Indian Journal of Advances in Chemical Science

Dehydration of Aqueous Isopropanol using Mixed-Matrix Blend Membranes of NaCMC/Gellan Gum-Loaded with Phosphotungstic Acid

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ABSTRACT

The present study focused on phosphotungstic acid (PWA) particles with different concentrations anchored on sodium carboxymethyl cellulose (NaCMC)/gellan gum blend membranes were prepared to evaluate its hydrophilic nature. The prepared membranes exhibited flux and selectivity values 0.389 Kg/m² h and 8172.81, the pervaporation index values is 3179.22 for the membrane with the highest loading of PWA (30%) at 30°C. The obtained results suggested that the incorporation of PWA particles is showed the highest PV performance. These membranes were also characterized using several techniques such as Fourier transform infrared, differential scanning colorimetry, thermogravimetric analysis, X-ray diffraction, and FE-scanning electron micrograph, which shows good interface interactions between filler and polymer blend membranes.

Key words: Phosphotungstic acid, NaCMC, Gellan gum, Blend membranes, Pervaporation studies, Isopropanol.

1. INTRODUCTION

The pervaporation (PV) technique is considered to be an energy-efficient alternative to conventional separation methods. It has been widely used to remove organics from water, dehydrate organic solvents, and separate organic solvent mixtures [1,2]. Particularly, PV is attractive for the separation of heat-sensitive, close-boiling, and azeotropic liquid mixtures. In general, PV involves sorbing components from the feed mixtures at the upstream side of a membrane, diffusing the absorbed components across the membrane, and then desorbing those components.

PV is one of the most significant techniques. It has many advantages over other techniques such as energy saving, cost effectiveness, and ecofriendly process. PV process comprises membrane for separation. It is unit operation, in which two components are separated using either polymeric or inorganic membrane through the combination of different permeation rates of the components. The separation membrane is the key element in PV equipments [3,4].

In continuation of our earlier studies [5-7], we have made an attempt to prepare the blend membranes comprising varying compositions of NaCMC/gellan gum (GG) with PWA as filler. To the best of our knowledge, this type of blend combination is used for the 1st time from its feed aqueous solution.

GG is an extracellular polysaccharide produced by fermentation of Sphingomonas paucimobilis (formerly Pseudomonas elodea) [8]. The polymer is a linear, anionic heteropolysaccharide based on a tetrasaccharide repeat unit of β -D-glucose, β -D-glucuronic acid, and α -L-rhamnose units in molar ratios of 2:1:1 [9]. It is a well-known biopolymer for its functional characteristics such as low water vapor permeability and smooth surfaces. Chemical structure of GG is formed by repeated units of tetrasaccharides and enhances the mechanical and barrier properties of films. It creates a highly organized structure and compacted network of biopolymers [10]. Sodium carboxymethylcellulose (NaCMC) is carboxymethyl ether of cellulose, a well-known natural polysaccharide comprising the fibrous tissue of plants. Due to its non-toxic, biocompatible, biodegradable, and abundantly availability, this material is being used in applications [11]. This material exhibits excellent acid and enzymatic hydrolysis resistance, as well as thermal stability. Due to its non-toxic, biocompatible, biodegradable, and abundantly availability [12], it is widely used in different fields from technological industries to the biological, pharmaceutical, petroleum, and medical fields [13]. It has also been used in membrane preparation for PV dehydration of several-organic compounds from their aqueous feed solutions.

However, phosphotungstic acid (PWA) $(H_3PW_{12}O_{40})$ is a material containing of polyanions and owns a unique discrete ionic structure [14]. As a good inorganic proton conductor, PWA has played an important role in developing proton conducting membranes [15]. It has been the rarely considered as a filler [16], in developing mixed-matrix membranes (MMMs) for PV studies. At the same time, the potential interactions between PWA and the host polymer would be responsible to achieve extraordinary separation performance of membrane.

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ISSN NO: 2320-0898 (p); 2320-0928 (e) **DOI:** 10.22607/IJACS.2023.1101005

Received: 13th December 2022; **Revised**: 22th December 2022; **Accepted**: 25th December 2022

2.1. Materials

Sodium carboxymethylcellulose (medium viscosity) was purchased from Merk, Mumbai, India. Gellen gum was purchased from SRL Mumbai, India. Glutaraldehyde (GA 50 wt % aqueous solution), concentrated (35%) hydrochloric acid (HCl), and acetone were purchased from Sd.fine chemicals, Mumbai, India. Phosphotunstic acid and isopropanol were purchased from Qualigens fine chemicals Mumbai, India. Deionised water with a conductivity of 20 μ S/cm was produced in the laboratory using Techno pilot plant (Vadodara, India.) through a nano filtration membrane module. All the chemicals were of analytical grade samples used without further purification and were used for all the experiments.

