Pervaporation Separation of Water-Isopropanol mixtures using Halloysite nanoclay (HNC) incorporated in the Poly (Vinyl alcohol) Membranes

U. Sajankumar ji Rao[1], K.Sreenivasulu[1], Y.Maruthi[1], P. Kumara Babu[1], G.Nagarjuna M.C.S.Subha[2], K. Chowdoji Rao[1*]

[1] Department of Polymer Science & Tech, S.K.University, Anantapuramu – 515003 A.P, India.
[2] Department of Chemistry, S.K.University, Anantapuramu – 515003 A.P, India.

Abstract- A solution casting technique was used to prepare Halloysite nanoclay (HNC) incorporated Poly (vinyl alcohol) (PVA) mixed matrix membranes (MMMs) and crosslinked with glutaraldehyde (GA). The prepared membranes were characterized by Fourier transform infrared spectroscopy, X-ray diffraction, Scanning electron microscopy, differential scanning calorimeter and thermo gravimetric analysis. Resulting membranes were tested for pervaporation (PV) separation of water-isopropanol mixture. The Degree of swelling of the membranes in various concentrations of water–isopropanol mixtures revealed an increase in the degree of swelling as the Halloysite nanoclay (HNC) loading was increased. The effect of clay loading and feed composition of water on pervaporation performance of the membranes was analyzed. The membrane containing 0.3wt. % of HNC loaded blend membrane (PVHNC-3) gave the highest selectivity of 2423 for 10 mass % of water containing feed mixture at 30 ^{0}C. Increase in water selectivity of the membrane was explained as due to a reduction in free volume by increasing clay content of the membrane. Selectivity and flux data are dependent on water composition of the feed mixture. The hindrance of water permeation at higher composition of water in feed mixture was explained as due to the formation of clusters of water molecules. These results showed that, when the water concentration of feed is increased, the selectivity decreased but flux increased. This Halloysite nanoclay (HNC) incorporated mixed matrix membranes (MMMs) are relatively hydrophilic, mechanically strong and thus suitable to be used for the pervaporation separation of isopropanol – water mixture.

Index Terms- Pervaporation, PVA membrane, Halloysite nanoclay, isopropanol-water mixtures.

I. INTRODUCTION

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 [1-3]. Over the last few decades, several commercial PV plants have been established all over the world especially for the dehydration of organic solvents. Therefore, much of the attention has now been focused toward the development of new membranes with better performance in the separation of azeotropic, isomeric and close boiling point systems.

The key for a successful PV dehydration separation process is preparation of membrane for achieving a simultaneous increase of both selectivity and permeation flux. However, most polymer membranes, including PVA, suffer from the inherent drawback of trade-off in aqueous solution between permeability and selectivity. To cross this trade-off hurdle, many modifying methods were carried out through chemical cross-linking, adding fillers [4], physical blending with other polymers [5], surface modification, copolymerization or hybridization. Among those methods, hybridization is of great interest owing to its applicability to improve both the stability and performance of membrane. In literature it is noticed that, researchers have prepared numerous organic – inorganic hybrid membranes, such as PVA/TEOS [6, 7], PVA / γ-aminopropyl triethoxy silane (APTEOS) [8], PVA / γ-glycidyloxy propyltrim ethoxysilane (GPTMS) [9], PVA / TEOS [10], PVA / AESP [11]. The hybridization effectively controls the swelling of hydrophilic polymer membrane in aqueous solution, but the permeation flux of membrane is usually depressed. Therefore, controlling the swelling degree and to retain the permeation flux simultaneously is the focus of modification for these membranes.

Many researchers are making continuous efforts to develop new polymeric membranes. Recently, several reports have been published in the literature using different types of hydrophilic polymers including poly (vinyl alcohol) (PVA), sodium alginate and chitosan as membranes in PV separation of aqueous-organic mixtures [12-16]. In view of the excellent film forming property and super hydrophilic nature, PVA is still attracting more interest for researchers and has been extensively studied as a membrane material.

PVA is one of the most important water soluble vinyl polymers, that exhibits excellent film forming, emulsifying and adhesive properties [17]. The hydroxyl groups in PVA can form strong hydrogen bonds between intra and intermolecular hydroxyl groups. This causes PVA to show high affinity towards water. Therefore, PVA is mainly used as a membrane material in PV for dehydration of solvents. PVA membranes usually give good permeation flux but low separation selectivity due to high swelling which limits the performance of these membranes in PV separations. To enhance the membrane performance, PVA needs modification to get good mechanical property and achieve better selectivity towards water [18-19]. Polymer – clay nanocomposite is a new class of composite materials consisting of a polymer matrix with dispersed clay nanoparticles. And these MMMs with

inorganic hybrid material with good hydrophilicity are chosen in the present study.

Nano-structured polymer-clay hybrid materials are currently the objects of intensive research because of their unique properties and low cost synthesis as clays is abundantly available in nature. The PVA reinforced with montmorillonite clay showed better thermal, mechanical, and water vapor transmission properties because of the nanoscale dispersion of the filler in the polymeric matrix [20]. The α – zirconium phosphate reinforced PVA matrix resulted in the increase in its storage modulus, tensile strength, and elongation at break with increase in the aspect ratio of the filler content[21].

Halloysite nanoclay (HNC) is naturally occurring silicate nanoclay ubiquitous in soils and weathered rocks. Halloysite nanoclay (HNC) deposits have been found in many geographic areas where they are present in a variety of particle shapes and hydration states. Halloysite is a unique nanoclay property [22], with a tubular morphology and low electrical and thermal conductivity. HNC have an empirical formula of $Al_2Si_2O_5(OH)_4$ $2H_2O$, which is chemically similar to kaolin clay. Halloysite is a two-layer mineral, characterized by its affinity to the monovalent cations. Those cations can act as "anchor" for the inner-sphere and interlayer cation-water complexes. Because this Halloysite plates easily dispersed and delamination in water, much easier than montmorillonite does. This Halloysite nanoclay (HNC) has better surface properties and this can form a new kind of interlayer space which can be resistant to the multivalent cations activity. Halloysite has a Si-tetrahedral sheet on one side and an Al-octahedral sheet on the other side. In this oxygen atoms of halloysite tetrahedra form a regular 6-fold hexagonal structure. This structure remains intact even after dehydration which suggests that either the "hole" water remains within the structure or that the rotation is blocked by physical forces [23-24]. In halloysite they cause a unique change in the structure resulting in layer separation which in other minerals from the kaolinite group is strongly bound together.

