as

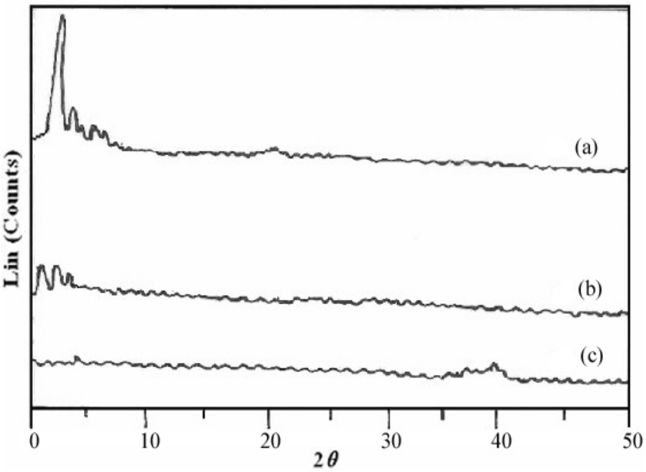

Fig. 1. X-RD curves of (a) Al-MCM-41 particles, (b) NaAlg/Al-MCM-41(3 wt.%) and (c) plain NaAlg membrane.

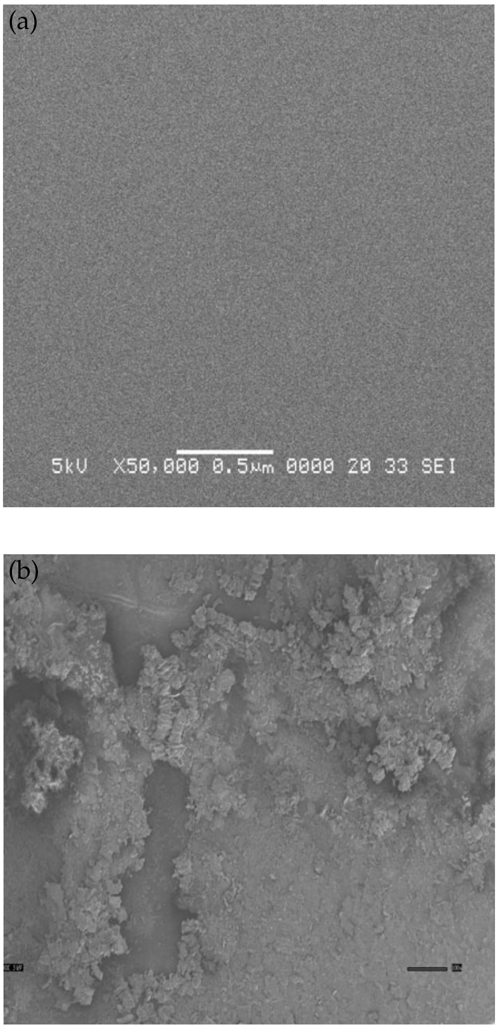

Fig. 2. SEM micrographs of (a) plain NaAlg and (b) NaAlg Al-MCM-41 (3 wt.%) membrane.

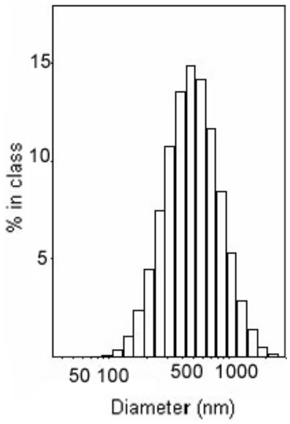

Fig. 3. Particle size distribution histogram of Al-MCM-41.

evidenced by the histogram plot of zetasizer as shown in Fig. 3.

3.2. *Ion-exchange capacity (IEC)*

The amount of residual hydroxyl groups present after crosslinking was estimated from IEC studies. Notice that the uncrosslinked NaAlg membrane had an IEC of 2.0519 meq/g, whereas the crosslinked NaAlg membrane exhibited an IECof 0.684 meq/g. The IEC, which is equivalent to the total number of free hydroxyl groups, has decreased after crosslinking [28], i.e., almost 60% of hydroxyl groups present in the uncrosslinked membranes are crosslinked with glutaraldehyde. However, there may be still some extra hydroxyl groups left for selective sorption and allow the diffusion of water molecules through hybrid composite membrane.

