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PERVAPORATION DEHYDRATION OF ISOPROPANOL USING BLEND MEMBRANES OF SODIUM ALGINATE (SA) AND HYDROXY PROPYL CELLULOSE (HPC)

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ABSTRACT

Sodium alginate (SA) and Hydroxy propyl cellulose (HPC) blend membranes(SA/HPC) were prepared by solution casting method, followed by crosslinking with gluteraldehyde (GA), were tested for the pervaporation (PV) dehydration of isopropanol. The blend membranes were characterized by Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (X-RD) to assess intermolecular interactions and crystallinity. Thermo gravimetric analysis (TGA) confirms that the stability increased with increase of SA content in SA / HPC blend membranes. The morphology of membranes was characterized by SEM studies, to confirm the chemical interaction and compatibility of these blend membranes. Sorption studies were carried out to evaluate the extent of interaction and degree of swelling of the membranes, in pure liquids as well as in mixtures of water and isopropanol. Pervaporation dehydration using crosslinked SA-HPC blend membranes were evaluated by the varying experimental parameters i.e., feed composition and membrane thickness. It was found that blend membrane containing 20 wt% HPC (SA-HPC-20) gave a high selectivity of 1314 and that the flux is of 0.1884 Kg /m² h for 10 wt % water containing feed mixture. Comparatively, a low selectivity of 607 was observed for pristine cross linked SA membrane with the same feed mixture. Flux of the pristine SA membrane increased from 0.092 to 0.137 Kg / m²h. For SA-HPC-20 membranes, flux increased from 0.1884 to 0.2879 Kg / m²h over the studied feed water compositions of 10-17.5 wt%. From the above results, it is concluded that the present blend membranes are a promising candidates for Pervaporation dehydration of isopropanol.

Keywords: Sodium alginate; Hydroxy propyl cellulose; Blend membranes; Isopropanol; Pervaporation*.*

1. INTRODUCTION

Membrane technology got much attention in last few decades and is found to be a good substitute for conventional energy - intensive separation process. The beauty of this process lies in its low energy demand, simplicity of design, low cost and eco friendly nature. Now-a-days this technology has been successfully used in-water treatment, food, pharmaceutical and chemical industries. Pervaporation (PV) is an efficient membrane process and potentially useful industrial method used for the separation of aqueous-organic and closely boiling mixtures [1-5]. The past two decades had witnessed substantial progress in both the fundamental and application aspect of pervaporation separation of liquid mixtures [6-7].

The successful performance of PV process largely depends on the physical and chemical properties of the membrane material. Hydrophilic membranes are widely used in PV dehydration of organic mixtures. Hydrophilic groups absorb water molecules preferentially, leading to high flux and

selectivity. Particularly, Sodium alginate (SA), due to its high hydrophilicity, good membrane applications and excellent chemical / thermal resistance properties, has been used as a membrane in PV dehydration studies. Sodium alginate (SA), which is one of the polysaccharides extracted from seaweed, is found to have an excellent performance as a membrane material for pervaporation-based dehydration of organic solvents [8]. However, a very high hydrophilicity of sodium alginate resulting from both of its carboxyl and hydroxyl groups, leads to a significant swelling of membrane in aqueous solution. Yeom and Lee [9] improved the membrane strength and stability of SA by crosslinking with GA. Huang *et al***.** [10] prepared stabilized SA membranes using a relatively simple method of ionic crosslinking.It has a linear chain structure of β-D-mannuronic acid (M) and α-L-guluronic acid (G) residues arranged in block wise fashion [11].

Another important natural polymer is hydroxyl propyl cellulose (HPC).It is a non ionic water soluble polymer, abundantly used in membrane studies. It is an alkyl-substituted hydrophilic cellulose derivative that not only has a particular phase transition behavior in aqueous solution [12] but also has many advantages such as excellent film forming properties, degradability, biocompatibility etc. [13]. It has been widely used in pharmaceutical applications [14-15], due to its excellent film forming property and hydrophilic nature; they act as acceptable barrier to oxygen and moisture [16-17].

Iso-propanol has been widely used in semiconductor and liquid crystal display industries as a water removing agent, also used as a solvent in many pharmaceutical industries and which forms an azeotrope at 14.7 mass% of water concentration [18].