However, the performance of PVA / Halloysite nanoclay (HNC) membranes was not well explored in this field. Isopropyl alcohol (IPA) is a widely used solvent in pharmaceutical and chemical industries. IPA forms an azeotrope with water at 87.5 wt. %, and most of its application needs high purity. In the industrial point of view, the dehydration of the azeotropic composition o f IPA is an important one. The separation of the azeotropic composition of the isopropanol (IPA) – water system is too difficult to carry out by using conventional methods such as distillation [25]. The results of some of the previous work for water – isopropanol alcohol pervaporative are summarized in Table.2 together with the result obtained in this work. From this table, it is obvious that the performance like flux and selectivity of HNC incorporated PVA membrane is better than the performance which was obtained from the membranes of other researchers.

II. EXPERIMENTAL

2.1 Materials

Poly(vinyl alcohol) (PVA) having a viscosity average molecular weight of 70,000 and degree of Hydroxylation 86 – 89 % , Acetone and Hydrochloric acid were purchased from S.d. fine chemicals, Mumbai, India. Halloysite nano clay (HNC) was purchased from Aldrich Chemical Company, Milwaukee, WI, USA. Iso-propanol was purchased from Qualigens finechemicals, 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.

2.2. Preparation of PVA / Halloysite nano composite membranes

MMMs of Poly (vinyl alcohol) (PVA) incorporated with Halloysite nano clay (HNC) membranes were prepared by solution casting and solvent evaporation technique. In order to prepare pure PVA solution, here we use powder form of PVA. For every 5 gr of PVA powder weighed, 90 ml of distilled water as a solvent used to dissolve PVA powder. As the resultant solution was non – clear then, it was stirred and heated. When the temperature reached 70 ^{0}C, rate of dissolution of PVA increased and the solution became clear one. Heating continued for about 30 minutes to let the temperature rises up to 90 ^{0}C. At this temperature, all the PVA powder was miscible. In separate flasks, 0.2, 0.3g of HNC was dispersed in 10 mL of water, sonicated for 2h, added individually to the previously prepared 5 wt % PVA 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 12h, take out the membrane from the cross linking bath, and wash with deionized water repeatedly then dry in an oven at 40 ^{0}C for 48h to eliminate the presence of residual acid, if any. The dried MMMs were peeled off and designated as Pristine PVA, PVHNC-2 and PVHNC-3 respectively. 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.

III. CHARACTERIZATION OF THE PVA/HALLOYSITE NANOCLAY NANOCOMPOSITE MEMBRANES

3.1. Fourier transform infrared spectroscopy (FT-IR)

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 Bomem MB – 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.

3.2. Scanning electron microscopy (SEM)

SEM micrographs of the MMMs 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.

3.3. 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.

3.4. 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 PVA 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 0^0 to 65^0 to identify any changes in crystal morphology and intermolecular distances between inter-segmental chains of the polymer.

3.5. 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 [26].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 [27].

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

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)

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

3.6. Membrane Swelling

The swelling experiments on the circularly cut membranes were performed at 30 ^{0}C gravimetrically [28] in 10, 12.5 and 15 wt. % water-containing fed mixtures. MMMs 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 [29].To do this, dry weight of the circularly cut (diameter=2.5 cm) disc shaped MMMs were stored in a desiccators over anhydrous calcium chloride maintained at 30^0C for about 24 h before performing the swelling experiments. This dry weight of the circularly cut (diameter = 2.5cm) MMMs 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

$$\text{Degree of swelling (S) (\%)} = \frac{(W_s - W_d)}{W_d} \times 100 \quad (3)$$

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

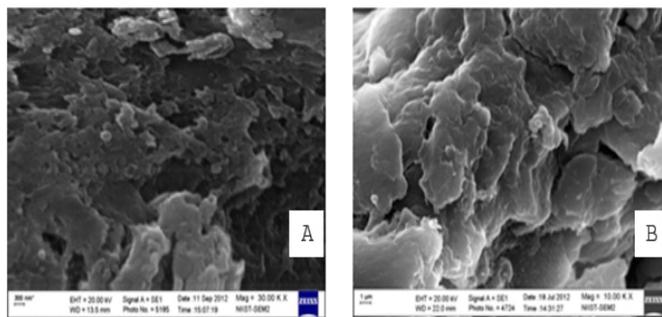## IV. Results and Discussion

4.1. FT-IR analysis

The FTIR spectra of Pristine PVA and Halloysite nanoclay (HNC) incorporated membranes (PVHNC-2, PVHNC-3) are shown in the Fig.1. In this the FTIR spectra of Pristine PVA showed a characteristic broad peak at 3200-3400 cm^{-1} indicating –OH stretching.The obtained FT-IR spectra of PVA are in good agreement with literature [30]. The bands around 2908 and 2858 cm^{-1} correspond to the asymmetric and symmetric stretching of – CH_2 – groups, respectively. The peaks at 1420 cm^{-1} can be attributed to C-H bending. From the FTIR spectra of clay loaded both the membranes it is noticed one broad characteristic peak at 3365 cm^{-1} which is assigned to –OH stretching, at 2980 cm^{-1} which is assigned to –CH_2 stretching. In these MMMs multiple bonds are shown between 1050 and 1165 cm^{-1} and are assigned Si-O stretching. By the incorporation of HNC content into pristine PVA, the intensity of these multiple bands was increased steadily. This is because of symmetric and asymmetric stretching bands of Si = O and Al =O which generally appear at the same frequency of C-O stretching. In this mixed matrix membranes, there was no absorption peak observed, suggesting that the Halloysite nanoclay (HNC) was physically blended within the polymer matrix. This also further ascertains the complete dispersion of nanoclay in the crosslinked PVA membranes.
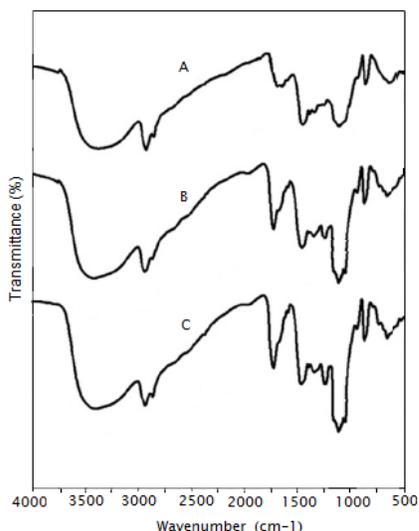
Fig.1: FTIR spectra of (A) Pristine PVA, and its HNC incorporated Composite membranes   (B) PVHNC-2, (C) PVHNC-3.