3.3. *FTIR*

Fig. 4 shows the FTIR spectra of crosslinked and uncrosslinked membranes. Curve (a) of Fig. 4 exhibits a peak at 3420 cm^{-1}, which corresponds to O-H stretching vibrations of NaAlg; curve (b) at 1620 cm^{-1} has a broad band, which refers to carboxyl groups of –COONa of NaAlg. In curve (b), the peak observed at 3420 cm^{-1} confirms the utilization of O-H groups of NaAlg during crosslinking reaction. A sharp peak at 1100 cm^{-1} refers to C-O-C stretching vibration due to crosslinking reaction.

3.4. *Pervaporation performance*

Flux and selectivity of all the membranes for both feed mixtures summarized in Table 1 indicate an increase with increasing loading of Al-MCM-41 into NaAlg matrix. In all the cases, except the 10 wt% Al-MCM-41 loaded NaAlg composite membrane, at higher water concentration of the feed, selectivity decreased and the infinite selectivity is attributed to polymer-filler contact and the adhesion. The present results follow the adsorption–diffusion–desorption principles for separation to take place due to the selective adsorption of water onto hydrophilic Al-MCM-41 particles. Since organic components did not cross through the membrane, they were retained in the feed. Flux increases due to an increase in the driving force for permeation. This effect is quite favorable for water transport since water molecules tend to occupy free channels of the hydrophilic molecular sieves in the composite membranes. This explains the marked increase in selectivity to infinity with a recovery of 100 wt.% water on permeate side. Composite membranes of this study are thus highly water selective due to small differences in molecular sieve compositions.

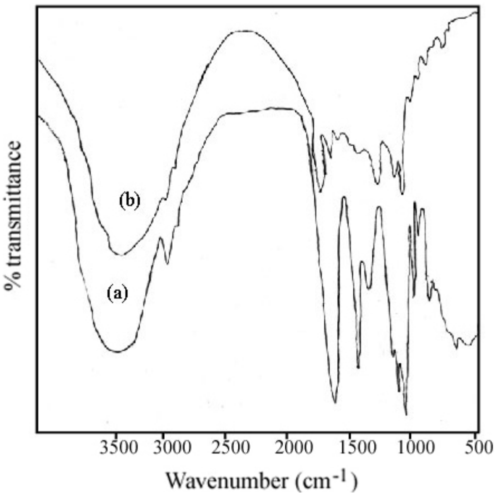

Fig. 4. FTIR tracings of (a) uncrosslinked NaAlg and (b) NaAlg /Al-MCM-41 (3 wt%) crosslinked NaAlg membranes.

Permeation flux of all the composite membranes is higher than that of the plain NaAlg membrane with an increasing amount of water in the feed. Flux ranged between 0.127 and 0.502 kg/m^2.h for 1,4-dioxane while for water–THF mixtures, flux ranged from 0.736 kg/m^2.h–0.334 kg/m^2.h. This indicates that due to the addition of Al-MCM-41 particles into NaAlg matrix, the separation characteristics of composite membranes improved considerably over that of plain NaAlg membrane.

In the present investigation, both permeation flux and selectivity values increased simultaneously with an increasing amount of Al-MCM-41 in NaAlg matrix. This is due to the fact that alumina of the zeolite will enhance hydrophilicity of the hybrid composite membranes. Additionally, the presence of zeolite particles creates free channels in the composite matrix, thus preferentially allowing water to transport through the membrane. Notice that for both 1,4-dioxane and THF dehydrations, complete removal of water on permeate side was possible with hybrid composite membrane containing 10 wt.%

Al-MCH-41. However, in case of water–1,4-dioxane, fluxes are smaller, while selectivities are higher than those observed for water–THF mixtures. For the plain NaAlg membrane, flux and selectivity for aqueous mixtures of THF are higher than those of 1,4-dioxane.

Table 1
Flux and selectivity data of water–1,4-dioxane and water–THF feed mixtures at 30°C

