ISSN: 2230-9926

Available online at http://www.journalijdr.com

IJDR

International Journal of Development Research
Vol. 5, Issue, 10, pp. 5736-5742, October, 2015

International Journal of
DEVELOPMENT RESEARCH

Full Length Research Article

PHOSPHOTUNGSTIC ACID LOADED SODIUM ALGINATE MEMBRANES FOR ENHANCED PERVAPORATIVE DEHYDRATION OF ISOPROPANOL

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ARTICLE INFO

Article History:
Received 30th July, 2015
Received in revised form
22nd August, 2015
Accepted 01st September, 2015
Published online 31st October, 2015

Key Words:
Pervaporation,
Phosphotungstic acid,
Sodium alginate,
Water-Isopropanol,
Membranes.

ABSTRACT

The Plain sodium alginate (NaAlg) and 5 wt % and 10 wt % phosphotungstic acid(PWA) incorporated NaAlg membranes have been fabricated by solution casting followed by solvent evaporation. The membranes formed were crosslinked with glutaraldehyde and tested for PV dehydration of isopropanol from their aqueous feed mixtures at water concentrations (5, 10, 15 and 25 wt %) at 30◦C. The crosslinking reaction was confirmed by Fourier transform infrared (FTIR) measurements. The selectivities of isopropanol - water feed mixtures were 1689 and 2134 with fluxes of 0.2283 and 0.2274 kg/m^2 h for 10 wt % water in the feed mixture for filled membranes containing 5 wt % and 10 wt % of (PWA) particles respectively. Flux data also improved considerably for both the feeds. However, the virgin crosslinked NaAlg membrane has selectivity and flux values of 653 and 0.067 kg/m^2 h, respectively, for Isopropanol – water, when tested for 10 wt % water containing feed. It is demonstrated that addition of PWA particles as fillers into the NaAlg matrix has improved both flux and selectivity values over that of the crosslinked virgin NaAlg membrane. Such improvements in the selective nature of the filled matrix membranes are attributed to the water absorbing capacity of the PWA particles.

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INTRODUCTION

Separation of water/organic liquid mixtures is one of the most important and difficult processes in the chemical industry. Traditional azeotropic distillation and extractive distillation are two techniques of choice for carrying out the separation. However, these techniques have many problems such as, process complexity, large equipment investment and high energy consumption. Pervaporation (PV) is an efficient membrane based process and has gained acceptance by chemical industries over the years because of its favorable economics, easy maintenance and simplicity of the process (Chapmann *et al*., 2008 and Huang, 2006). Therefore, much of the attention has now been focused towards the development of new robust membranes with better performance. As an account of this organic-inorganic hybrid materials have attracted considerable attention and popularly termed as mixed matrix membranes (MMS) materials (Peng, 2006; Sudhakar, 2011; Sajankumarji Rao, 2014 and Lokesh *et al*., 2008).

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Such hybrid membranes are typically composed of polymeric and inorganic materials in which inorganic fillers with specific physico-chemical characteristics are specially dispersed into a bulk of the polymeric membranes. This seems to be a facial and feasible solution to have a good flux and high selectivity with desirable mechanical properties of inorganic materials and tenable flexibility with an excellent processability of polymeric materials (Lokesh, 2008).

Among the family of polysaccharides, NaAlg has been the most widely used polymer in fabricating PV separation membranes in addition to its usage in drug delivery (Okuno, 1992; Zhang *et al*., 1997; Chanachi, 2000; Cao, 2000 and Soppimath, 2001). NaAlg is water-soluble having good membrane forming properties; it can be readily crosslinked with glutaraldehyde or Ca^{2+} ions. Alginate is a linear chain structure of (1–4)-linked β-D-mannuronic acid (M) and α-L-guluronic acid (G) residues arranged in a blockwise fashion. These blocks are constructed in three different ways: homopolymeric MM blocks, homopolymeric GG blocks and heteropolymeric sequentially alternating MG blocks (Fischer *et al*., 1955; Haung, 1966). The presence of α-L-guluronic acid in various ratios and molecular weight alters physico-chemical