Fig. 2: SEM image of (A) MMMs of PVHNC-2 (B) MMMs of PVHNC-3.

### 4.2. Scanning electron microscopy (SEM)

Fig. 2 illustrates the Scanning electron microscopy (SEM) of cross linked HNC loaded membranes (PVHNC-2 and PVHNC-3). From these micrographs, it is observed that surface view of these membranes were uneven. This might be due to increased cross linking segments by the incorporation of HNC content in pure PVA membrane. It may be due to increased hydrophilic property of the membrane by the dominancy of Si, Al and –OH groups over the crosslinking segments. From the SEM graphs it is also noticed that the homogeneous mixing of HNC is attributed to hydrophilic nature of nanoclay with a lower silica alumina ratio value and their presence is responsible to create channels between inter phase of the polymer and clay particle surfaces that are more selective to water than IPA. However, particle agglomeration is seen in case of PVHNC-3 due to its relative hydrophobic nature compared to nanoclay with a lower silica alumina ratio, where these channels are formed in the interphase they are less selective to water.

4.3. Differential Scanning Calorimetry (DSC)

DSC is the technique used to determine the quantity of heat either absorbed or released when substances undergo physical or chemical changes. Differential scanning calorimetric measurements were carried out for PVHNC-2 and PVHNC-3 membranes and the resulting thermograms are presented in Fig.3. The change in physical properties in the polymer membranes due to crosslinking and incorporation of Halloysite nanoclay (HNC) can be reflected in their glass transition temperature (T_g) and melting point (T_m) values which have been confirmed by the DSC results. The DSC thermograms of PVHNC-2 and PVHNC-3 mixed matrix membranes show a value of T_g at 110 ^{0}C and 130^0 C melting temperatures are around 325 ^{0}C to   350^0 C respectively. From these it is evident that the increase in $T_{g \& }T_m$ values of these membranes was due to increase in the HNC content. This is due to decrease in free-volume of the PVA matrix which confirms the cross linking reaction between hydroxyl group of PVA and Al, Si and the carboxylic groups of HNC in the mixed matrix membranes. This is attributed due to the increased crystallinity of PVA by chemical crosslinking reaction with HNC molecule. This is attributed due to reduced crystallinity of PVA by the incorporating HNC then they form chemical cross linking in these MMMs, which breaks the molecular symmetry of PVA of mixed matrix membranes to some extent.
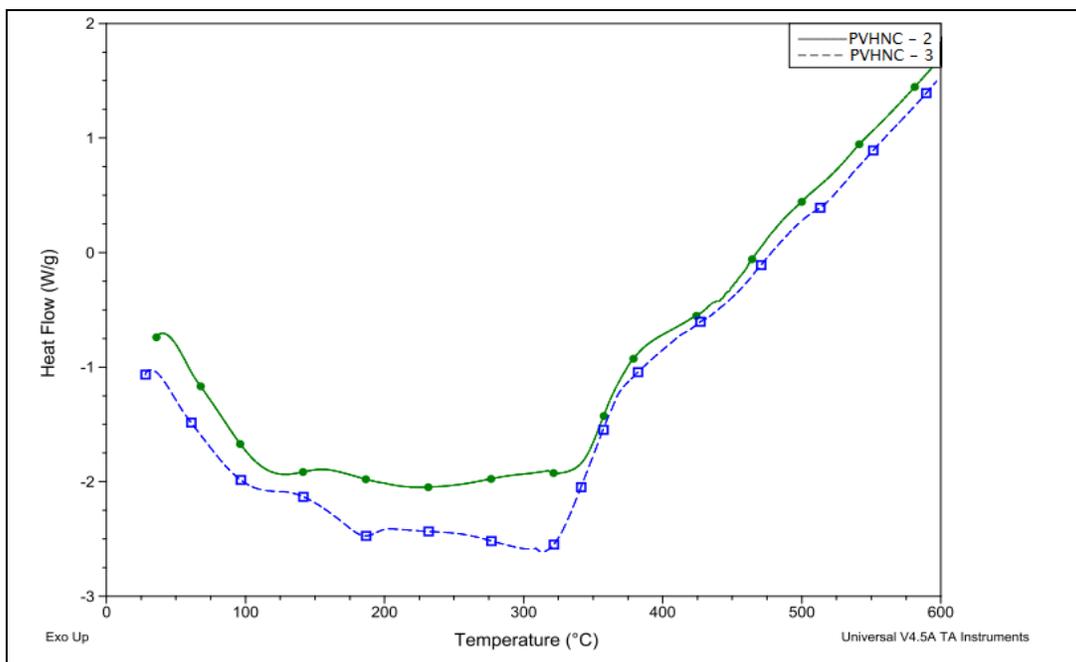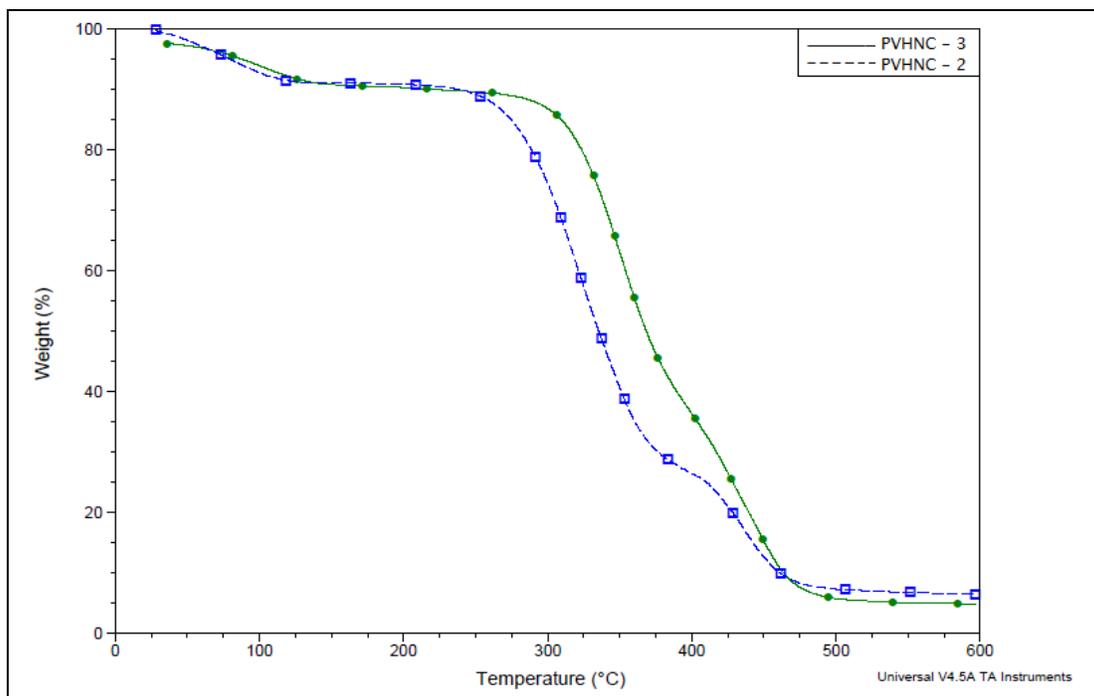
Fig. 3: DSC. Thermograms MMMs of the PVHNC-2 and PVHNC-3.