Wt. % of water in feed	Wt. % of water in permeate	Flux (kg/m^2.h)	α
A. Water-1,4-Dioxane			
Plain NaAlg membrane			
10	96.8	0.111	268
15	92.1	0.131	103
20	91.71	0.143	49
30	91.5	0.151	32
40	90.1	0.169	17
NaAlg/Al-MCM-41 (3 wt.%)			
10	99.6	0.127	2477
15	99.5	0.142	1052
20	98.9	0.156	375
30	98.6	0.166	164
40	97.7	0.192	65
NaAlg/Al-MCM-41 (6 wt.%)			
10	99.9	0.227	8173
15	99.6	0.243	1560
20	99.3	0.26	560
30	98.9	0.28	219
40	98.6	0.32	105
NaAlg/Al-MCM-41 (10 wt.%)			
10	100	0.301	∞
15	100	0.322	∞
20	100	0.367	∞
30	100	0.467	∞
40	100	0.502	∞
B. Water–THF			
Plain NaAlg membrane			
10	98.02	0.131	619
15	97.03	0.154	280
20	96.9	0.174	201
30	94.8	0.192	87
40	94	0.224	36
NaAlg/Al-MCM-41 (3 wt.%)			
10	99.3	0.334	1489
15	99	0.337	159
20	98.2	0.341	219
30	97.9	0.356	107
40	97	0.495	48
NaAlg/Al-MCM-41 (6 wt.%)			
10	99.4	0.439	1537
15	99.07	0.456	604
20	98.7	0.497	309
30	98.2	0.619	128
40	97.5	0.649	59
NaAlg/Al-MCM-41 (10 wt.%)			
10	100	0.461	∞
15	100	0.495	∞
20	100	0.527	∞
30	100	0.684	∞
40	100	0.736	∞

3.5. *Effect of feed composition*

The PV results presented in Table 1 vary depending upon the composition of water of the feed for both plain and hybrid mixed membranes. Flux and selectivity for water–1,4-dioxane and water–THF feed mixtures are displayed, respectively, in Figs. 5 and 6. Notice that selectivity for the 10 wt.% Al-MCM-41 loaded NaAlg membrane is not presented due to infinite value. Also, flux and selectivity increased for both the feed mixtures with increasing concentration of water. NaAlg is highly hydrophilic and so is Al-MCM-41. Thus the matrix NaAlg/Al-MCM-41 membranes would transport more of water than either of the organic components due to hydrophilic–hydrophilic interactions.

For 10 wt.% water containing feed mixture, selectivity to water is quite high for all the membranes. For instance, a value of 268 for pure NaAlg increased to infinity for hybrid composite membrane containing 10 wt.% of Al-MCM-41. With increasing wt.% of water in the feed, selectivity decreased drastically. On the other hand, for 15 wt.% water-containing feed, selectivities dropped to almost half the original values with plain NaAlg as well as the 3 wt.% Al-MCM-41 loaded hybrid composite membrane. However, in the case of the hybrid composite membrane loaded with 6 wt.% of Al-MCM-41, selectivity for 15 wt.% water-containing feed mixture dropped nearly five-fold. With a subsequent increase in water composition of the feed, i.e., up to 40% of water, selectivity dropped considerably. The infinite values of selectivity were observed for the 10 wt.% Al-MCM-41 loaded composite membrane at all compositions of water in the feed, and hence membrane performance might have been affected by the extent of Al-MCM-41 particles present in the NaAlg matrix.

In case of water–THF feed mixtures, similar trends are observed as those of the water–1,4-dioxane mixtures. However, differences in the interaction parameters and thermodynamic properties of water–THF as compared to water–1,4-dioxane, flux and selectivity values are higher for water–THF than for water–1,4-dioxane. At 10 wt.% water in the feed, selectivities for NaAlg, NaAlg/Al-MCM-41 (3 wt.%), NaAlg/Al-MCM-41 (6 wt.%) and NaAlg/Al-MCM-41 (10 wt.%) membranes are, respectively, 619, 1489, 1537 and infinity, while their fluxes are 0.131, 0.334, 0.439 and 0.461 kg/m^2.h. With increasing water content of the feed mixture, flux increased, but