properties of the polymer (Moe, 1995). In the previous literature, NaAlg is known to have PV performances that exceed those of poly(viny1 alcohol) (PVA) (Huang *et al*., 1991), ion-exchange resins (Tsuyumoto, 1991) as well as other polysaccharides with similar chemical structures such as chitosan (Ugarami, 1990) and cellulose (Neel, 1986). This prompted the other to choose NaAlg as a polymer to fabricate membrane for this particular separation study.

Phosphotungstic acid (PWA) has been the rarely studied filler (Kim, 2008 and Lakshminarayana, Nogami, 2009), in developing mixed matrix membranes (MMMs). However the potential interactions between PWA and the host polymer would be responsible to achieve extraordinary separation performance of membrane. The PWA consists of Keggin unit as a primary structure, i.e., the polyanion $[PW_{12}O_{40}]^{3-}$, and a secondary structure, i.e., a regular three-dimensional assembly of the hetero polyanions with counter cations (protons) and additional water molecules (Teli *et al*., 2007 and Misono, Catal, 1987). This Keggin unit consists of a central PO_4 tetrahedron surrounded by four W_3O_{13} sets, linked together through oxygen atoms of which, four types can be distinguished; the central oxygen atom belonging to PO_4 tetrahedron is shared by three tungsten atoms, while the edge-sharing oxygen atoms bridge two tungsten atoms of the same set. The corner-sharing oxygen atoms bridge two tungsten atoms of different sets and terminal oxygen atoms are associated with a single tungsten atom. The bridging and terminal oxygen atoms are on the periphery of the structure, which are available to associate with protons or water molecules to form hydrates that are thought to enhance selectivity to water.

Also, hydrogen-bonding is likely to be established between PWA and the Sodium alginate polymer matrix. Due to these advantages, PWA-loaded Sodium alginate membrane is selected to investigate the PV separation of Isopropanol. Three membranes were fabricated unfilled pristine sodium alginate membrane and two MMMs incorporated with 5, 10 wt. % of phosphotungstic acid (PWA) particles. All the membranes were characterized by a variety of characterization techniques and their PV performances were evaluated for isopropanol dehydration. In many chemical engineering unit operations, we often encounter aqueous streams containing isopropanol and its azeotropic separation is very difficult to achieve by the conventional techniques discussed before. It may be noted that water- isopropanol, form azeotrope at 12.6, wt % of water. In order to achieve its effective separation, the membrane based PV separation technique would be quite attractive and efficient. In conitinuation of our research on pervaporation studies (Sudhakar, 2011 and Lokesh, 2008) our present study is aimed to demonstrate the many fold improvement in water selectivity over that of pristine NaAlg by incorporating 5 and 10 wt % of phosphotungstic acid (PWA) particles into NaAlg matrix and crosslinking it with glutaraldehyde and the results are presented here.

MATERIALS AND METHODS

Sodium alginate (SA) having a viscosity of average molecular weight of 50,000, tungstophosphoric acid hydrate (Phosphotungstic acid) (PWA), acetone , and hydrochloric acid were purchased from S.D fine chemicals, Mumbai. India. Isopropanal was purchased from qualigens fine chemicals, Mumbai, India and glutaraldehydrate was purchased from Merck chemicals, Mumbai. Deionized water having a conductivity of 20 µS/cm was used for the preparation of feed solution, which was generated in the laboratory itself.