2.2. Preparation of PWA-Filled NaCMC-GG Blend Membranes

NaCMC (0.5 g) and GG (0.3 g) were individually dissolved in 40 mL of deionized water in two separate beakers with constant stirring for about 24 h at room temperature and were then filtered and mixed thoroughly for the blend solution preparation of 50% NaCMC + 30% of GG and considered this as stock solution of polymer blend mixture. In separate beakers, 0.2, 0.4, and 0.6 g of PWA were taken and dissolved each in 20 mL of water. To the above prepared blend solution (50% NaCMC& 30% GG), 10, 20, and 30 wt. % PWA solutions were added and stirred for about 12 h. Both the solutions (polymer blend mixture and PWA solution) were then mixed for 24 h and kept overnight to release any gases. The resulting solution was filtered to remove suspended particles and poured on to a clean dust-free glass plate to fabricate membranes of uniform thickness. Then, this was dried at 30°C and finally peeled off from the glass plate. Thus, the prepared membranes were then crosslinked in a bath containing water-acetone mixture (30:70) along with 2.5 mL of GA (cross-linking agent) and 1 mL of conc. HCl as catalyst for a period of 2-4 h. The cross-linked membranes were repeatedly rinsed with water and methanol solutions at least four to 5 times, followed by soaking in methanol for 24 h (to remove the unreacted GA). The nascent blend membrane was designated as NaCMC/GG (50/30)-0%, while the MMMs containing 10, 20, and 30 wt. %, PWA were designated as NaCMC/GG (50/30)-10%, NaCMC/GG (50/30)-20%, and NaCMC/GG (50/30)-30%, respectively. The average membrane thickness was around $50 \pm 3 \,\mu\text{m}$ as was measured by micrometer screw gauge at various points of the membrane. The structure of NaCMC/ GG interaction with PWA is shown in Figure 1. The membrane is supported by a stainless steel porous plate which is embedded with an SS mesh/screen. Teflon gaskets are fixed by means of high-vacuum silicone grease on either side of the membrane, and the sandwich is placed between the two glass column couplers and secured tightly. The effective membrane area in contact with feed is almost 20 cm² in all cases. The feed side pressure is maintained at atmospheric pressure and the vacuum in the downstream side at about 0.5 mmHg using a vacuum pump (INDVAC, Model- IVP-150, Bangalore, India).

2.3. PV Experiments

PV experimental setup (Figure 2). The procedure used in PV has been described in earlier studies [17]. The PV cell consists of two bellshaped B-24 size glass column reducers/couplers clamped together with external padded flanges by means of tie rods to give a vacuum tight arrangement. The top half of it is used as the feed chamber.

Permeate composition was determined by measuring refractive index (RI) and comparing it with the established graph of RI versus liquid mixture composition. Permeate was collected in liquid nitrogen cold traps for a period of 8 h followed by analyzing the compositions of the feed and permeate at 30°C using Abbe Refractometer (Atago, Model:



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Figure 1: Diagrammatic representation of the preparation of cross-linked NaCMC and GG blend membrane with phosphotungstic acid.



Figure 2: Diagrammatic representation of laboratory PV equipment (SM: Stirring; CT: Condenser trap; PC: Permeate collector; SR: Stirring rod; MA: Membrane assembly; MG: McLeod Gauge; FC: Feed chamber; DF: Dewar flask; VP: Vacuum Pump; TV: Teflon Valve; VR: Vacuum Release).

DR-A1, USA) and comparing with standard graph of RI versus mixture composition. From the PV data, flux, J_i is calculated as given below:

$$Ji = \left(\frac{Wi}{At}\right) \tag{1}$$

Here, W_i represents the mass of water in permeate (kg), A is the membrane area (m^2) and t represents the permeation time (h).

Membrane selectivity, α , is the ratio of permeability coefficients of water to that of isopropanol, which is calculated from their respective concentrations in feed and permeate as given below:

$$\alpha = \left(\frac{Y_A}{1 - Y_A}\right) \left(\frac{1 - X_A}{X_A}\right) \tag{2}$$

Where "XA" is the mole fraction of water in feed and "YA" is its mole fraction of water in permeate. In all cases, results were obtained in triplicate, but averages (3% standard error) are reported. Calculated values of flux and selectivity are presented.