4.4. Thermo gravimetric analysis (TGA)

The TGA used to determine by monitoring the weight loss of the sample in a chosen atmosphere as a function of temperature. The thermal stability of the Halloysite nanoclay (HNC) incorporated MMMs of PVHNC-2 and PVHNC-3 were analyzed using thermo gravimetric analysis under nitrogen atmosphere and the resulting thermograms are shown in Fig.4. The two nano clay filled membranes (PVHNC-2 & PVHNC-3) exhibited there consecutive steps for weight loss. It can be seen that the first weight loss of about 10 % occurred around 80-150° C which is due to desorption of physically absorbed water molecules in the membranes. The second weight loss was of about 75 % occurred between the temperature ranges of 200 ^{0}C to 375 ^{0}C which corresponds to the degradation of crosslinker [31]. The third weight loss occurred between 400 ^{0}C and 490 ^{0}C, which is presumably related to the degradation of main-chain backbone of crosslinked membranes that could be attributed to thermal oxidation of PVA. From these TGA results, it is further justified that the residual amounts of membranes were increased with increasing the HNC content. This represents that thermal stability of membranes increased due to the increase in the HNC concentration. In the PVHNC-2, the major two weight loss stages took place from 250 to 360 ^{0}C and followed by a further smaller weight loss from 370 to 470 ^{0}C. On the PVHNC-3, the major weight loss took place from 320 to 460 ^{0}C. The increase in the thermal stability was due to permeability of volatile degradation product to the material and maximize the heat insulation. On addition of nanofillers HNC clay to the polymer matrix and its stability is enhanced. This TGA study indicates that the mixed matrix membranes can be effectively used in PV experiments at temperature up to 150 ^{0}C.

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

4.5. X-ray diffraction (XRD)

The X-ray diffractogram of the pristine PVA, PCHNC-2 and PVHNC-3 mixed matrix membranes were shown in Fig.5. Generally, when the polymer contains crystalline domains the diffraction peaks are sharp and these intensities are high where as for amorphous polymer they are broad. In this the Pristine PVA showed broad peaks around 12^0 of 2θ, indicating the intermolecular distance of the amorphous part and a peak arising at the 22^0 of 2θ, due to sharp semi crystalline nature. In case of PVHNC-2 which showed the peaks at 8.9^0 and 19.6^0 of 2θ and PVHNC-3 which showed the peaks at 9.2^0 and 20.2^0 of 2θ. Here the two mixed matrix membranes (PVHNC-2 and PVHNC-3) peak intensity is lesser than Pristine PVA membrane. As the content of HNC was increase in pure PVA, the intensity of this was decreased gradually as can be seen from the X-RD patterns. This is because of the increased amorphous domains in HNC incorporated PVA membranes. The crystallinity was high in case of pure PVA membranes due to the presence of hydroxyl groups in its side chain. However in HNC incorporated PVA membrane the hydroxyl group of PVA reacted with HNC molecules resulting in a decreased crystallinity.
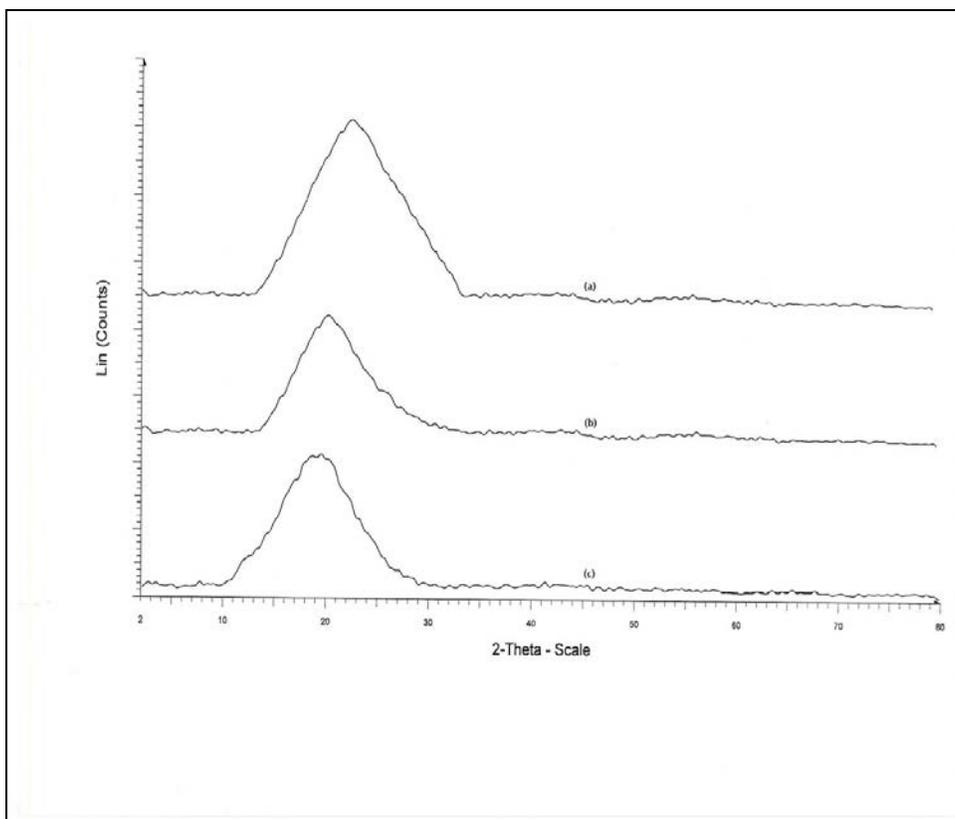
**Fig. 5: XRD spectra of (a) Pristine PVA and MMMs of (b) PVHNC-2 (c) PVHNC -3**