Materials

Preparation of membranes

Membranes were prepared by dissolving 4gm of SA in 100ml of distilled water at room temperature by constant stirring on a magnetic stirrer (Remi Equipment Model 2MLH, Mumbai, India) for 24 hr. To this 4% of SA solution different amounts of 5 & 10 wt % PWA with respect to weight of polymer were prepared separately and added to the alginate solution. Above mixture was stirred 24 hr in order to get homogenous solution. The resulting solution was mixed thoroughly and then filtered to remove any suspended particles. It was then poured on a clean glass plate leveled perfectly on a table top kept in a dust free atmosphere and dried at the ambient temperature (30OC) to obtain dense non-porous membrane. Dried membranes were peeled off carefully from the glass plate and immersed in cross linking bath containing water: Acetone mixture (30:70) along with 2.5 ml of HCl, 2.5 ml of Glutaraldehydrate (GA). After allowing 12 Hrs, take out the membrane from the cross linking bath and washed with deionized water repeatedly, then dried in an owen at 60^{o} C to eliminate the presence of residual acid, if any. Membrane thickness was measured by a micrometer screw gauge at different positions on the flat surface of the membrane and the thickness the membranes were around 35-40 um. The pristine NaAlg membrane was also prepared in the same manner in the absence of PWA.

Pervaporation experiments

Pervaporation (PV) apparatus consists of stirred stainless steel cell through which retentate is circulated to the feed tank. Effective surface area of the membrane in the cell is 28.27 cm2 with a radius of 3.0 cm and volume capacity of the cell is about 250 cm3. Temperature of the feed mixture is maintained constant using a thermostatic water jacket. The Pervaporation (PV) cell is provided with an efficient three-blade stirrer powered by a DC current motor in the feed compartment. Turbulent flows were obtained even at low rotation of the stirrer, i.e., < 200 rpm speed. Mass transfer limitations due to concentration polarization are negligible. The permeate is collected in a glass container, cooled in a Dewar flask with liquid nitrogen. The vacuum is maintained by a two-stage vacuum pump. The experimental procedure remained the same as reported elsewhere (Misono, 1987). Weight of the permeate vapors collected in a Dewar flask with liquid nitrogen trap was measured and its composition was determined by measuring its refractive index by comparing it with the standard graph of refractive index Vs. mixture composition of the feed system. The Selectivity, α of a given membrane can be estimated by using the following equation (Hung, 1999).

$$\alpha = \left(\frac{Y_A}{1-Y_A}\right)\left(\frac{1-X_A}{X_A}\right) \qquad (1)$$

Where XA is mole fraction of water in feed and YA is the mole fraction of water in permeate. Flux, J (Kg/m2 h), was calculated from the weight of liquid permeated, W (Kg), effective membrane area, A (m2) and actual measurement time, t (h)

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

Membrane Swelling

The swelling experiments on the circularly cut membranes were performed at 30oC gravimetrically (Harogoppad and Aminabhavi, 1991) in 5-30wt% water-containing fed mixtures. Membrane samples with compositions ranging from 5 to 30 wt % water at 30oC ± 0.5oC in an electronically controlled incubator (WTB Binder, model BD-53, Tuttilgen, Germany) as per procedures reported previously (Aminabhavi, 1996). Initial weights of the circularly cut (dia=2.5 cm) disc shaped membranes were stored in a desiccators over anhydrous calcium chloride maintained at 30oC for about 24 h before performing the swelling experiments. Mass of the soaked samples were measured using a single-pan Adam digital microbalance (model AFP 210L) having a sensitivity of ±0.01mg. The swollen membranes were weighed immediately after careful blotting to remove surface adhered water. The percent degree of swelling (DS) was calculated as

$$\text{Degree of Swelling (\%)} = \left(\frac{W_s - W_d}{W_d}\right) X\,100 \quad (3)$$

Where WS and Wd are the mass of the swollen and dry membranes, respectively.

Fourier Transform Infrared Spectroscopy (FTIR) analysis

FTIR Spectra measurements were recorded in the wavelength region of 4000-400 cm1under a N2 atmosphere at a scan rate of 21cm-1 using Bomem MB-3000 (Make: Canada) FTIR spectrometer, equipped with attenuated total reflectance a (ATR). About 2mg of the sample was ground thoroughly with KBr, and pellets were made under a hydraulic pressure of 600 kg/cm2.