2.4. Sorption Experiments

The degree of swelling (DS) of PWA incorporated NaCMC/GG blend membranes was determined in different compositions of water and isopropanol mixtures for 24 h at 30°C using an electronically controlled oven (WTB Binder, model-BD-53, Germany). The masses of the dry membranes were first determined. The dry membranes were equilibrated by soaking in different compositions of the mixture in a sealed vessel, at 30°C for 24 h and, then, the swollen membranes were immediately blotted the tissue paper carefully and weighed on a single pan Adam digital microbalance (model AAA 160L, Switzerland) having a sensitivity of ± 0.01 mg. The % DS was calculated as:

Degree of swelling (s) (%) =
$$\frac{(w_s - w_d) \times 100}{W_d}$$
 (3)

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

2.5. Measurement of RI

RI N^D, for sodium-D line was measured using the thermostatically controlled Abbe Refractometer (Atago, Model: DR-A1, USA) with an accuracy of ± 0.001 . The instrument directly gives the values of N^D.

3. CHARACTERIZATION TECHNIQUES

3.1. Fourier-Transform Infrared (FTIR) Spectroscopic Studies

Dispersion of different amounts of PWA acid in the NaCMC/ GG blend membrane was studied by FTIR (Bomem, MB-3000, Canada) spectrophotometer. About 2 mg of the sample was grounded thoroughly with KB_r, and pellets were made under a hydraulic pressure of 600 kg/cm². Dry membranes were characterized in the range of 4000–400 cm⁻¹ at a scan rate of 25 cm⁻¹ under N₂ atmosphere.

3.2. Differential Scanning Calorimetry (DSC) Studies

DSC thermograms of PWA-loaded NaCMC/GG blend membranes were obtained on a differential scanning calorimeter (Model-SDTQ600, USA). Thermograms were recorded from 30°C to 600°C at a heating rate of 10°C/min in a nitrogen atmosphere.

3.3. Thermogravimetric Analysis (TGA)

Thermal stability and degradation behavior of nascent NaCMC/GG blend membrane as well as PWA loaded composite membranes were evaluated by thermogravimetry (Model-SDTQ600, USA). The oxidative degradation of 6-9 mg of liquid nitrogen crushed membrane samples taken was carried out under a constant flow of nitrogen gas at 50 mL min⁻¹, over the temperature range of $40-600^{\circ}$ C with a ramp rate of 10° C min⁻¹ in an aluminum pan.

3.4. X-Ray Diffraction (X-RD) Analysis

To investigate a change in membrane structure with cross-linking density, a wide-angle X-ray diffractometer (Jain University, Karnataka) with a scintillation counter detector using Cu K α - radiation as a source was used to identify any changes in the crystal structure and intermolecular distances between intersegmental chains after modification.

3.5. Scanning Electron Micrograph (SEM) Studies

SEM (Jain University, Karnataka) of surface was taken for the unfilled NaCMC/GG membrane and PWA filled (GG/NaCMC-PWD) membranes, using software controlled digital scanning electron microscope.

4. RESULTS AND DISCUSSION

4.1. FTIR Analysis

The FTIR spectra of pure NaCMC, GG, PWA, pristine blend membrane, and PWA-loaded membranes are illustrated in Figure 3.



Figure 3: Fourier Transform Infrared spectra of phosphotungstic acid (PWA)-loaded blend composite membrane pure NaCMC (a), Pure GG (b), pure PWA (c), pure blend (d), and PWA-loaded membrane (e).

Wevenumber (cm⁻¹)

2000

1500

1000

500

2500

The FTIR spectrum of plain NaCMC shows a band at 3425 cm⁻¹ corresponding to the aliphatic stretching vibration. The peaks at 1604 and 1388 cm⁻¹ were due to asymmetric stretching vibrations of -COO group. The band at 1018 cm⁻¹ represents the -C-O-C- stretching. In case of plain membrane, the -OH stretching frequency 3317 cm⁻¹ shifted toward lower side indicating the development of hydrogen bonding between NaCMC with GG and the intense peak at 1072 cm⁻¹ indicated the formation of acetal between NaCMC and GG by GA. The spectrum of pure GG significantly shows absorption peaks of carboxylic group. The characteristic bands at 1606 cm^{-1} and 1416 cm^{-1} were assigned to the asymmetric and symmetric stretching peaks of the -COO group, respectively. Finally, the broad stretching peak at 3382 cm⁻¹ was due to -OH. The FTIR spectra of PWA shows four characteristic bands (keggin-type) at around 1080 cm⁻¹, 987 cm⁻¹, 779 cm⁻¹, and 516 cm⁻¹ and they are, respectively, attributed to P-Oa, W-Od, W-Ob-W, and W-Oc-W. A strong and broad band appeared at around 3425 cm⁻¹ in PWA-loaded blend membrane. All these changes show a strong evidence of the intermolecular interactions, crosslinking, and good molecular compatibility between NaCMC and GG.