0.131, 0.334, 0.439 and 0.461 kg/m^2.h. With increasing

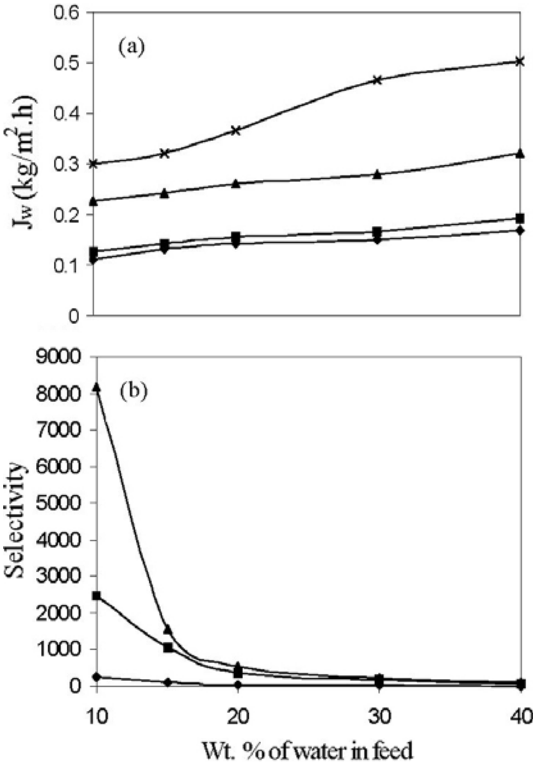

Fig. 5. Flux and selectivity of water–1,4-dioxane feed for (♦) plain NaAlg, (■) NaAlg/Al-MCM-41(3 wt.%) and (▲) NaAlg/Al-MCM-41 (6 wt.%) and (×) NaAlg/Al-MCM-41 (10 wt.%) membranes.

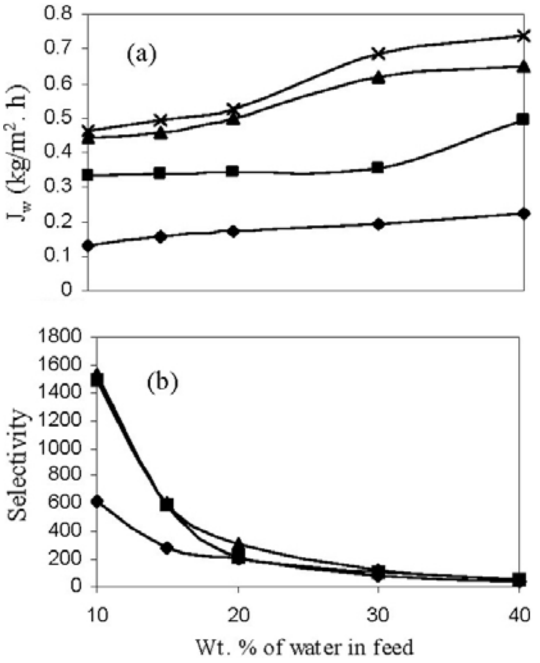

Fig. 6. Flux and selectivity of water–THF feed for (♦) plain NaAlg, (■) NaAlg/Al-MCM-41 (3 wt.%) (▲) NaAlg/Al-MCM-41 (6 wt.%) and (×) NaAlg/Al-MCM-41 (10 wt.%) membranes.

water content of the feed mixture, flux increased, but selectivity decreased for all the membranes. By increasing the filler content up to 10 wt.% of MCM-41 in the NaAlg membrane, infinite value for selectivity was observed for all compositions, i.e., 10–40 wt.% of water in the feed. These results are displayed in Fig. 6 (curve a) and (curve b).

Both flux and selectivity for water increased simultaneously by increasing the filler content in NaAlg membrane. These effects are demonstrated in Fig. 7 (curves a and b) for 10 wt.% water-containing feed mixtures for both the feeds. The mass transport through membrane is a complex phenomenon because the interaction between liquid feed components and the membrane would result in membrane swelling affecting the PV data. Fig. 8 (curves a and b) compares the plots of %degree of swelling of plain NaAlg and Al-MCM-41 loaded NaAlg hybrid composite membranes at 30°C for 10–40 wt.% water containing feeds of 1,4-dioxane and THF. Notice that membranes are swollen to a lesser extent in water-1,4-dioxane than in water–THF feeds due to stronger interactions (hydrogen bond type) between THF and water than between 1,4-dioxane and water. For both the feed mixtures, initially, swelling increased with increasing amount of the filler particles. Also, Al-MCM-41-incorporated NaAlg membranes were swollen to a greater extent in both the feeds mixtures than the plain NaAlg membrane.

