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MIXED MATRIX BLEND MEMBRANES OF SODIUM ALGINATE – HYDROXY PROPYL CELLULOSE LOADED WITH HALLOYSITE NANO CLAY USED IN PERVAPORATION TECHNIQUE FOR DEHYDRATION OF ISOPROPANOL MIXTURE AT 30 ^{0}C.

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ABSTRACT

Mixed matrix blend membranes (MMMs) of Sodium alginate (SA) - Hydroxy propyl cellulose (HPC) were prepared by incorporating with Halloysite nanoclay (HNC) by solution casting technique and characterized by various physico-chemical techniques like FTIR, SEM and TGA. Pervaporation experiments of these membranes were investigated for the separation of isopropanol / water mixture at 30 ^{0}C. Membrane performance showed dependence on the extent of Halloysite nanoclay (HNC) loading. The 0.3 wt % HNC-loaded blend membrane SA-HPCL-3 had the highest selectivity of 2359, which declined considerably at higher loading of HNC. The flux of 0.3 wt % HNC-loaded membrane of SA-HPCL-3 was higher than that of pristine SA-HPC blend membrane. The effect of feed water composition was studied on the PV performance. Solubility selectivity was higher than diffusion selectivity. Degree of swelling was smaller after HNC loading exhibiting better separation ability.

KEYWORDS: Pervaporation; Halloysite nanoclay, SA/HPC blend membrane, Isopropanol-water mixture.

INTRODUCTION

Membrane – based pervaporation process has been intensively studied for separation of aqueous-organic mixtures [1-3] and more recently, even organic-organic solutions [2-4] because of their economic advantage and ability to separate isomeric and azeotropic mixtures. In PV separation studies of aqueous organic mixtures, several types of membranes have been used including those of blends, composites, etc. The successful performance of PV process largely depends on the physical and chemical properties of the membrane material. Generally, the membrane material that contains a large number of hydrophilic groups is preferred for the dehydration process. Out of these, cellulose and its derivatives, the next most common natural polymer is Sodium alginate mainly considered. From these points of view, natural high molecular weight polymers, polysaccharides, are worthy of consideration as a membrane materials for dehydration. They possess good affinity towards water molecules as shown in several studies dealing with the dehydration of alcohols through polysaccharide membranes. Alginic acid membrane [5] and generated cellulose membranes [6] are reported to show a good selectivity in the dehydration of water-alcohol mixtures. Among the hydrophilic polysaccharide type polymers, alginate membrane has gained special interest because it showed the highest flux and separation factor among the hydrophilic materials tested for the pervaporation dehydration [7-8]. Hydroxy propyl cellulose [HPC] is another important biopolymer used in PV dehydration studies. In order to improve PV separation characteristics of water-isopropanol mixtures, in this work, blending of SA with HPC is considered to limit the excessive swelling of SA. Hydroxy propyl cellulose (HPC) which is an alkyl-substituted hydrophilic cellulose derivative that not only has phase transition behavior in aqueous solution [9] but also good biocompatible film forming material. The incorporation of zeolite or porous fillers in dense membrane can improve the separation performance of the membranes [10-14] due to combined effect of molecular sieving action, selective adsorption, and difference in diffusion rates.

Isopropanol has been widely used in semiconductor and liquid crystal display industries as a water-removing agent [15]. Among the many aqueous –organic mixtures, separation of water from this mixture with isopropanol is a challenging task, because the system forms an azeotrope at 14.7 mass % of water, hence its separation by conventional distillation is not feasible. So, this isopropanol can be recycled by several methods, including pervaporation process. In the present study, because of its hydrophilic nature we have chosen Halloysite nanoclay (HNC) which is to be added to the blend membrane for better pervaporation separation. This Halloysite is a clay mineral, chemically similar to kaolin, typically formed by hydrothermal alteration of alumino silicate minerals [16]. Halloysite belongs to family of alumino silicate ($Al_2Si_2O_5(OH)_4.nH_2O$) which has a hollow tubular structure [17]. It is naturally occurs as small cylinders which average 30 nm in diameter with lengths in between 0.5 and 10 micrometers[17-18]. Mainly on this microscopic scale halloysite usually occurs as nanotubes, which average diameter is a few dozen of nanometers and lengths is in the range of few micrometers. Sometimes, depend on deposit, these nanotubes split open and unroll to form laths or spatula shapes [19]. Additionally, because of biocompatibility of the halloysite they are frequently used in environmental protection and industry for example as sorptive material in biofilters or coagulant for water and sewage treatment plants.