4.2. DSC Analysis

Fransmittance (%)

4000

3500

3000

DSC spectra of pure NaCMC (4a), pure GG (4b), pure PWA (4c), blend (4d), and PWA-loaded blend membranes (4e, 4f, 4g) are shown in Figure 4.

Initially, all the films showed endothermic peaks between 50°C to 90°C, corresponding to the loss of crystalline water molecules in the films formed during drying process. An exothermic sharp peak appeared in Figure 4a at 300°C can be attributed to the thermal degradation of NaCMC. The DSC curve of GG (Figure 4b) shows exothermic peaks between 190°C and 250°C, which may be attributed to the disintegration of the intermolecular side chain and main chains, respectively. The DSC curve of PWA (Figure 4c) shows exothermic peak at 260°C.

In Figure 4d, pure blend film exhibits endothermic peaks at 80°C and exothermic peak at 180°C, while PWA-loaded blend membranes

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(Figure 4e-g) show that the melting temperature increased after blending with PWA. The GG molecules strengthened the blend films, and thus, the loaded membranes emerged as a better performing membrane compared to pristine membrane. This result indicates that PWA-loaded membranes are more stable.

4.3. TGA Analysis

TGA thermograms in pure NaCMC (a), GG (b), pure PWA (c), and pristine blend membrane (d) and PWA-loaded blend membranes are shown in Figure 5.

The thermal stability of pure NaCMC, GG, PWA, pristine blend membrane, and PWA-loaded membranes was analyzed under atmosphere of nitrogen using TGA and the resulting thermograms are shown in Figure 5. From Fig, it can be observed that all degradation curves experience three degradation stages. There is a small weight loss at temperature below 100°C, due to loss of water followed by steep loss of weight which may be due to degradation of molecular stability. It is concluded that incorporation of PWA, though it is in small quantity considerably increased the thermal stability of blend membranes. These results are in good agreement with Alshorifi *et al.* [18] from their synthesis of acid catalyst using PWA and UiO-66 (Zr).

4.4. X-RD Analysis

To study the effect of PWA on the morphology of NaCMC/GG blend membrane, X-RD patterns were employed and the patterns, thus, obtained are presented in Figure 6. X-RD patterns of pristine blend membrane (a), PWA filled blend membranes (b and c), and pure PWA (d) are shown in Figure 6.

From Figure 6d, it is clearly evident that the PWA was crystalline nature. The pattern of pristine blend membrane (a) exhibits sharp peak at $2\theta=5^{\circ}$ and two broad peaks at $18-24^{\circ}$. Incorporation of PWA drastically decreases the intensity of sharp peaks that can be seen from the patterns (b and c). This is due to decreased semicrystalline domains in the membrane matrix due to the presence of PWA. The results concluded that the crystalline PWA was observed even with low concentration of PWA [19]. Further, as evidenced by the SEM results, one can see the PWA particles dispersed in the matrix.

4.5. SEM Analysis

Figure 7 represents the suface and cross-sectional SEM images of pure PWA (a and b), pristine blend membrane (c and d), and PWA-loaded NaCMC-GG blend membranes (e, f, g, and h), respectively, at two different resolutions.



Figure 4: DSC spectra of pure NaCMC (a), Pure GG (b), pure phosphotungstic acid (PWA) (c) pure blend (d), and PWA loaded blend membranes (e-g).



Figure 5: TGA thermograms in pure NaCMC (a), GG gum (b), pure phosphotungstic acid (PWA) (c), pristine blend membrane (d), and PWA loaded blend membranes (e and g).