In continuation of our research on separation of different aqueous organic liquid mixtures [19-21, 22] we thought of preparing blend membranes of SA and HPC, since such developed blend membranes have not been reported so far in the literature. Particularly, the developed blend membranes were found to be much better properties than these individual polymer membranes.

The present study reports on the preparation of the blend membranes of sodium alginate (SA) and hydroxy propyl cellulose (HPC), which are cross linked with GA, for dehydration of iso-propanol. The work also exposes the effect of varying water concentration in the binary feed mixture on membrane flux and selectivity, and the results are incorporated in this paper.

2. EXPERIMENTAL 2.1. Materials

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 was purchased from Aldrich Chemical Company, Milwaukee, WI, USA. Iso-propanol was purchased from Qualigens fine chemicals, Mumbai, India, and glutaraldehyde 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.

2.2. Preparation of membranes

SA/HPC blend membranes were prepared by solution casting and solvent evaporation technique. In brief by dissolving 4gm of SA and HPC in 100 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 this 4% of SA solution, different amounts of HPC (20, 40, and 60 wt %) were added. The membranes thus prepared are designated as SA-HPC-20, SA-HPC-30 and SA-HPC-40 respectively, while the pristine SA and HPC membranes was designated as SA and HPC. 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 $(30^{\circ}C)$ 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 Gluteraldehyde (GA). After allowing 12 h, take out the membrane from the cross linking bath, and washed with deionized water repeatedly then dried in an oven at 60° 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 area of the membrane and the thicknesses of the membrane prepared were around of 35-40 µm.

Scheme 1. Structural representation of Sodium alginate-Hydroxypropyl cellulose blends membrane crosslinked with gluteraldehyde.

2.3. 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 threeblade 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 [22]. Weight of the permeate vapours 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 [23].

$$
\left(\frac{Y_A}{1 - Y_A}\right) \left(\frac{1 - X_A}{X_A}\right) \tag{1}
$$

Where $X_{\rm A}$ is mole fraction of water in feed and $Y_{\rm A}$ is the mole fraction of water in permeate. Flux, J (Kg/m²h), was calculated from the weight of liquid permeated, W (Kg), effective membrane area, A (m^2) and actual measurement time, t (h)

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

2.4. Membrane Swelling

The swelling experiments on the circularly cut membranes were performed at 30° C gravimetrically [24] in 10, 12.5, 15 and 17.5 wt. % water-containing fed mixtures. Blend samples with compositions ranging from 10 to 17.5 wt % water at $30^{\circ}\text{C} \pm 0.5^{\circ}\text{C}$ in an electronically controlled incubator (WTB Binder, model BD-53, Tuttilgen, Germany) as per procedures reported previously [25]. Initial weights of the circularly cut (dia=2.5 cm) disc shaped blend membranes were stored in a desiccators over anhydrous calcium chloride maintained at 30° C 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 ± 0.01 mg. The swollen membranes were weighed immediately after careful blotting to remove surface adhered water. The percent degree of swelling (DS) was calculated as

Degree of switching (S)
$$
(\%) = W_s-W_d x 100
$$
 (3)

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

2.5. Fourier transform infrared spectral (FTIR) analysis

 FTIR Spectra measurements were recorded in the wavelength region of 4000-400 $\rm cm^{-1}$ under a $\rm N_2$ atmosphere at a scan rate of 21cm^{-1} using Bomem MB-3000 (Make :Canada) FTIR spectrometer, equipped with attenuated total reflectance

(ATR). About 2mg of the sample was ground thoroughly with KBr, and pellets were made under a hydraulic pressure of 600 kg/cm^2 .

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 pristine SA and SA-HPC blend membranes. The X-rays of 1.5406 Åwavelengths were generated by a Cu Kα radiation source. The angle of diffraction (2 θ) was varied from 0[°] to 65[°] to identify any changes in crystal morphology and intermolecular distances between inter-segmental chains of the polymer.

2.7. 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 \pm 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 $(\pm 0.01^{\circ}C)$. 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.

2.8. 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.

2.9. 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 10^0 C/min under N_2 atmosphere at a purge speed of 100 mL/min.