In continuation of our research work on pervaporation studies using natural polymer blends [20-22] this paper deals with the development of novel mixed matrix SA-HPC blend membranes incorporated with the Halloysite nanoclay (HNC) in different concentrations for the PV separation of water-isopropanol mixture at room temperature at different and feed water compositions to investigate the improvement in membrane performances. The results of this study revealed that Halloysite nanoclay (HNC) incorporated blend membranes performance is better than the Pure SA-HPC blend membranes in dehydration of isopropanol.

MATERIALS AND METHODS

Sodium alginate (SA) having a viscosity average molecular weight of 500,000, Acetone and Hydrochloric acid were purchased from S.d. fine chemicals, Mumbai, India. Hydroxy propyl cellulose (HPC) with a molecular weight of ≈15,000 and Halloysite nano clay (HNC) were purchased from Aldrich Chemical Company, Milwaukee, WI, USA. Iso-propanol was purchased from Qualigens fine chemicals, Mumbai, India, and Gluteraldehyde was purchased from Merck chemicals, Mumbai, India. Deionized water having a conductivity of 20μS/cm was used for the preparation of feed solution, which was generated in the laboratory itself.

Preparation of membranes

MMMs of SA/HPC blends incorporated with Halloysite nano clay(HNC) membranes were prepared by solution casting and solvent evaporation technique. In brief, different ratios of SA and HPC so as to make 4 gms were dissolved in 90 mL of distilled water individually at room temperature by constant stirring on a magnetic stirrer (Remi Equipment Model 2MLH, Mumbai, India) for 24 h to get homogeneous solution of SA/HPC blend. In separate flasks, 0.2, 0.3gm of HNC was dispersed in 10 mL of water, sonicated for 2h, added individually to the previously prepared SA/HPC blend solution. The whole mixture was stirred for 24 h, filtered and poured onto a perfectly aligned clean glass plate in a dust free environment for casting the membranes using a doctor's blade. The membranes after drying at ambient temperature (30 ^{0}C) were peeled off from the glass plate, immersed in a cross-linking solution bath containing water and acetone mixture (30:70) along with 2.5 mL of Con. HCl, 2.5 mL of Gluteraldehyde (GA). After allowing for 12 h, take out the membrane from the cross linking bath, and wash with deionized water repeatedly then dry in an oven at 40 ^{0}C to eliminate the presence of residual acid, if any. The dried MMMs were peeled off and designated as SA-HPCL-2, SA-HPCL-3 respectively. The resulting solution was mixed thoroughly and then filtered to remove any suspended particles. Membrane thickness was measured by a micrometer screw gauge at different positions on the flat surface area of the membrane and the thicknesses of the membrane prepared were around 35-40 μ.

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 cm^2 with a radius of 3.0 cm and volume capacity of the cell is about 250 $cm^{3.}$ 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 [23]. 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 was estimated using the following equation [24].

$$\alpha_{PV} = \left(\frac{y_A}{1-y_A}\right)\left(\frac{1-x_A}{x_A}\right) \longrightarrow \quad (1)$$

Where X_A is mole fraction of water in feed and Y_A is the mole fraction of water in permeate.

Flux, J (Kg/m^2 h), was calculated from the weight of liquid permeated, W (Kg), effective membrane area, A (m^2) and actual measurement time, t (h)

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

Membrane Swelling

The swelling experiments on the circularly cut membranes were performed at 30^0C gravimetrically [25] in 10, 12.5 and 15 wt. % water-containing fed mixtures. MMMs of Blend samples with compositions ranging from 10 to 15 wt % water at 30 ^{0}C ± 0.5 ^{0}C in an electronically controlled incubator (WTB Binder, model BD-53, Tuttilgen, Germany) as per procedures reported previously [26]. To do this, dry weight of the circularly cut (diameter = 2.5 cm) disc shaped MMMs of blend membranes were stored in a desiccators over anhydrous calcium chloride maintained at 30 ^{0}C for about 24 h before performing the swelling experiments. This dry weight of the circularly cut (diameter = 2.5cm) MMMs of blend membranes were taken, 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 surface to remove the adhered water. The percent degree of swelling (DS) was calculated as

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

Where W_S and W_d are the mass of the swollen and dry membranes, respectively.