X-ray diffraction (XRD)

A Siemens D 5000 (Germany) powder X-ray diffractometer was used to study the solid-state morphology of the pristine SA and SA-HPC blend membranes. The X-rays of 1.5406 Å wavelengths were generated by a Cu Kα radiation source. The angle of diffraction (2θ) was varied from 0o to 65o to identify any changes in crystal morphology and intermolecular distances between inter-segmental chains of the polymer.

Measurement of refractive index

Refractive index, ND for sodium–D line was measured using the thermostatically controlled Abbe Refractometer (Atago 3T, Japan) with an accuracy of ± 0.001. Refractometer was fitted with hollow prism casings through which water was circulated. The experimental Temperature of the prism casing was observed with a digital display (±0.01ºC). The instrument directly gives the values of ND. Permeate composition was determined by measuring refractive index and comparing it with the established graph of refractive index versus mixture composition.

Scanning electron microscopy (SEM)

SEM micrographs of the beads were obtained under high resolution (Mag: 300X, 5kv) Using JOEL MODEL JSM 840A, Scanning electron microscope (SEM), equipped with phoenix energy dispersive. SEM micrographs were taken at Anna University, Chennai.

Thermo gravimetric analysis (TGA)

TGA curves of blend membranes of different compositions were recorded using TA instruments differential scanning calorimeter (Model – SDT Q600, USA).The analysis of the samples was performed at heating rate of 10oC/min under N2 atmosphere at a purge speed of 100 mL/min.

RESULTS AND DISCUSSION

FTIR studies

Fig.1.Shows FTIR Spectra of uncross linked NaAlg (a) and crosslinked10 wt % PWA filled NaAlg (b). From curve (a) the peak observed at 3420 cm-1 corresponding to O–H stretching vibrations of the hydroxyl group of NaAlg. The strong bands appeared at around 1620 and 1416 cm-1 are assigned, respectively, to antisymmetric and symmetric COO− stretching vibrations of the carboxyl group of sodium alginate (Hung, 1999). In the curve 1 (b) a peak at 3420 cm-1 conforming the utilization of O-H groups during cross linking with glutaraldehyde. The sharp peak appeared at 1250 cm-1 assigned to the formation of an acetal ring and ther linkage as a result of the reaction between the hydroxyl group of alginate and the aldehydes of Glutaraldehyde (as shown in Fig. 2).

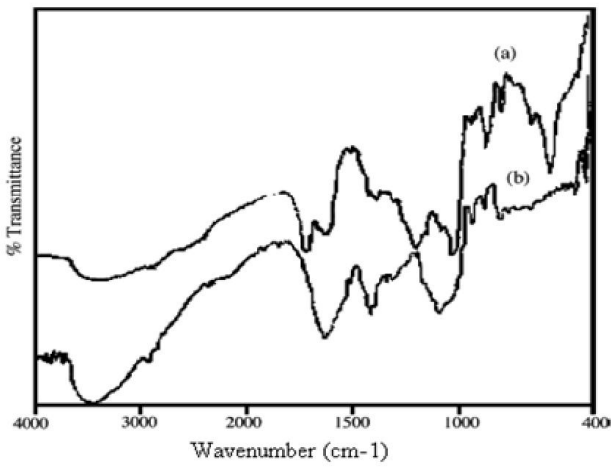

Fig. 1. FTIR tracings of (a) uncrosslinked NaAlg and (b) PWA loaded crosslinked NaAlg Membranes

TGA studies

Fig. 3. Shows the TGA thermograms of crosslinked NaAlg (a) and 5 wt % and 10 wt % PWA filled NaAlg (b and c) membranes respectively. These curves showed the thermal

stability of the system under study. These thermo grams further revealed that 2 stage thermal degradation process. The first stage transition diffusion occurred in the temperature range of 105-200oC and the second stage in the range of 204-310oC. The weight loss in the first stage is attributed to loss of volatile products like dehydration etc and the weight loss is the second stage is attributed to the decrosslinking of polymer networks and decomposition of PWA.