3. RESULTS AND DISCUSSIONS

3.1. Fourier Transform Infra-Red spectroscopy (FTIR)

The FTIR spectra of the cross linked and uncross linked SA-HPC blend membranes variations are displayed in Fig.1 All the membranes synthesized (Fig.1(a)-(f)) showed characteristic peaks appearing in the range 3010-3460 cm⁻¹ corresponding to O-H stretching vibrations of both SA and HPC. The

characteristic of SA band appeared at 736 cm-1 [26]**.** The strong band at 1753 cm⁻¹ could be indicative of the free carboxyl group of SA, whereas the band at 1520 cm^{-1} were assigned to the presence of salified carboxy group. The strong bond appeared around 1620 and 1416 cm⁻¹ assigned to anti symmetric and symmetric-COO– stretching vibrations of the carboxyl group respectively [27]. In detail, 1530 cm⁻¹ band is assigned to the anti symmetric and symmetric COO stretching vibration of the salified carboxyl group, respectively. The bands appearing in the range of $1064-1114$ cm^{-1} in the cross linked blend membrane correspond to C-O-C linkages of stretching vibrations. This band appears due to the formation of an ether linkage as a result of the reaction between hydroxyl group and glutaraldehyde. Such changes in the spectra confirmed the successful crosslinking of glutaraldehyde with SA-HPC blend membranes [28].

Fig.1. FTIR Spectra of (a) Crosslinked SA-HPC-40 (b) Uncross linked SA-HPC- 40 (C) Crosslinked SA-HPC-30 (d) Uncross linked SA-HPC – 30 (e) Crosslinked SA-HPC- 20 (f) Uncross linked SA-HPC 20

3.2. X-ray diffraction studies (XRD)

Fig.2. X-RD diffractogram of (a) SA-HPC -20 (b) SA-HPC-40 (c) Pure SA and (d) Pure HPC

X-RD curves of cross linked SA-HPC-20 (curve a), SA-HPC-40(curve b), pristine SA (curve c) and pristine HPC (curve d) membranes are displayed in Fig.2. The pattern of

sodium alginate shows a broad peak at $2\theta=14^\circ$. The two different peaks were observed in the case of SA/HPC blend membranes at a 2 θ value of 8^0 , 13^0 suggesting that their structures remain independent in the blend. Broad peaks appear in SA-HPC-40 at 13^0 and in SA-HPC-20 at 8^0 represent the amorphous nature of the polymer blend matrix.

3.3. Thermo gravimetric analysis (TGA)

Thermo gravimetric analysis provided quantitative information on the process of weight loss. The thermal stability and degradation behavior of the pristine SA, pristine HPC and blended SA-HPC membranes are shown in Fig. 3. From the thermograms, it is clear that under nitrogen flow non-oxidative degradation occurred in two stages for all the membranes. TGA curve of pristine SA (Fig.3a) membrane showed a single weight loss stage in the range $175-250$ °C, followed by a final decomposition at 250 °C on the other hand; pristine HPC (Fig.3b) membrane showed a single weight loss stage in the ranges between $180-220$ °C and followed by a final decomposition between $250-310^0$ C, respectively. The TGA curve of SA-HPC-40, SA-HPC-30 blends (Fig.3e, 3d.), shows weight loss stage occurring at $180-280$ °C followed by a final decomposition at 280° C. The SA-HPC-20 blend membrane (Fig.3c) on the other hand, shows two step weight loss between $215-250^{\circ}\text{C}$ and $260-315^{\circ}\text{C}$, corresponding to the decomposition of SA and HPC polymers, respectively. Thermal degradation studies indicate that the crosslinked blends can be effectively used in PV experiments at temperature up to 150° C, but we did not attempt to investigate up to such a high temperature.

Fig.3. TGA Curve of (a) Pristine SA (b) Pristine HPC (c) SA-HPC-20 (d) SA-HPC-30 (e) SA-HPC 40

3.4. Swelling studies

Degree of swelling of the pristine SA membrane followed by the sequence: Isopropanol ≤ 1 , 4 dioxane \leq THF and trend is similar to the flux data. Since Degree of swelling upon the extent of interaction of water molecules with the membrane materials and hence, higher selling would mean higher thermodynamic interactions.