Fourier transform infrared spectral (FTIR) analysis

FTIR Spectra measurements were recorded in the wavelength region of 4000-400 cm^{-1} under N_2 atmosphere at a scan rate of 21cm^{-1} using BomemMB –3000 (Make:Canada) FTIR spectrometer, equipped with attenuated total reflectance (ATR). About 2mg of the sample was grinded thoroughly with KBr, and pellets were made under a hydraulic pressure of 600 kg/cm^2.

Measurement of refractive index:

Refractive index, (N^D) 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 (± 0.01^0C). The instrument directly gives the values of N^D. 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 MMMs of SA/HPC blends 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) and Differential Scanning Calorimetry (DSC):

TGA / DSC curves of MMMs at 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 10 ^{0}C/min under N_2 atmosphere at a purge speed of 100 mL/min.

X-ray diffraction (XRD)

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

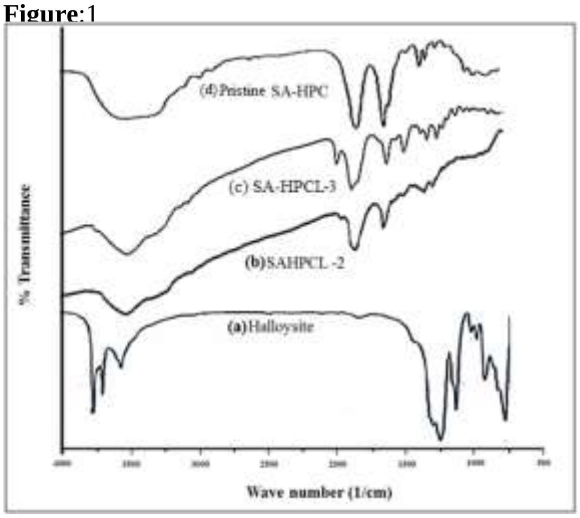
RESULTS AND DISCUSSION

FT-IR analysis:

Fig. 1 shows the spectra of HNC (a), HNC loaded SA-HPC blend membrane (b&c) and pristine SA-HPC blend membrane (d). The Al-OH peaks at 3700 cm^{-1} and 3630 cm^{-1} and Si-O vibrations at 1113 cm^{-1} and 1032^{-1} , which are characteristic peaks of HNC, were observed in the FTIR Spectroscopy of pure HNC (a) and HNC incorporated SA-HPC blend membranes (b&c). The multiple bonds that appeared between 1200 and 1000 cm^{-1} were assigned to C-O stretching. On incorporation of, the Halloysite nanoclay into SA-HPC blend membranes, the intensity of C-O stretching increased and this was predominant with increase of amount of nanoclay as clearly demonstrated in spectra (b) & (c). This is expected due to Si-O-Si stretching clay material as it overlaps at the same frequency of C-O.

A characteristic peak at 3508 cm^{-1} in all the membranes and pristine HNC corresponding to O-H stretching vibrations of SA & HPC blend polymers and HNC filler. From this spectra it can be seen that the – OH bond is shifted slightly to a lower frequency which supports the enhanced hydrogen bonding occurring between the –OH groups present in clay (Si-OH and Al-OH) as well as with OH groups present in SA & HPC blend membranes. This confirms the incorporation of clay and its reaction with the polymers in the blend membranes.

Figure:1



FTIR spectra of the (a) Halloysite nanoclay(HNC), blend membranes of (b) SA-HPCL-2, (c) SA-HPCL-3 and (d)pristine SA-HPC blend membranes.