V. MEMBRANE PERFORMANCE

5.1. Swelling Experiments

In general, the hydrophilic membrane swells appreciably in aqueous solution. The swelling property of membrane is important for Pervaporation dehydration separation process since it affects the membrane perm selectivity. The polymer chains for swollen membrane would become more flexible and hence the permeates pass through the swollen membrane more easily.

The mechanism of degree of swelling depends on the microstructure of the membrane, affinity of the penetrates towards membrane and mutual interaction between them. Therefore, the degree of swelling of course plays an important role in PV process that controls the transport of permeating molecules under the influence of chemical potential gradient [32]. This study of the effects of feed composition and HNC content on membrane swelling, the percent degree of swelling of the Pristine PVA membrane, PVHNC-2 and PVHNC-3 mixed matrix membranes was plotted as a function of mass % of water in the feed at $30\ ^{0}$ C as shown in Fig.6. It is clearly noticed that the degree of swelling was increased for all the membranes with increasing amount of the mass % of water in the feed. This is due to the interaction between water molecules and the membrane, owing to the presence of interactive hydrophilic groups (-OH and –COO) in the membrane matrix. This is expected since water is more polar than IPA, which preferentially interacts with membrane resulting in an increase in degree of swelling, which increased with increasing the clay content in the membranes at all feed compositions. This may be due to the presence of Al-OH, Si-OH groups in the clay and –OH groups in PVA which dominates the hydrophilic properties of the mixed matrix membranes.
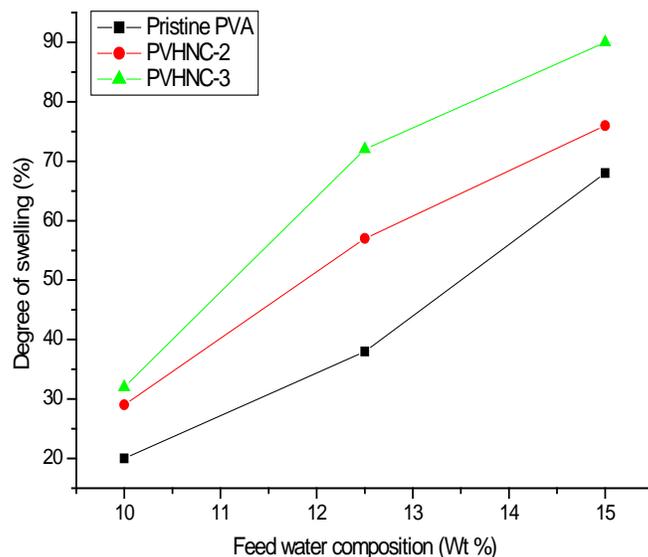
Fig. 6: Degree of swelling of Pristine PVA membrane and MMMs of PVHNC-2, PVHNC-3.

VI. PERVAPORATION STUDIES

6.1. Influence of HNC Loading on PV Performance

The Pervaporation performances of PVHNC-2, PVHNC-3 mixed matrix membranes have been evaluated by calculating flux and selectivity through the Pervaporation results. The PV performance of mixed matrix membranes (MMMs) is closely related to its structure and the incorporating nanoclay in an efficient way to modify the structure of PVA membrane. The effect of feed water concentration on PV performance was studied with the MMMs for various feed compositions ranging from 10-15 wt. % of water in feed at room temperature. The framed network and the more compact structure in HNC incorporated PVA results in the decrease of the free volume of membrane. This was because of incorporation of HNC into the membrane matrix which not only changed the membrane hydrophilicity but also its structure.

In PV process, the overall selectivity of a membrane is generally explained on the basis of interaction between membrane and the permeating molecules, molecular size of the permeating species and pore diameter of the membrane [33]. Fig. 7 displays the effect of water composition on the selectivity for all the membranes. It is observed that the selectivity of all the membranes was decreased with increasing the mass % of water in the feed. This is because of increased membrane swelling and plasticized upstream membrane layer, which allow some of IPA molecules to escape into the permeate side along with water molecules and this causes a negative impact on the membrane's selectivity. From Fig.7, it is also observed that selectivity was increased significantly from membrane PVHNC-2 to PVHNC-3 upon increasing the clay content. This is attributed to decreased crosslinking density that changed the membranes morphology. As a result, the mobility of polymeric chains apparently increased and the absolute free-volume diffused the permeates through the membrane also increased due to the hydrophilic nature of clay. Thus, water molecules having relatively small molecular size can diffuse through the crosslinked membranes easily rather than isopropanol molecules having large molecular size.