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The pristine blend film Figure 7c and d showed a smooth and homogeneous surface morphology, suggesting high miscibillity. From the cross-sectional images displayed in Figure 7e-h, it could be concluded that in the NaCMC-GG, the zeolite filled blend membrane displays better interfacial morphology than NaCMC-GG-0 membrane. The two polymers and incorporated zeolite were homogeneously intermixed and in the state of a polymer composite membrane. Further, no agglomerations are seen in the polymer blend before and after zeolite incorporation.



Figure 6: X-RD patterns of pristine blend membrane (a), phosphotungstic acid (PWA) filled blend membranes (b and c), and pure PWA (d).



Figure 7: SEM images of pure phosphotungstic acid (PWA) (a and b), pristine membrane, (c and d), and PWA-loaded membranes (e-h) at different resolutions.

4.6. Sorption Studies

The mechanism of sorption depends on the microstructure of membrane, affinity of penetrants toward membrane, and mutual interaction between the penetrants. Therefore, the degree of sorption plays an important role in PV process that controls the transport of permeating molecules under the influence of chemical potential gradient.

The variation of dynamic sorption of pristine blend membrane and PWA-loaded blend membrane with 10, 20, 30, and 40% watercontaining feed mixtures are shown in Figure 8. Percentage of swelling data of ethanol and water mixtures for different blend membranes (0%, 10%, 20%, and 30% PWA) at 30°C is presented in Table 1.

From the results presented in Table 1, it is observed that at each water feed composition, the DS increased with increasing PWA loading. Ryu *et al.* [20] discovered a similar observation, while synthesizing a sulfonated poly(arylene ether) membrane with PWA and graphene oxide. Swelling results are in good agreement with the observed Tg values of the blend membranes. Pristine blend membrane swells in water, lowering its selectivity to water, but in the presence of PWA, membranes swelling becomes more rigid. This is due to the hydrophilic-hydrophilic interactions of blend membranes and PWA particles that are responsible for higher selectivity to water than feed mixtures. Similarly, the DS increased with increasing concentration of PWA content in the membrane matrix and is attributed to the hydrophilic nature of PWA.

4.7. Membrane Performance through PV Studies

PV studies have been carried out with and without loading PWA in different blend membranes at 30°C for 10, 20, 30, and 40% water containing feed mixtures and the obtained selectivity, flux, and PSI values are incorporated in Table 2.

4.7.1. Effect of PWA on pervaporation

Figure 9 demonstrates the feed composition and PWA content on the total permeation flux for all the membranes under study at 30° C

The permeation flux increased almost linearly for all the membranes with increasing water composition in the feed. This is due to an increased selective interaction between water molecules and the membrane, as NaCMC/GG blend membrane and PWA contain active groups, which are capable of absorbing water molecules. However, this interaction is increased proportionally with increasing PWA content in the membranes (a to d). This is mainly attributed to enhancement of hydrophilicity in the membrane matrix due to the presence of large number of –OH groups in PWA. These findings are consistent with those of Venkatesulu *et al.* [21], who found similar increasing behavior in their composite membranes.

Table 1: Percentage swelling data of ethanol and water mixtures at 30°C for different blend membranes (loaded with 0%, 10% 20, and 30% of PWA).

% of water in the feed	% of Swelling						
	0% PWA	10% PWA	20% PWA	30% PWA			
10	32.75	39.09	47.82	52.69			
20	48.57	56.79	66.44	72.81			
30	62.72	70.24	80.57	85.98			
40	68.66	75.66	85.34	90.81			

PWA: Phosphotungstic acid

Table 2: The results of membrane performance PV studies at 30°C.

Feed compositions		Percentage of permeation		Selectivity	Flux (kg/m ² h)	PSI
Water X	IPA (1-x)	Water y	IPA (1-y)	Α		
NaCMC/GG-0						
10	90	98.88	1.12	794.57	0.243	193.0809
20	80	98.57	1.43	275.72	0.258	71.13583
30	70	98.11	1.89	121.12	0.293	35.48917
40	60	98.02	1.98	74.257	0.376	27.92085
NaCMC/GG-1	0%					
10	90	99.52	0.48	1866.00	0.267	498.222
20	80	99.47	0.53	750.71	0.305	228.9687
30	70	99.24	0.76	304.68	0.384	116.9987
40	60	99.04	0.96	154.75	0.467	72.26825
NaCMC/GG-2	0%					
10	90	99.71	0.29	3094.44	0.328	1014.979
20	80	99.51	0.49	812.32	0.377	306.2471
30	70	99.38	0.62	374.01	0.434	162.3207
40	60	99.21	0.79	188.37	0.495	93.24484
NaCMC/GG-3	0%					
10	90	99.89	0.11	8172.81	0.389	3179.226
20	80	99.71	0.29	1375.31	0.467	642.2699
30	70	99.57	0.43	540.30	0.489	264.2078
40	60	99.31	0.69	215.89	0.535	115.5018



Figure 8: Degree of swelling of pristine blend membrane (a) and PWA-loaded blend membranes (b-d).