Scanning electron microscopy (SEM):

The morphology of the HNC incorporated blend membranes (SA-HPCL-2 and SA-HPCL-3) were examined by SEM and the results are shown in Fig.2. From the Fig.2 (a) many clusters can be seen at the low-magnification micrograph. It is also seen from Fig.2 (b) that a close up view of one of the clusters. This indicates that the HNC particles are uniformly distributed in the blend membranes of SA-HPC. The adhesion of clay surface and the blend membranes is because of the formation of hydrogen bonding between the active surface groups of clay (Si-OH and Al-OH) with the active surface groups(-OH) of blend membranes.

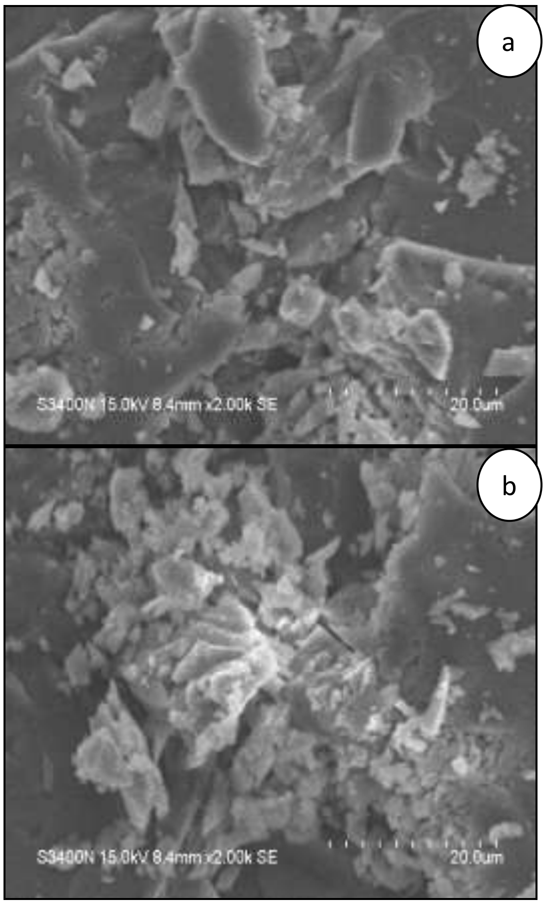


Fig.2: SEM images of (a) MMMs of SA-HPCL-2 and (b) MMMs of SA-HPCL-3.

Differential Scanning Calorimetry (DSC):

The DSC curve of the Halloysite nanoclay filled SA-HPCL-2 and SA-HPCL-3 mixed matrix membranes are shown in Fig.3, From this figure it is noticed that SA-HPCL-2 shows T_g and T_m at 76 ^{0}C and 266 ^{0}C respectively and where as the SA-HPCL-3 shows T_g and T_m at 78 ^{0}C and 276 ^{0}C respectivelly. The higher values of T_g and T_m for SA-HPCL-3 than SA-HPCL-2 is due to the higher amount of HNC content, this can be attributed to the more hydrogen bonding interactions between the blend polymer and HNC particles. This could be attributed to the decrease of molecular chain mobility of SA-HPC polymer with increasing HNC loading.

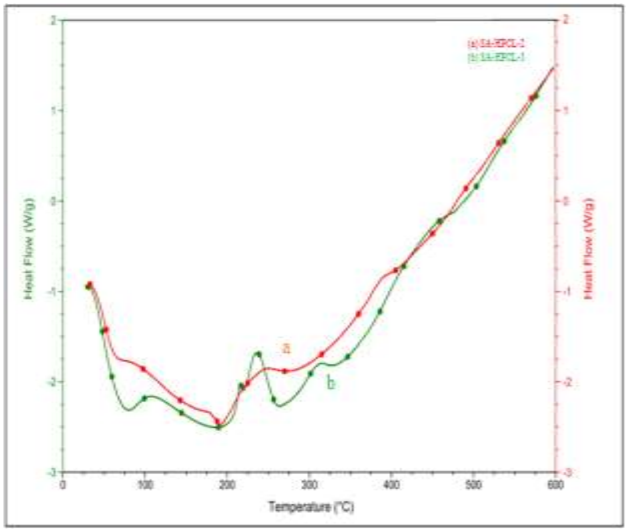


Fig. 3: DSC. Thermograms MMMs of the (a)SA-HPCL-2 and (b) SA-HPCL-3.