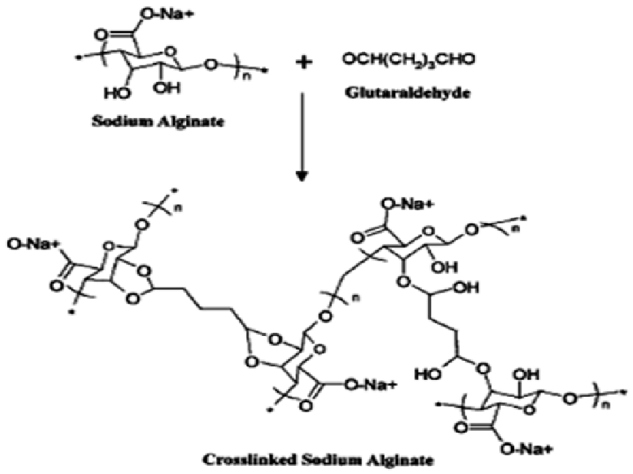

Fig. 2. Schematic chemical structure of crosslinked SA

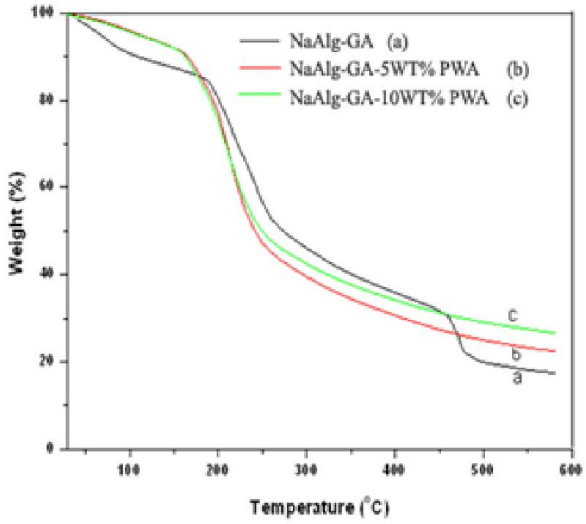

Fig. 3. Thermograms of crosslinked NaAlg (a), 5 wt % PWA filled NaAlg (b) and 10 wt % PWA filled NaAlg membranes

It is important to have uniform dispersion of particles in the NaAlg matrix to exhibit enhanced effects of flux and selectivity during PV dehydration experiments.