4.7.2. Membrane performance in terms of selectivity

Selectivity of a membrane in pervaporation process is generally explained on the basis of interaction between membrane and the permeating molecules, and the molecular size of the permeating species. Figure 10 displays the effects of feed composition and PWA content on the selectivity for all the membranes under study at 30°C.

It is observed that the selectivity of water was decreased almost exponentially for all the membranes with increasing mass% of



Figure 9: (a-d) Effect of Wt% of water in the feed on flux and its phosphotungstic acid incorporated for different blend membranes.

water in the feed. At higher concentration of water in the feed, the membrane swells greatly due to establishing strong interaction between membrane and the water molecules. Therefore, a decrease of selectivity is apparent at higher concentration of water, irrespective of the content of PWA in the membrane matrix [22]. On the contrary, the selectivity was increased significantly from membrane a to d at all feed compositions with increasing PWA content in the membrane matrix. This is attributed to increased selective interaction between

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Figure 10: (a-d) Effect of Wt% of water in the feed on selectivity with its phosphotungstic acid incorporated for different blend membranes.

membrane and the water molecules, due to the establishment of hydrogen bonding, enhanced hydrophilicity, and shrinkage in cell size. However, in the present study, both permeation flux and selectivity increased simultaneously with increasing PWA concentration in the membrane, due to the hydrophilic nature of PWA molecules.

4.7.3. Effect of feed water composition

From the PV studies results, to assess the intrinsic membrane permeability of water and isopropanol as a function of % of feed water, the variation is presented in Figure 11.

From the plot, it is clearly noticed that mass % of water in permeate decreased over the range of water composition of the feed mixture. It has been widely accepted that under reduced pressure conditions the transport of a volatile organic mixture through a pervaporation membrane comprises of three steps: A sorption step at the membrane upstream face, followed by diffusion through the polymer film and desorption into the vacuum. Furthermore, the PWA particles will act as the reinforcing bridge between the polymer chain segments of NaCMC and GG to establish this bridge through the electrostatic interactions.

4.7.4. Effect of PV Separation Index

The variation of PV separation index with % of water in the feed is shown in Figure 12.

PSI is the product of the total permeation and the separation factor characterized as the membrane separation ability. This index can be used as a relative guideline for the design of PV membrane separation processes with an optium flux and selectivity. The results in Table 2 indicates that the PSI values increase with increasing PWA content in the membrane signifying that the membranes incorporated with a higher amount of PWA showed better performance for the separation of IPA/water mixtures. This was due to the incorporation of PWA into the membrane matrix which changes not only the membrane's hydrophilicity but also its structure and may have a significant effect on the diffusion. The results and discussions are supported by the already published results [23-30].



Figure 11: (a-d) Effect of Wt% of water in the feed on water permeate and its PWA incorporated for different blend membranes.



Figure 12: (a-d) Effect of Wt% of water in the feed on PSI and its phosphotungstic acid incorporated for different blend membranes.

5. CONCLUSIONS

PWA filled MMMs are prepared by blending NaCMC/GG in different compositions followed by chemical cross-linking with GAto study the PV dehydration of isopropanol. The excellent hydrophilicity of both membrane constituents was exploited to develop water selective PV membranes. PWA forms the hybrid mixed-matrix with NaCMC/GG gum, which exhibited an improved PV performance. Selectivity and flux values of 30 wt% PWA zeolite incorporated MMMs were superior as compared to lower amount of PWA incorporated MMMs. This could be due to increased hydrophilicity as a result of more number of OH groups in 30 wt% PWA zeolite membranes compared to loaded % of PWA membrane. However, molecular sieving effect, selective sorption/adsorption by the filler particles, as well as the selective diffusion increases the mobility of the preferentially permeating water molecules in the MMMs. The present experimental data suggest that PWA filled MMMs can be employed successfully in PV-aided method.