Generally in PV experiment, we are maintaining constant room temperature, flux values increase and selectivity values decrease due to thermal motion of polymer chain and formation of nanoclay micro clusters. However, the flux and selectivity get the better values of PVA mixed matrix membrane increased after incorporation of HNC particles, due to the presence of Halloysite nanoclay (HNC) particles into the continuous polymer phase is shown to be an attractive method of coupling an easy process ability of polymers with superior separation properties, Halloysite nanoclay-polymer mixed matrix membranes are quite useful in PV dehydration studies. In the present study, it shows that by adding 0.3wt % HNC into PVHNC-3 membrane, thus MMMs sorption capacity has increased, as PVHNC mixed matrix membrane and Halloysite nanoclay particles are hydrophilic in nature. So, the overall membrane performance can be explained clearly on the basis of solution-diffusion theory [34]. Then the PVA membrane incorporated with HNC the result of mixed matrix membrane can exhibit excellent potential to break the azeotropic balance, which shows the membrane prepared in this work is useful for the separation of isopropanol-water mixtures by pervaporation (PV) experiment.

6.2. Effect of feed water composition on the PV performance

PV studies have shown that membrane performance is affected by the water content in the feed mixture. In PV, the effect of feed 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 Fig.7 & 8. It is observed that the flux was increased with increase of the water composition in the feed. This is mainly because of increased membrane swelling. This is expected due to an establishment of greater interaction between the membrane and the water molecules as membrane contains a large number of hydrophilic groups such as –OH, -COOH and –CH$_2$, which prefer water molecules rather than IPA. On the contrary, the selectivity was decreased exponentially with increasing the 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, as 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.

1: Pervaporation data of the Pristine PVA and MMMs of PVHNC-2, PVHNC-3 for feed mixture of water –IPA at 30 ^{0} C.

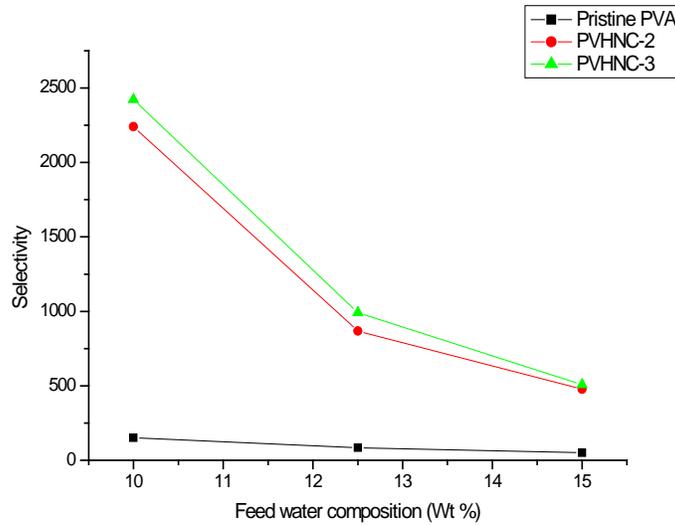| Wt.%. of water in feed	Wt.%. of water in permeate	Flux (J) (Kg/m^2 h)	Selectivity (α)
Pristine PVA			
10.0	94.32	0.1600	151
12.5	92.32	0.1804	84
15.0	90.08	0.2681	50
PVHNC-2			
10.0	99.60	0.3643	2241
12.5	99.20	0.3878	868
15.0	98.84	0.4021	477
PVHNC-3			
10.0	99.63	0.3725	2423
12.5	99.30	0.3985	992
15.0	98.91	0.4096	508

Fig. 7: Selectivity vs. wt. % of water in feed mixture for pristine PVA membrane and MMMs of PVHNC-2, PVHNC-3.
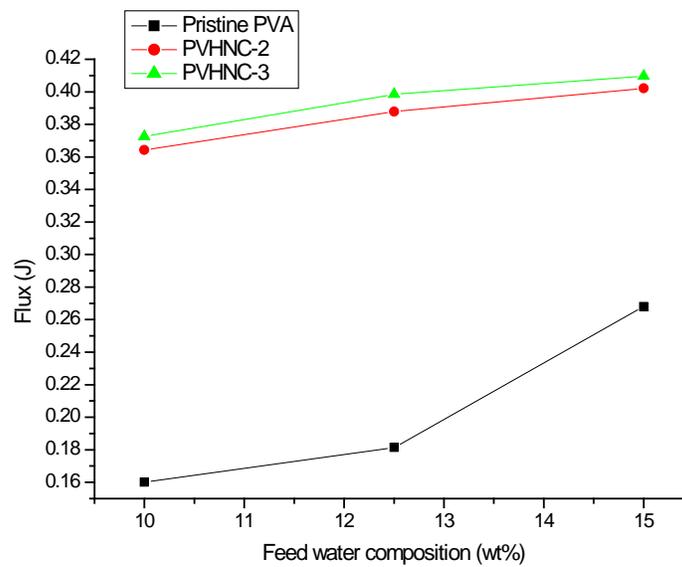

Fig. 8: Flux vs. wt. % of water in feed mixture for pristine PVA membrane and MMMs of PVHNC -2, PVHNC-3.

6.3. Comparison of PV results with literature

In the present study, we have demonstrated the variation of Halloysite nanoclay (HNC) in mixed matrix membrane (MMMs) of PVA to study the PV performance. As shown in Table.2, these HNC incorporated MMMs give better selectivity values compared to the other literature like, H-ZSM5 Zeolite with silica alumina ratio of 10 and 20 % when loaded into PVA membrane [35] and PVA incorporating Sulfophthalic acid (SPTA) [36]. In this study the results obtained are almost comparable or even better than those of the previously discovered polymeric membranes. The 0.2 and 0.3wt % of Halloysite nanoclay (HNC) filled PVHNC mixed matrix membrane have the good separation values compared to the literature.