Thermo Gravimetric analysis (TGA):

The thermal stability of the MMMs of SA-HPC blend incorporated with Halloysite nanoclay (HNC) was analyzed by the thermo gravimetric analysis. The TGA curves of SA-HPCL-2 and SA-HPCL-3 are shown in Fig.4. It can be observed that the primary weight loss occurs just above 100 ^{0}C for these two samples, which may be due to the loss of water molecules. SA-HPCL-2 showed two weight loss stages in the range 210 - 500 ^{0}C and SA-HPCL-3 shows the two weight loss stages in the range 180 - 600 ^{0}C. Mixed matrix membrane with incorporation of HNC shows increase in thermal stability of the membranes. The present TGA studies indicate that the MMMs can be effectively used in PV experiments at temperatures up to 150 ^{0}C.

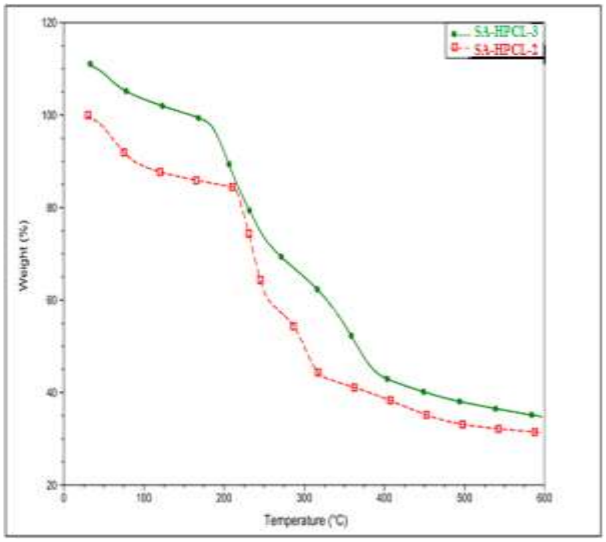


Fig. 4: TGA. thermograms of the MMMs of the SA-HPCL-2 and SA-HPCL-3.

Membrane Performance

Swelling Experiments:

In order to study the effect of the feed composition and clay loading on the membrane swelling, the percentage degree of swelling of all the membranes were plotted with respect to water composition in the feed at 30 ^{0}C and shown in Fig.5. It is observed that the degree of swelling is increased almost linearly for all the membranes with increase in the mass % of water in the feed. This is due to increased interaction between water molecules and the membrane, owing to the presence of interactive groups (-COOH,-OH) in the membrane matrix. This is expected since water is more polar than IPA, which preferentially interacts with membrane resulting in an increased degree of swelling. On the other hand, the degree of swelling increased with increase in clay content in the membrane at all feed compositions.

In this study, swelling increases slightly with increase in amount of Halloysite nanoclay (HNC) in the mixed matrix membranes (MMMs). This could be due to the increased void space and nature of the penetration of liquid molecules which could exert an influence on swelling. Degree of swelling increases with increase in HNC composition in the MMMs, because the presence of HNC molecules in the polymer chain segments move quite rapidly allowing the higher amount of liquids to penetrate into the free volume pores of the MMMs. Degree of swelling for SA-HPCL-3 membrane was higher than that observed for pristine SA-HPC blend membrane and SA-HPCL-2 membrane due to higher-level hydrophilic nature of HNC molecules interact more with solvent molecules which in terms leads to more swelling. This increased swelling is due to the presence of HNC particles that creates the three – dimensional channel network with a symmetric opening. Increase in HNC content leads to the increase of membrane swelling.

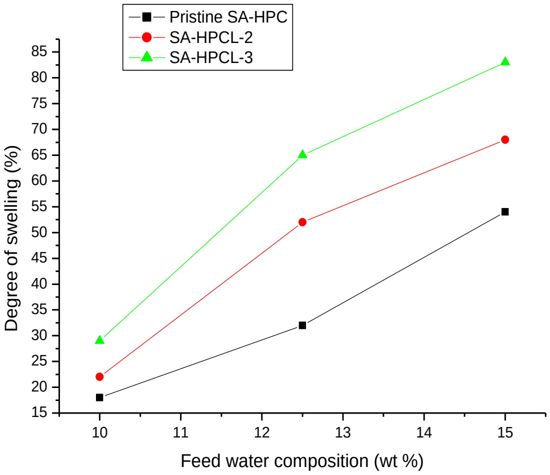


Fig.5: Degree of swelling of Pristine SA/HPC blend membrane and MMMs of SA-HPCL-2, SA-HPCL-3.