6. REFERENCES

- R. W. Baker, (2012) *Membrane Technology and Applications*. New York: JohnWiley and Sons. p. 588.
- L. M. Vane, (2019) Review: Membrane materials for the removal of water from industrial solvents by pervaporation and vapor permeation, *Journal of Chemical Technology and Biotechnology*, 94(2): 343-365.
- E. Trovatti, S. C. Fernandes, L. Rubatat, D. S. Perez, C. S. Freire, A. J. Silvestre, C. P. Neto, (2012) Effect of gelatin addition on properties of pullulan films, *Composites Science and Technology*, 72: 1556-1561.
- W. C. Lin, C. C. Lien, H. J. Yeh, C. M. Yu, S. H. Hsu, (2013) Bacterial cellulose and bacterial cellulose-chitosan membranes for wound dressing applications, *Carbohydrate Polymers*, 94: 603-611.
- U. S. Rao, K. V. Sekharnath, H. Sudhakar, K. C. Rao, M. C. Subha, (2014) Mixed matrix membranes of sodium alginate and hydroxy propyl cellulose loaded with phosphotungstic heteropolyacid for the pervaporation separation of water-isopropanol mixtures at 30 °C, *International Journal of Scientific and Technology Research*, 3: 129-137.
- P. Upendra, P. K. Babu, Y. Maruthi, U. S. K. Rao, M. C. Subha, K. C. Rao, (2015) Phosphotungstic acid loaded sodium alginate membranes for enhanced pervaporative dehydration of Isopropanol, *International Journal of Development Research*, 5(10): 5736-5742.
- K. V. Sekharnath, U. S. Rao, Y. Maruthi, P. K. Babu, A. Parandhama, C. Madhavi, M. C. Subha, (2016) Mixed matrix blend membranes of NaCMC/HPC loaded with phosphotungstic acid for the dehydration of aqueous Isopropanol by pervaporation technique, *Indian Journal of Advances in Chemical Sciences*, 2(4): 412-418.
- G. R. Sanderson, (1990) Gellangum. In: P. Harries (ed.), *Food Gels*. New York: Elsevier Science Publishing Company. p. 201-232.
- E. Miyoshi, (2007) Dierenteects of mono-saccharides and disaccharides on the solgel transition in gellan gum aqueous solutions, *Development and Environment*, 7: 31-43.
- D. Charpentier, G. Mocanu, A. Carpov, S. Chapelle, L. Merle, G. Muller, (1997) New hydrophobically modified carboxymethylcellulose derivatives, *Carbohydrate Polymers*, 33: 177-186.
- A. Parandhama, C. Madhavi, K. C. Rao, M. C. Subha, (2019) Phosphotungstic acid loaded mixed matrix blend membranes of poly(vinyl alcohol)/gellan gum for pervaporation dehydration of isopropanol, *Journal of Advanced Scientific Research*, 10(3): 35-44.
- S. G. Adoor, V. Rajineekanth, M. N. Nadagouda, K. C. Rao, D. D. Dionysiou, T. M. Aminabhavi, (2013) Exploration of nanocomposite membranes composed of phosphotungstic acid in sodium alginate for separation of aqueous-organic mixtures by pervaporation, *Separation and Purification Technology*, 113: 64-74.
- B. Van der Bruggen, P. Luis, (2014) Pervaporation as a tool in chemical engineering: A new era?, *Current Openion Chemical Engineering*, 4: 47-53.
- 14. N. Ghaemi, F. Nasirmanesh, (2018) Synthesis of a hybrid organic-inorganic polyethersulfone membrane incorporated with phosphotungstic acid: Controversial formance in removal of dinitroaniline herbicides from water, *Journal of Cleaner*

Production, 182: 259-271.