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
PVA-H-ZSM5	30	10	144-138	568	[36]
PVA-SPTA(M4)	40	10	0.060	1991	[37]
PVHNC -2	30	10	0.3643	2241	Present work
PVHNC -3	30	10	0.3725	2423	

VII. CONCLUSIONS

The Pervaporation results of PVHNC-2 & PVHNC-3 membranes indicates that it is possible to enhance both flux and selectivity over that of pristine PVA membrane. The present experimental data indicated that due to the strong intercalated structure of PVA formed with Halloysite nanoclay (HNC) galleries, it is possible to obtain the layered crystalline structures in the PVA matrix. It was observed that the crystalline and hydrophilic nature of nanoclay particles could hinder the transport of organic components of the mixed aqueous media to offer an easy passage to water molecules through the membranes. An increase in flux and selectivity of the PVHNC-3 membrane can be attributed to the increase of membrane swelling as a result of more number of water selective sites available for such hydrophilic – hydrophilic interactions, but selectivity has decrease due to a decrease in crystallinity in addition to increased plasticization effect of the PVA membrane in the presence of a large amount of water during Pervaporation technique.

The effect of change in content of HNC particles and change in feed water concentration on flux and selectivity was investigated for the PV dehydration of IPA from the different water % of feed mixture. The results clearly show improved membrane performance due to the presence of hydrophilic nature of HNC particles and PVA. The 0.3 wt. % HNC incorporated mixed matrix membranes have shown the better selectivity of 2423. Pervaporation (PV) through HNC incorporated membranes provides the alternative to the industrial purification of aqueous organic liquid mixtures. These PV experimental results of the present study clearly explain the PV dehydration of IPA as influenced by the amount of HNC particles incorporated into the PVA mixed matrix membranes.

VIII. ACKNOWLEDGEMENT

REFERENCES

[1] Chapman, P. D.; Oliveira, T.; Livingston, A. G.; Li, K. Membranes for the dehydration of solvents by pervaporation. Journal of Membrane Science, 2008, 318, 5-37.

[2] Huang, Z.; Shi, Y.; Wen, R.; Guo. Y. H.; Su, J. F.; Matsura, T. Multilayer poly (vinyl alcohol)-zeolite 4A composite membranes for ethanol dehydration by means of pervaporation. Separation and Purification Technology, 2006, 51, 126-136.

[3] Chapman, P. D.; Tan, X.; Livingston, A. G.; Li, K.; Oliveira, T. Dehydration of tetrahydrofuran by pervaporation using a composite membrane. Journal of Membrane Science, 2006,268, 13-19.

[4] Mali, M. G.; Gokavi, G. S. Sorption and permeation studies for isopropanol + water mixtures using alginate based highly water selective nanocomposite membranes. Journal of Polymer Research, 2012, 19, 9976.

[5] Lin, W. H.; Li, Q.; Zhu, T. R. New Konjac Glucomannan-PVA Composite Membrane for Application in Pervaporation Dehydration of Caprolactam Solution. Chemical Engineering and Technology, 2012, 35, 1069-1076.

[6] Uragami, T.; Mastugi, H.; Miyata, T. Pervaporation Characteristics of Organic – Inorganic Hybrid Membranes Composed of Poly (vinyl alcohol-co-acrylic acid) and Tetraethoxysilane for water/Ethanol Separation. Macromolecules, 2005, 38, 8440 - 8446.

[7] Guo, R. L.; Hu, C. L.; Pan, F. S. PVA-GPTMS/TEOS hybrid pervaporation membrane for dehydration of ethylene glycol aqueous solution. Journal of Membrane Science, 2006, 281,454 – 462.

[8] Zhang, Q. G.; Liu, Q. L.; Jiang, Z. Y. Anti-trade-off in dehydration of ethanol by novel PVA/APTEOS hybrid membranes. Journal of Membrane Science, 2007, 287, 237 - 245.

[9] Pen, F. B.; Lu, L. Y.; Sun, H. L.; Wang, Y.; Wu, H.; Jian, Z. Correlations between free volume characteristics and pervaporation permeability of novel PVA-GPTMS hybrid membranes, Journal of Membrane Science, 2006,275, 97 - 104.

[10] Sajjan, A. M.; Jeevan Kumar, B. K.; Kittur, A. A.; Kariduraganavar, M. Y. Development of novel grafted hybrid PVA membranes using glycidyltrimethylammonium chloride for pervaporation separation of water – isopropanol mixtures. Journal of Industrial and Engineering Chemistry, 2013,19, 427 - 437.

[11] Premakshi, H. G.; Kariduraganavar, M. Y.; Mitchell, G.R. Development of Composite anion – exchange membranes using poly(vinyl alcohol) and silica precursor for pervaporation separation of water – isopropanol mixtures. RSC Advances, 2016, 6,11802 – 11814.

[12] Kahya, S.; Solak, E. K.; Sanli, O. Sodium alginate / Poly(vinyl alcohol) alloy membranes for the pervaporation,vapour permeation and vapour permeation with temperature difference separation of dimethylformamide / water mixtures: A comparative study. Vacuum, 2010, 84, 1092 - 1102.

[13] Kulkarni, S. S.; Kittur, A. A.; Aralaguppi, M. I.; Kridurganavar, M. Y. Synthesis and characterization of hybrid membranes using poly(vinyl alcohol) and tetraethylorthosilicate for the pervaporation separation of water – isopropanol mixtures. Journal of Applied Polymer Science, 2004, 94, 1304 – 1315.

[14] Kittur, A. A.; Tambe, S. M.; Kulkarni, S. S.; Kariduraganavar, M. Y. Pervaporation separation of water-acetic acid mixtures through NaY Zeolite – incorporated Sodium alginate membranes. Journal of Applied Polymer Science, 2004,94, 2101 – 2109.

[15] Alghezawi, N.; Sanli, O.; Aras, L.; Asman, G. Separation of acetic acid – water mixtures through acrylonitrile grafted poly(vinyl alcohol) membranes by pervaporation. Chemical Engineering and Processing: Process Internsification, 2005, 44, 51 - 58.

[16] Jiraratananon, R.; Chanachai, A.; Huang, R. Y. M.; Uttapap, D.Pervaporation dehydration of ethanol – water mixtures with chitosan / hydroxyethylecellulose(CS / HEC) composite membranes :I.Effect of operating conditions. Journal of Membrane Science, 2002,195, 143 - 151.