Results of Degree of swelling (S) of pristine SA membrane, pristine HPC as well as SA-HPC blend membranes (viz., SA-HPC-20, SA-HPC-30, SA-HPC-40) measured as a function of wt % of different ratios of water-isopropanol feed mixtures (10-17.5 % at 30 \degree C) are displayed in Fig.4. Degree of Swelling is a dynamic process, which depends upon the mutual diffusion of solvent molecules in response to polymer segmental relaxation processes [29]. Flux values depend upon the equilibrium membrane swelling. Lower value of membrane swelling resulted in lower permeation fluxes, suggesting a linear relationship between the equilibrium swelling and the flux. Formulations containing higher amount of SA showed higher swelling rates than the formulations containing lower amount of SA. This increase in swelling rate is due to more hydrophilic nature of SA, there by leading to higher water uptake.

Fig. 4.Degree of swelling vs. wt % of water in feed mixture at 30⁰C

For pristine HPC membrane, Degree of swelling increased systematically with increasing feed water composition, but for SA-HPC blend membranes, Degree of swelling increased steadily up to 30 wt% of water in the feed mixture, which increased considerably with a maximum sorption value of 55 wt%. For instance, equilibrium swelling is higher for SA-HPC-40 membrane than for SA-HPC-30, SA-HPC-20; for all the blend membranes, swelling is higher than the pristine SA membrane, indicating their higher hydrophilicity. The increase in swelling for blend membranes is due to flexible nature of molecular chain as well as due to increase of molecular weight. In diffusion controlled swelling, molecules in the outer layer of membrane first undergo relaxation followed by diffusion of solvent molecules in to the bulk [30]. This means that water molecules are absorbed more preferentially than isopropanol and hence, this will diffuse out more easily through the blend membranes than the pristine SA membrane. This can be explained as due to the plasticization effect of the blend membrane in the presence of HPC making it more hydrophilic than the neat SA membrane. In addition, the hydroxy propyl group of HPC is bigger than carboxyl group (-COO⁻) of SA.

This shows that the blend membranes of SA-HPC compositions interacts extensively with water and is capable of being highly selective towards the same during separation. However, absorption of large amounts of water at high feed concentration could cause enhanced swelling and subsequently a fall in membrane selectivity due to plasticization of the polymer chains. Therefore, the flexibility of the blend membranes increases to create more free volume. This type of affinity of membranes to water molecules would result in increased water sorption. This would allow water molecules to diffuse out more easily, resulting in a higher amount of sorbed water.

3.5. Scanning electron microscopy (SEM)

Fig.5. SEM images of (a) Pure HPC (b) pure SA, and (c) SA-HPC-20 blend membrane

The SEM images of pristine HPC (a), pristine SA (b), and blended SA-HPC-20 (c) membranes (Fig. 5) show that the membranes casting were proper as they all depict non-porous structures. Accordingly, such membranes may be considered to be of dense structures, which are essential for pervaporation studies. Macroscopically, (a), (b) membranes appear opaque. The fig .5 (a) and (b) membrane has a thick and dense top layer almost without any pores, which is supported by a porous sub layer similar to the so called sponge structure. Typical SEM images of SA-HPC-20 Suggest smooth surfaces for all membranes with no phase separation, in these blend membranes has no pores, suggesting a homogenous and more

3.6. Pervaporation studies

uniform distribution.

3.6.1. Membrane performance

Table.1. Pervaporation data of water + isopropanol feed mixture at 30⁰C for pristine SA and variations SA-HPC blend membranes

Extensive research has been done in finding a suitable membrane having a preferential interaction with the specific component of a mixture in order to maximize the membrane performance such as flux and selectivity. In this present research, the PV performance of pristine SA, pristine HPC and SA-HPC blend variations of membranes has been investigated for the feed (water/Iso propanol) mixtures containing 10,

12.5, 15 and 17.5 wt. % of water. The hydrophilic SA –HPC blend membranes are used for the dehydration of isopropanol will possibly exert an interaction with water molecules of the feed mixture, since it interacts more preferentially than Iso propanol. Flux and selectivity data for 10, 12.5,15 and 17.5 wt. % water containing feed mixture presented in Table 1.This data shows that permeation flux increases with increasing SA content of the blend. Selectivity also increases initially with increasing SA; however, selectivity is high at SA content of 80wt % (SA-HPC-20), but low at lower amounts of SA, i.e., in case of SA-HPC-30,SA-HPC-40 blend membranes, the selectivity was reduced. This may be due to molecular structure and hydrophilic nature of SA, SA-HPC blending compositions, which transports huge number of water molecules than isopropanol. From this, one can conclude as noted before that the polymer plasticization effect would be the responsible factor for decreased selectivity [31, 32]. An increase of SA content in the blend matrix, leads to a more flexible polymer network, this indicats higher free volume in the membrane, resulting in the increase of permeation rates.