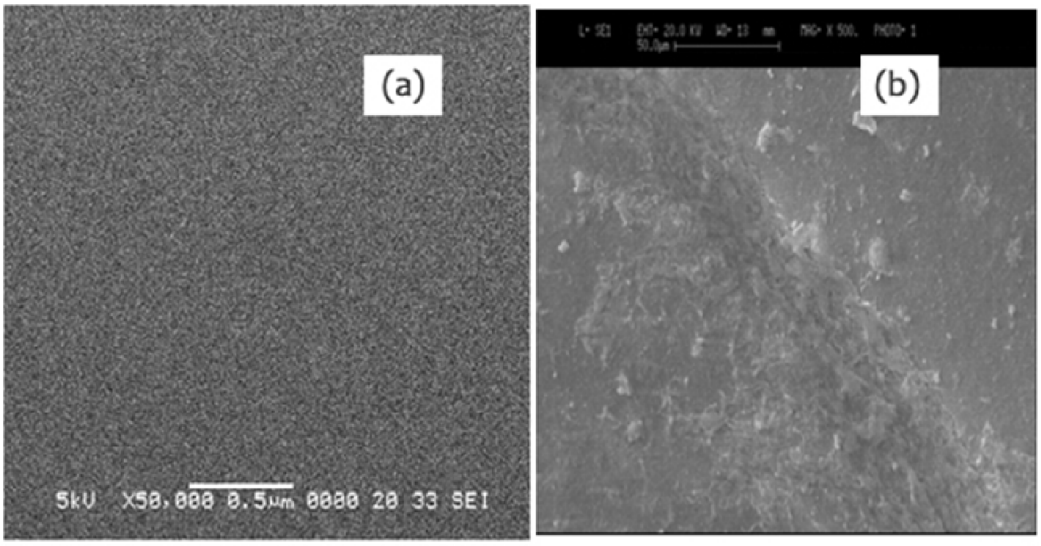

Fig. 4. SEM photo graphs of (a) virgin NaAlg and (b) 10 wt% PWA filled NaAlg Mixed Matrix Membrane

Table.1. Tensile strength and % elongation at break of pristine NaAlg and PWA -filled NaAlg mixed matrix membranes

Membrane type	Tensile strength(N/mm^2)	Elongation at break (%)
0 wt % of PWA +NaAlg	20.01	7.6
5 wt.% of PWA + NaAlg	59.12	5.0
10 wt.% of PWA + NaAlg	91.4	3.2

SEM studies

Fig 4. Shows the surface SEM image of (a) virgin NaAlg and (b) 10 wt % PWA filled NaAlg-mixed matrix membrane. Notice that PWA particles are uniformly distributed at the molecular level in the NaAlg matrix. During pervaporation experiments most of the water molecules are absorbed on to PWA particles and transported through the pores of the particles that are uniformly embedded in the NaAlg matrix.

Mechanical properties

The values of Tensile strength and elongation at break of 5 wt % and10 wt % PWA -loaded NaAlg membranes as well as pristine NaAlg membrane in dry state are given in Table.1. These values suggest that mixed matrix membranes exhibit higher tensile strengths than the pristine NaAlg. This enhancement is attributed to the interaction of filler particles with NaAlg matrix. NaAlg chains in the presence of PWA

filler particles will experience a restriction in chain segmental mobility, resulting in an increase of rigidity or tensile strength, thereby reducing elongation at break. Such enhancement will be more pronounced for 5 wt % and 10 wt % PWA loaded mixed matrix membranes than the pristine NaAlg membrane. However, the PWA loaded mixed matrix membranes exhibited a high-mechanical strength due to higher interaction/ compatability with NaAlg matrix. It is evident from the results given in Table.1 that with increase of PWA concentration the tensile strength also increases and elongation at break decreases.

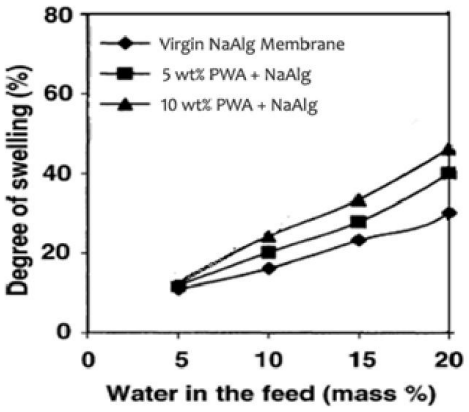

Fig.5: Degree of swelling Vs. wt.% of water in the feed. Symbols: ( ) Prisitne NaAlg; ( ) 5 wt.% PWA filled NaAlg-mixed matrix membranes; ( )10 wt.% PWA filled NaAlg-mixed matrix membranes at 30^0 C

concentration is increased in the feed, since water causes a greater degree of swelling than those of Isopropanol with the SA membrane.