[17] Benguergoura, H.; Aouak, T.; Moulay, S. Use of pervaporation technique to monitor the oxidation of primary alcohols: n-propanol and n- butanol, Journal of Membrane Science, 2004,229, 107-116.

[18] Chiellini, E.; Corti, A.; Antone, S. D.; Solaro, R. Biodegradation of poly (vinyl alcohol) based materials. Progress in Polymer Science, 2003, 28, 963- 1014.

[19] Schildtnecht,C.E.Poly(vinyl alcohol) properties and Applications, Wiley Interscience, New York(1973).

[20] Peng. F.; Lu, L.; Sun, H.; Pan, F.; Jiang, Z. Organic – Inorganic Hybrid Membranes with Simultaneously Enhanced Flux and Selectivity. Journal of Industrial and Engineering Chemistry, 2007, 46, 2544 – 2549.

[21] Adoor, S. G.; Sairam, M.; Manjeshwa, L. S.; Raju, K. V. S. N.; Aminabhavi, T. M. Sodium montmorillonite clay loaded novel mixed matrix membrane sof poly(vinyl alcohol) for pervaporation dehydration of aqueous mixtures of isopropanol and1,4 - dioxane. Journal of Membrane Science, 2006, 285, 182 - 195.

[22] Liu, C.; Yang. Y. Effects of α – zirconium phosphate aspect ratio on the properties of polyvinyl alcohol nanocomposites. Polymer Testing, 2009, 28, 801 - 807.

[23] Du, M.; Guo, B.; Jia, D. Newlyemerging applications of Halloysite nanotubes : a reviw. Polymer International, 2010, 59, 574 – 582.

[24] Joussein, E.; Petit, S.; Churchman, J.; Theng, B.; Righi, D.; Delvaux, B. Halloysite clay minerals – a review. Clay Minerals, 2005, 40,383 - 426.

[25] Singh, B. Why Does Halloysite Roll? – A New Model. Clays and Clay Minerals, 1996, 44, 191 - 196.

[26] Lee, Y. M.; Nam. S. Y.; Ha, S. Y. Pervaporation of water / isopropanol mixtures through polyaniline membranes doped with poly(acrylic acid). Journal of Membrane Science, 1999,159, 41 – 46.

[27] Lokesh, B. G.; Krishna Rao, K. S. V.; Mallikarjuna Reddy, K.; Chowdoji Rao,K.; Srinivasa Rao, P. Novel nanocomposite membranes of sodium alginate filled with polyaniline – coated titanium dioxide for dehydration of 1,4 – dioxane / water mixtures. Desalination, 2008, 233, 166 - 172.

[28] Boddeker, K.W. Terminology in Pervaporation. Journal of Membrane Science, 1990, 51, 259 – 272.

[29] Harogoppad, S.B.; Aminabhavi, T.M.Diffusion and sorption of organic liquids through polymer membranes.5.Neoprene, styrene-butadience-rubber,ethylene-propylene-diene terpolymer, and natural rubber versus hydrocarbons (C8-C16). Macromolecules, 1991, 24, 2598 – 2605.

[30] Adoor, S. G.; Rajineekanth, V.; Mallikarjuna, N. N.; Chowdoji Rao, K. Exploration of nanocomposite membranes composed of phosphotungstic acid in sodium alginate for separation of aqueous – organic mixtures by pervaporation. Separation and Purification Technology, 2013,113, 64 - 74.

[31] Cheng, H .K. F.; Sahoo, N. G.; Tan, Y. P.; Pan, Y.; Bao, H.; Li, L.; Chan, S. H.; Zhao, J. Poly(vinyl alcohol) nanocomposites filled with Poly(vinyl alcholo)-Grafted Graphene Oxide.ACS Applied Materials and Interfaces, 2012,4, 2387 - 2394.

[32] Kim, D. S. ; Park, H. B.; Lee, Y. M .; Park, Y. H.; Rhim, J . W.Pervaporation and Characterization of PVDF/silica hybrid membranes containing Sulfonic acid Groups.Journal of Applied Polymer Science, 2004, 93, 209-218.

[33] Choudhari, S. K.; Kariduraganavar, M. Y.Development of novel composite membranes using quanternized chitosan and Na+ - MMT clay for the pervaporation dehydration of isopropanol. Journal of Colloid and Interface Science, 2009, 338, 111 – 120.

[34] Rachipudi, P. S.; Kittur, A. A.; Choudhari, S. K.; Varghese, J. G. ; Kariduraganavar, M. Y.

[35] European Polymer Journal, 2009, 45, 3116 - 3126.

[36] Binning, R. C.; Lee, R. J.; Jennings, J. E.; Martin, E. C. Separation of Liquid Mixtures by Permeation. Industrial & Engineering Chemistry, 1961, 53, 45 – 50.

[37] Suhas, D. P.; Aminabhavi, T. M.; Raghu, A. V. Mixed matrix membranes of H-ZSM-5-loaded poly(vinyl alcohol) used in Pervaporation dehydration of alcohols: Influence of Silica / alumina ratio. Polymer Engineering & Science, 2014, 54, 1774 - 1782.

[38] Rachipudi, P. S.; Kariduraganavar, M. Y.; Kittur, A. A.; Sajjan, A. M. Synthesis and Characterization of Sulfonated – poly (vinyl alcohol) membranes for the pervaporation dehydration of isopropanol. Journal of Membrane Science, 2011, 383, 224 – 234.

AUTHORS

First Author – U. Sajankumar ji Rao, Department of Polymer Science & Tech, S.K.University, Anantapuramu – 515003 A.P, India.

Second Author – K.Sreenivasulu, Department of Polymer Science & Tech, S.K.University, Anantapuramu

Third Author – Y.Maruthi, Department of Polymer Science & Tech, S.K.University, Anantapuramu

Fourth Author – P. Kumara Babu, Department of Polymer Science & Tech, S.K.University, Anantapuramu

Fifth Author – G.Nagarjuna M.C.S.Subha, Department of Chemistry, S.K.University, Anantapuramu – 515003 A.P, India.

Sixth Author – K. Chowdoji Rao, Department of Polymer Science & Tech, S.K.University, Anantapuramu