3.6.2. Effect of feed water composition

This effect is attributed to polymer plasticization as seen with the pristine SA and variations of SA-HPC blend membranes due to swelling, which would facilitate transport of water molecules from feed to permeate side manifested by hydrophilic–hydrophilic interactions. SA membranes have higher flux values with a reasonably good selectivity at increasing water concentration of the feed mixture. Flux and selectivity results at 30˚C are presented in Table.1. The flux for pristine SA membrane has increased from 0.092 to 0.137 $kg/m²$ h for varying feed concentrations of water from 10 to 17.5 wt.%. As the feed water concentration increases, the selectivity of pristine SA membrane decreases considerably from 607 to 245 and same as the SA-HPC-20 membrane decreased from 1314 to 39. Similar to this observation, wt. %. Water removed in the permeate also decreased from 98.54 to 98.12. On the other hand, the PV performance of pristine SA membrane was developed by blending with pristine HPC (i.e., 10, 12.5, 15and 17.5 wt %). For instance, flux for SA-HPC-20 membrane increased from 0.1884 to 0.2879 Kg/m²h, while for SA-HPC-30 membrane, it increased from 0.179 to 0.270 $Kg / m²h$ at an in increasing amount of water in the feed from 10 to 17.5 wt.%. In the case of SA-HPC-40 membrane, flux has increased from 0.1600 to 0.2681 Kg /m² h.

The preferential interaction with water molecules causes the membrane to swell, leading to plasticization and unrestricted and quicker transport of both volatile components through the barrier. On swelling, the polymer chains become more flexible and hence the transport through the membrane becomes easier for both the feed components resulting in high flux [33].

Fig .6. Selectivity vs. wt. % of water in feed mixture for pristine SA membrane and blend membranes of SA-HPC various compositions.

Fig .7. Flux vs. wt. % of water in feed mixture for pristine SA membrane and blend membranes of SA-HPC various compositions.

3.6.3. Comparison of PV results with literature

Table. 2. Comparisons of PV performance of the present crosslinked SA-HPC-20 blend membrane with literature data for water-isopropanol separation.

In the literature, many types of membranes have been used to study PV dehydration of isopropanol. Table.2. compares flux and selectivity data of the present blend membranes with those of the literature data. A comparison of all the membranes was made under similar feed conditions and temperature. In this present research below table gives a comparison of the PV performance data of other similar properties of blend membranes used in PV separation of water + isopropanol mixtures [34-37]. It is realized that the performance of the pristine SA membrane is not satisfactory due to larger free volume between the polymer chains. However it is clear that the membrane property of SA was improved by blending with HPC and hence, the present SA - HPC-20 blend membrane exhibited much higher values of flux and selectivity for water $+$ isopropanol mixture that most of the published data.

4. CONCLUSIONS

Sodium alginate (SA) and hydroxy propyl cellulose (HPC) blend membranes were prepared for different compositions of (SA-HPC-20, SA-HPC-30, SA-HPC-40).HPC Viz, 20, 30, and 40 mass% for dehydration of isopropanol. The effect of water permselective characteristic of SA could be prepared by blending with HPC to yield good flux and high selectivity. Membrane characterization confirmed that the extent of cross linking by FTIR and DSC technique. The crosslinked SA-HPC blend membranes are useful for the dehydration of the isopropanol. The balance between blend compatibility and hydrophilicity is important to obtain high permeation flux and selectivity for dehydration of isopropanol. Swelling results indicate that the effect of HPC content on sorption is important to induce changes in pervaporation characteristics of SA-HPC blend membranes. With increasing feed water composition, the membrane performance exhibited a reduction in selectivity and improvement in flux due to increased swelling. On the whole, the PV separation of SA-

HPC-20 blend membrane is better than pristine SA membrane as well as that of SA-HPC-40 blend membranes.

5. ACKNOWLEDGEMENTS

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