For the 3 wt.% Al-MCM-41-loaded NaAlg membrane, the % DS was higher than observed for the plain crosslinked NaAlg membrane. For 10 wt.% Al-MCM-41

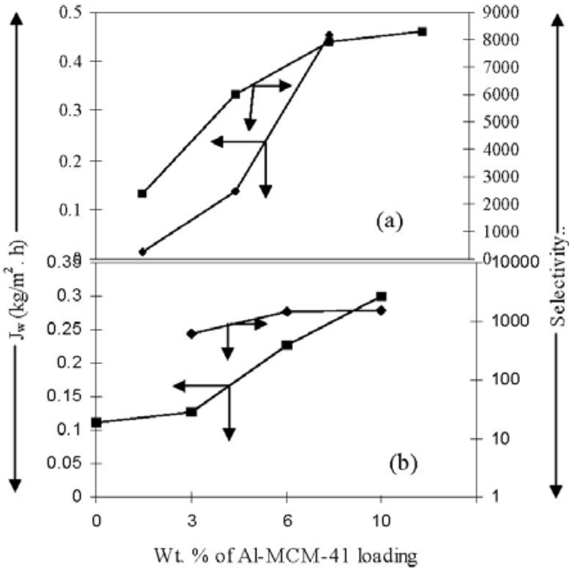

Fig. 7. Flux (■) and selectivity (♦) data at 10 wt.% of water in the feed vs. wt.% loadings of Al-MCM-41 in NaAlg for (a) water–1,4-dioxane and (b) water–THF feed mixtures.

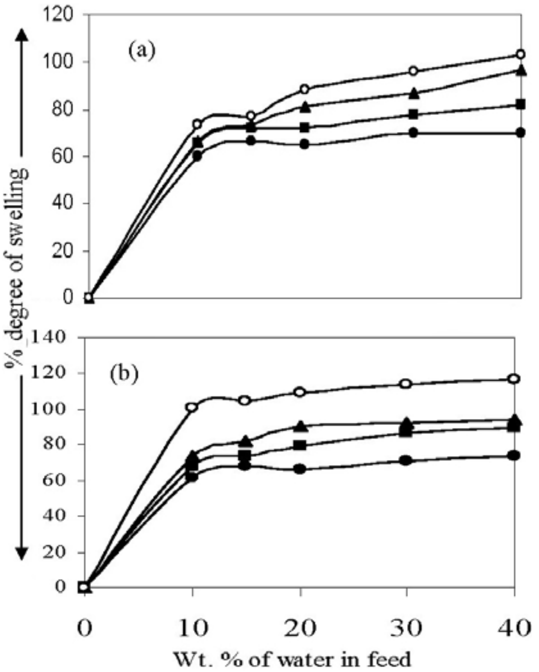

Fig. 8. Swelling curves of (●) plain NaAlg, (■) NaAlg/Al-MCM-41 (3 wt.%) and (▲) NaAlg/Al-MCM-41 (6 wt.%) and (○) NaAlg/Al-MCM-41 (10 wt.%) for (a) water–1,4-dioxane and (b) water–THF feed mixtures.

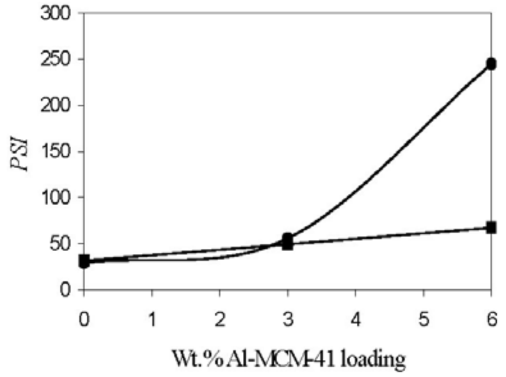

Fig. 9. PSI curves for 10 wt.% water containing feeds (●) water–1,4-dioxane and (■) water–THF mixtures.

containing membrane, the % DS was highest of all the membranes due to increased hydrophilicity of hybrid composite membranes. The filler particles would occupy the free volume spaces in the NaAlg matrix that otherwise would have been held by hydroxyl groups of NaAlg. The free volume inside the membrane may be in the form of static holes (unfilled spaces) or can be created or destroyed as a result of molecular motions (dynamic free volumes) of the polymer chains. Principally, there are two mechanistic models that influence the PV results: (1) the solution–diffusion model and (2) the pore-flow model. The former is widely accepted and the present PV results can be explained by the solution–diffusion concepts. With increasing concentration of Al-MCM-41, the NaAlg membrane would absorb large amounts of water because the adsorption of water also takes place in the porous structure of Al-MCM-41 particles. Hence, the overall uptake of water by the membrane is enhanced.