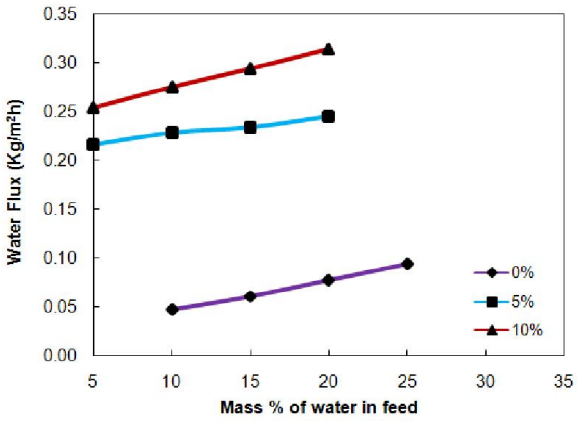

Fig. 6. Water Flux Vs Mass % of water in feed for various percentages of PWA filled NaAlg membrane for water Isopropanol mixtures at 30^0 C

When the polymer matrices are filled with PWA the degree of swelling increases more than that of a pure sodium alginate membrane. This effect becomes more prominent when the PWA content in the membrane is increased, which is clearly viewed in Fig.5. As a consequence, adsorption of water molecules increases remarkably and this, in turn becomes responsible for an enhanced swelling with an increase of PWA content in the membrane.

Table 2: Pervaporation results of PWA filled NaAlg membrane for water-Isopropanol mixtures at 30^0 C

Sl. No.	Mass% of water in the feed	Water flux Kg/m^{2}h	Selectivity (α)	Mass% of water in the permeate	PSI	Enrichment factor (β)
0% PWA filled NaAlg Membrane:						
1	10	0.047	678.00	98.69	31.90	14.09
2	15	0.061	342.00	98.37	20.88	9.36
3	20	0.077	222.00	98.23	16.97	7.02
4	25	0.094	145.00	97.97	13.45	5.59
5	30	0.104	96.00	97.63	9.92	4.65
5% PWA filled NaAlg Membrane:						
1	5	0.215	5918.50	99.68	1275.97	19.93
2	10	0.228	1689.11	99.47	384.66	12.43
3	15	0.233	711.63	99.21	165.05	6.70
4	20	0.244	404.16	99.02	97.79	4.78
10% PWA filled NaAlg Membrane:						
1	5	0.253	14596.38	99.87	3695.68	19.97
2	10	0.275	2133.85	99.58	586.70	12.44
3	15	0.293	638.27	99.12	186.51	6.70
4	20	0.313	396.00	99.00	123.10	4.78

Pervaporation studies on water isopropanol mixture

Swelling studies

In an effort to study the effect of feed composition on the membrane swelling, the percent degree of swelling was plotted as a function of different mass % of water in the feed mixture in case of swelling studies of PWA filled NaAlg membrane for water Isopropanol mixture at 30°C as shown in Fig. 5. It is observed that the degree of swelling increased almost linearly with increasing mass% of water in the feed. This is due to an increase of strong interaction offered by hydroxyl and COO− groups of SA with the water molecules. The interaction becomes more and more predominant when the water

Membrane performance on Flux and Selectivity

Fig. 6. Shows the effect of feed composition on the water permeation flux for all the membranes. It is observed that the water permeation flux increased almost linearly for all the PWA -incorporated SA membranes with increasing amount of water in the feed. This is due to an increase of selective interactions between water molecules and PWA -incorporated SA membrane. However, for pure sodium alginate membrane the permeation flux increased linearly with mass% water in the feed. This may be due to the saturation of interactive groups (COO− and OH) of sodium alginate at higher concentration of water in the feed. But, this is not the case with PWA -incorporated SA membranes, wherein an increase of PWA

content in the membranes enhances the selective interaction between the water molecules and membrane. This property is mainly attributed to a combined influence of ionic species present in the PWA cages and porous nature of PWA, which together lead to an increase of water adsorption as evidenced in the swelling study. These, in turn become responsible for a higher permeation flux with increasing water concentration in the feed.