Pervaporation studies

Influence of HNC Loading on PV Performance:

In the PV process, the overall performance of the membranes can be assessed basing on the flux and selectivity values. In order to calculate these parameters the developed membranes were subjected to a Pervaporation experiment with 10 to 15 % of water in the feed. The resulting data of both flux and selectivity are presented in Figs.6 & 7.

It is observed that the clay-loaded composite membranes exhibited higher separation selectivity with lower permeation flux compared to pristine membranes. As the content of clay was increased in the pristine membrane, the selectivity decreased. However, the permeation flux increased with increase in the amount of clay. This complex transport phenomenon can be explained on the basis of decreased free volume and establishment of a tortuous path.In polymer-clay composite membranes, the incorporated clay usually exits in the forms of exfoliated, intercalated, and flocculated states [27, 28]. The extent of each state depends on the ratio between polymer and the incorporated clay. This favors the molecular level interaction between the polymer and the clay, resulting in decreased free volume. In addition, a high aspect ratio of layered silicates caused them to act as a barrier, offering more resistance to diffusion by creating tortuosity to the diffusion pathway. This has suppressed the diffusion of both water and IPA molecules. However, the diffusion of IPA molecule was affected significantly as the kinetic diameter of IPA molecule was affected significantly as the kinetic diameter of IPA molecule is almost four times bigger than that of water molecule [29]. Obviously, transport of IPA molecules were less preferred as compared to water molecules, resulting in decreased selectivity and flux. On further increase of the amount of clay, the decrease in selectivity was due to micro-phase separation occurring between organic and inorganic matrix, which has resulted from the shift of exfoliation state to intercalation followed by flocculation. The decrease in flux accounted for the lower degree of swelling at higher mass % of clay.

Effect of feed water composition:

In PV, the effect of feed water composition is also an important factor, and thus we have carried out a PV study at different mass % of water in the feed and resulting data is presented in Table.1. and shown in Fig. 6 & 7. It is observed that the flux is increased with increase of the water composition in feed. This is mainly due to increase of membrane swelling, this is expected because of establishment of greater interaction between the membrane and the water molecules as in this membrane contains a huge number of hydrophilic and carboxylic groups such as –OH, CH_2 and COO^-, which preferentially, interacts with water molecules rather than isopropanol. On the other hand the flux values decreased with increase of water feed in case of HNC filled blend membranes. This is because with increase of water the ionic interactions are more with clay which contain more –OH groups.

On the contrary, the selectivity was decreased exponentially with increasing mass % of water in the feed. At a higher concentration of water in the feed, a small amount of water dissolves in the membrane, which in turn acts as a plasticizer for the membrane, leading to more flexible polymeric chains in the matrix. In addition, water is more polar in nature, its absorption in the membrane might have weakened the interaction between polymer and clay material, resulting in a somewhat loose structure, which becomes responsible for facilitating the diffusion of some of the IPA molecules in association with water molecules.

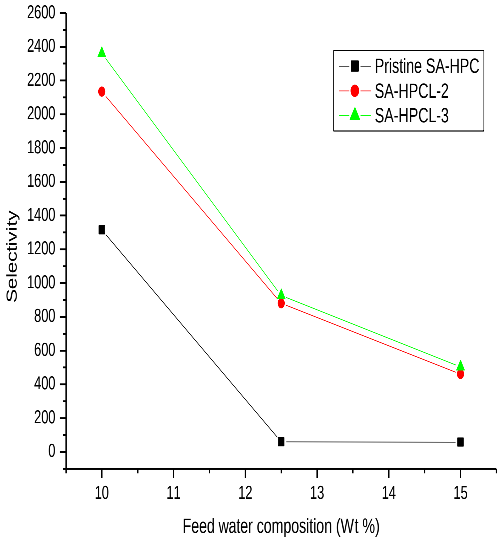


Fig.6: Selectivity vs. wt. % of water in feed mixture for pristine SA/HPC blend membrane and MMMs of SA-HPCL-2, SA-HPCL-3.