3.7. Pervaporation separation index (PSI)

Fig. 9 displays the variation of PSI with the extent of loading Al-MCM-41 in the NaAlg membrane at 30°C for 10 wt.% water-containing feed. The PSI values increased linearly with increasing Al-MCM-41 content, signifying that membranes that contained a higher amount of filler would show improved PV performance for both water–1,4-dioxane and water THF–feed water mixtures. The incorporation of Al-MCM-41 particles into the NaAlg membrane would not only affect membrane hydrophilicity, but also its rigidity. Thus, increased hydrophilic–hydrophilic interactions between Al-MCM-41 and NaAlg exert a significant effect on diffusion of water through composite membranes by retaining organic components on the feed side.

4. Comparison of present PV data with literature

A comparison of PV data with literature results presented in Tables 2 and 3, respectively, for water–1,4-

Table 2
Literature comparison of PV dehydration data for different types of NaAlg-based membranes with 10 wt.% water in 1,4-dioxane at 30°C

Membrane type	Flux, *J* (kg/m^2.h)	α	Ref.
Plain/blends/grafted NaAlg membranes			
NaAlg/Al-MCM-41 (10 wt. %)	0.300	∞	Present work
5 wt. % PVA + 95 wt. % NaAlg blend	NA	63	[29]
pAAm-*g*-NaAlg	0.075	83	[30]
Dense NaAlg membrane[a]	0.305	1,898	[31]
NaAlg (GA + UFS crosslinked)	0.092	268	[32]
NaAlg-HEC-5 blend	0.085	60	[32]
Mixed matrix membranes of NaAlg			
SBA-15 (10 wt. %)-filled NaAlg	0.04	∞	[17]
Fe-SBA-15 (10 wt. %)-filled NaAlg	0.049	∞	[17]
Na^+MMT (10 wt. %) filled NaAlg	0.089	∞	[18]
$AlPO_4$-5 (20 wt. %)-filled NaAlg[b]	0.103	45,244	[19]

NA, not available; PVA, poly(vinyl alcohol); pAAm, polyacrylamide; HECm hydroxyethylcellulose; GA, glutaraldehyde; UFS, urea-formaldehyde sulfuric acid; $AlPO_4$-5, alumino-phosphate
[a] 5 wt.% of water in the feed at 60°C.
[b] 18.1 wt.% of water in the feed.

Table 3
Literature comparison of PV dehydration data for different types of NaAlg-based membranes with 10 wt.% water in THF dehydration at 30 °C

Membrane type	Flux, *J* (kg/m^2.h)	α	Ref.
Plain/blends/grafted NaAlg membranes			
NaAlg/Al-MCM-41 (10 wt. %)	0.131	∞	Present work
5 wt. % PVA + 95 wt. % NaAlg blend	NA	216	[29]
pAAm-*g*-NaAlg	0.012	303	[30]
Dense NaAlg membrane[a]	0.36	∞	[31]
NaAlg-HEC-10 (GA + UFS crosslinked)	0.15	1,516	[32]
PHEMA (20 wt. %)- NaAlg[c]	0.034	857	[11]
Mixed matrix membranes of NaAlg			
Na$^+$MMT (10 wt.%) filled NaAlg	0.118	∞	[18]
$AlPO_4$-5 (20 wt. %)-filled NaAlg)[b]	0.110	19,879	[19]

NA, not available; PHEMA, poly(hydroxyethylmethacrylate)

[a] 5 wt.% of water in the feed at 55 °C.
[b] 6.7 wt.% of water in the feed.
[c] 5 wt.% of water in the feed.

dioxane and water–THF mixtures suggest that the present membranes are better in extracting 100% of water on the permeate line than the published data for other types of NaAlg-based membranes.

5. Conclusions

To improve membrane performance, one can generally follow two distinct strategies, i.e., either to synthesize new polymers with specific chemical architectures or to modify the existing polymers by incorporating suitable fillers. This paper reports results obtained according to the latter route. It is realized from the literature that fillers like zeolites can improve separation properties of membranes, provided that appropriate zeolite and polymer combinations are chosen. The mesoporous Al-MCM-41 zeolite-filled NaAlg hybrid composite membranes of this study had not been previously reported in the literature. The novel hybrid composite membranes studied here were effective in PV dehydration of 1,4-dioxane and THF.

The addition of even a small amount of Al-MCM-41 particles into NaAlg membranes has improved both flux and selectivity to water over that of the plain NaAlg membrane. Such improvements are attributed to hydrophilic nature of Al-MCM-41 particles, whose addition to another hydrophilic polymer like NaAlg greatly improved the overall membrane performance.

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