- W. Shi, H. Li, R. Zhou, X. Qin, H. Zhang, Y. Su, Q. Du, (2016) Preparation and characterization of phosphotungstic acid/PVA nanofiber composite catalytic membranes via electrospinning for biodiesel production, *Fuel*, 180: 759-766.
- Y. Li, H. Wang, Q. Wu, X. Xu, S. Lu, Y. Xiang, (2016) A poly(vinyl alcohol)-based composite membrane with immobilized phosphotungstic acid molecules for direct methanol fuel cells, *Electrochemica Act*, 224: 369-377.
- 17. G. Venkatesulu, P. K. Babu, Y. Maruthi, C. Madhavi, A. Parandhama, M. C. Subha, K. C. Rao, (2016) Design and application of H-ZSM-5 zeolite loaded hydroxy propyl cellulose/ poly (vinyl pyrrolidone) mixed matrix membranes for dehydration of ethanol by pervaporation, *Indian Journal of Advances in Chemical Science*, 4: 496-505.
- F. T. Alshorifi, D. E. Tobbala, S. M. El-Bahy, M. A. Nassan, R. S. Salama, (2022) The role of phosphotungstic acid in enhancing the catalytic performance of UiO-66 (Zr) and its applications as an efficient solid acid catalyst for coumarins and dihydropyrimidinones synthesis, *Catalysis Communications*, 169: 106479.
- A. A. Ibrahim, R. S. Salama, S. A. El-Hakam, A. S. Khder, A. I. Ahmed, (2021) Synthesis of tungestophosphoric acid supported on Zr/MCM-41 composite with excellent heterogeneous catalyst and promising adsorbent of methylene blue, *Colloids Surface A Physicochemical Engineering Aspects*, 631: 127753.
- 20. S. K. Ryu, A. R. Kim, M. Vinothkannan, K. H. Lee, J. Y. Chu, D. J. Yoo, (2021) Enhancing physicochemical properties and single cell performance of sulfonated poly (arylene ether)(SPAE) membrane by incorporation of phosphotungstic acid and graphene oxide: A potential electrolyte for proton exchange membrane fuel cells, **Polymers**, **13**: 2364.
- G. Venkatesulu, P. K. Babu, Y. Maruthi, U. S. Rao, M. C. Subha, C. Rao, (2016) Composite membranes comprising of hydroxypropyl cellulose-poly(vinyl alcohol) incorporated with inorganic fillers for dehydration of ethanol by pervaporation. *Indian Journal of Advances in Chemical Sciences*, 2(1): 174-179.
- Y. Maruthi, P. K. Babu, M. C. Subha, K. Chowdojirao, (2018), Phospotungstic acid loaded mixed membranes of sodium alginate karayagum for dehydration of aqueous organic mixtures, *Indian Journal of Chemical Technology*, 25: 459-467.
- K. V. Sekharnath, U. S. Rao, Y. Maruthi, P. K. Babu, K. C. Rao, M. C. Subha, (2015) Halloysite nanoclay-filled blend membranes of sodium carboxyl methyl cellulose/hydroxyl propyl cellulose for pervaporation separation of water-isopropanol mixtures, *Indian Journal of Advances in Chemical Science*, 3: 160-170.
- U. S. Rao, Y. Maruthi, K. V. Sekharnath, P. K. Babu, K. C. Rao, M. C. Subha, (2014) Mixed matrix blend membranes of sodium alginate-hydroxy propyl cellulose loaded with phosphomolybdic acid used for pervaporation dehydration of isopropanol mixture at 30°C, *Indian Journal of Advances in Chemical Science*, 3: 11-18.
- H. Sudhakar, Y. Maruthi, U. S. Rao, C. V. Prasad, M. C. Subha, S. Sridhar, K. C. Rao, (2013) Improved pervaporation performance of 13X zeolite filled chitosan membranes, *Indian Journal of Advances in Chemical Science*, 2: 21-31.
- B. V. Naidu, K. S. Rao, T. M. Aminabhavi, (2005) Pervaporation separation of water+ 1, 4-dioxane and water+ tetrahydrofuran mixtures using sodium alginate and its blend membranes

with hydroxyethylcellulose-a comparative study, *Journal of Membrane Science*, **260**: 131-141.

- K. S. Rao, M. C. Subha, M. Sairam, N. N. Mallikarjuna, T. M. Aminabhavi, (2007) Blend membranes of chitosan and poly (vinyl alcohol) in pervaporation dehydration of isopropanol and tetrahydrofuran. *Journal of Applied Polymer Science*, 103: 1918-1926.
- K. S. Rao, B. V. Naidu, M. C. Subha, M. Sairam, N. N. Mallikarjuna, Aminabahvi, T. M., (2006) Novel carbohydrate polymeric blend membranes in pervaporation dehydration of

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- K. S. Rao, B. G. Lokesh, P. S. Rao, K. C. Rao, (2008) Synthesis and characterization of biopolymeric blend membranes based on sodium alginate for the pervaporation dehydration of isopropanol/ water mixtures, *Separation Science and Technology*, 43(5): 1065-1082.
- B. G. Lokesh, K. S. Rao, K. M. Reddy, K. C. Rao, P. S. Rao, (2008) Novel nanocomposite membranes of sodium alginate filled with polyaniline-coated titanium dioxide for dehydration of 1, 4-dioxane/water mixtures. *Desalination*, 233: 166-172.