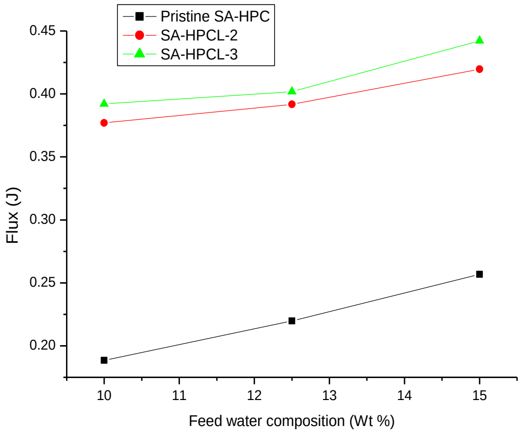


Fig.7: Flux vs. wt. % of water in feed mixture for pristine SA/HPC blend membrane and MMMs of SA-HPCL-2, SA-HPCL-3.

Table.1. Pervaporation data of MMMs of SA-HPCL-2, SA-HPCL-3 for feed mixture of water –IPA at 30 ^{0} C.

Wt. %. of water in feed	Wt. %. of water in permeate	Flux (J) (Kg/m^2 h)	Selectivity (α)
Pristine SA/HPC			
10.0	99.32	0.1884	1314
12.5	89.52	0.2197	60
15.0	89.50	0.2567	58
SA-HPCL-2			
10.0	99.58	0.4196	2133
12.5	99.21	0.3918	879
15.0	98.80	0.3770	461
SA-HPCL-3			
10.0	99.62	0.4315	2359
12.5	99.25	0.3945	926
15.0	98.86	0.3842	485

Comparison of PV results with literature:

In the present study, after incorporating the Halloysite nanoclay (HNC) particles into the MMMs of SA-HPC, membrane properties have improved. In the literature, many different types of membranes were used to study the PV dehydration of isopropanol from a aqueous mixtures due to their widespread applications in chemical engineering and pharmaceutical disciplines.Flux and selectivity values of the present membranes are comparable with the other important membranes used in the literature. In some cases, the present MMMs gave the better performance than those published in the literature. Now a days, there is a greater tendency to use the MMMs by incorporating zeolites or similar particulates of fillers such as nanoclay or metal complexes into polymeric materials. In this study results obtained are almost comparable or even better than those previously discovered polymeric membranes. The 0.3wt % of Halloysite nanoclay (HNC) filled SA-HPCL-3 mixed matrix membrane have superior selectivity as compared to magnesium aluminum silicate filled NaAlg membranes [30].

Table.2.Comparison of PV performance of the present MMMs with literature data for water-isopropanol separation.

Membrane	Temperature (^{0}C)	Wt. %. of water in feed	Flux (Kg/m^{2}h)	Selectivity (α)	Reference
Na Alg-MAS-15	40	10	0.070	2036	[30]
Two play nano composite NaAlg and CS	30	10	0.554	2010	[31]
NaAlg+5wt % Al-MCM-41	30	10	0.110	1516	[32]
SA-HPCL-2	30	10	0.4196	2133	Present work
SA-HPCL-3	30	10	0.4315	2359	

CONCLUSION

This paper explains the pervaporation studies of water-isopropanol mixture by using the mixed matrix blend membranes of Sodium alginate and Hydroxy propyl cellulose. Here the SA-HPC blend membranes are loaded with Halloysite nanoclay particles and crosslinked with glutaraldehyde. The better membrane performances was achieved for 0.3 wt.% of HNC particles incorporated in SA-HPCL-3 mixed matrix membranes with a selectivity of 2359 and a water flux of 0.4315 Kg/m^2 h values compared to the SA-HPCL-2 and pristine SA-HPC blend membrane. So, the Halloysite nanoclay loaded mixed matrix membranes of this study are thus better than Pristine SA-HPC membrane with regard to dehydration of aqueous isopropanol. From the above results it is concluded that the hydrophilicity nature of both the polymer and clay are responsible for the high selectivity and flux values.

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