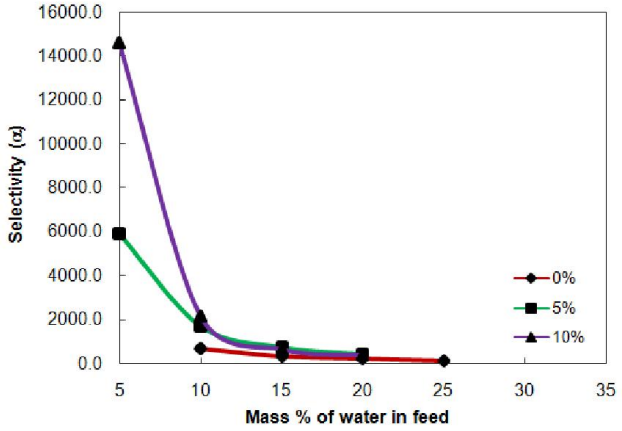

Fig. 7. Water Selectivity Vs Mass % of water in feed for various percentages of PWA filled NaAlg membrane for water Isopropanol mixtures at 30^0 C

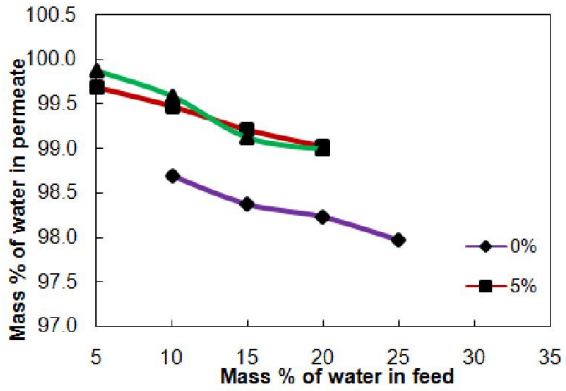

Fig. 8. Mass% of water in permeate Vs Mass % of water in feed for various percentages of PWA filled NaAlg membrane for water Isopropanol mixtures at 30^0 C

Fig.7 displays the effect of water composition on the selectivity for all the membranes. It is observed that the selectivity decreased exponentially for all the membranes with increasing water concentration in the feed. This is due to a greater swelling with increasing water concentration in the feed, owing to an increase of selective interaction between the membrane and water molecules. On the contrary, the selectivity increased from 5 wt % to 10 wt % PWA filled NaAlg membrane. Further, it can be clearly observed from the values given in Table 2 that, both the permeation flux and selectivity increased with increasing PWA content in the membrane.

Effect of feed water composition

Table 2 illustrates the relationship between membrane performance and water composition in different water isopropanol mixtures for the pristine NaAlg 5 wt % and 10 wt % of PWA -loaded NaAlg membranes at ambient temperature. Permeation flux increases with increasing water content of the feed, which is caused due to higher concentration of water molecules within the membrane. At the same time, wt % of water in permeate line (see Fig.7) and selectivity values decreased for all the water - isopropanol mixtures of this study. There is a two-fold increase in the permeation flux for isopropanol mixtures because of the hydrophilic nature of the PWA used and its interaction with NaAlg matrix. For all the feed mixtures, flux values of PWA -loaded NaAlg membranes are higher than that of the pristine NaAlg membrane Membrane performances were also studied by Pervaporation Separation Index (PSI) and Enrichment factor β data. These results are incorporated in Table 2. From these results it is noticed that PSI and β values follow a decreasing trend with increasing amount of water in the feed. The β values of all the membranes decreasing systematically with an increasing composition of water in the feed. The value of PSI also follows as same trends as those of β.

Conclusions

Sodium alginate membranes, incorporated with higher amounts of PWA, showed better performance while separating Isopropanol - water mixtures. An increase of PWA content in the membrane results in increase of both flux and selectivity, attributed to a significant enhancement of hydrophilic character, selective adsorption, and molecular sieving action, including a reduction of pore size of the polymer matrix. The PV separation index data also indicated that the higher the loading of PWA, the better the membrane performance. For Isopropanol - water mixture the highest separation selectivity was found to be 14596 with a flux of 0.2532 kg m^{-2} h^{-1} for the membrane with the highest loading of PWA at 30°C for 5 mass % of water composition in the feed.

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