Development and Characterization of Silicotungstic Acid-loaded Sodium Polymeric Composite Membranes for Pervaporation Applications

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Efforts have been focused on the membrane synthesis, specifically enhancing membrane properties through the incorporation of zeolites into a polymer matrix. This study emphasizes the development of sodium carboxymethyl cellulose (NaCMC)/poly(vinylpyrrolidone-*co*-vinyl acetate) [P(Vp-*co*-VAc)] matrix composite membranes *via* solution casting method, incorporating varying amounts of silicotungstic acid (STA) (5, 10, and 15 wt.%) for the pervaporation dehydration of a water-isopropanol mixture. The developed films were characterized by FTIR, DSC, TGA, XRD and SEM techniques. Among all the STA-loaded membranes, the optimum pervaporation performance was observed in the MSTA15 membrane, which had a flux equal to 0.533 kg/m^2 h at 35 ºC and a separation factor of 118.52 for a 40 wt.% water-isopropanol feed composition. The developed membrane exhibits a good hydrophilic nature and a molecular sieve effect. Furthermore, STA-loaded membranes showed the improved pervaporation performance compared to pristine membranes. These results of this study suggested that the STA-loaded composite membranes act as prominent materials for the effective dehydration of isopropanol.

Keywords: Poly(vinylpyrrolidone), Vinyl acetate, Sodium carboxymethyl cellulose, Silicotungstic acid, Composite membranes.

INTRODUCTION

Pervaporation (PV) has indeed garnered significant attention over the past two decades, both in academic research and industrial applications, due to its distinct advantages over traditional separation methods like distillation and adsorption. Liquid mixtures can be separated using the membrane-based process of pervaporation, especially when more traditional techniques like distillation are difficult or ineffective [1]. Pervaporation process is mainly employed for the dehydration of various alcohols and one of such commercial applications of pervaporation is the isopropanol (IPA). The membrane used for this method should exhibit high permeation flux and high separation selectivity [2]. Furthermore, suitable membranes with a significant permeability rating, adequate selectivity and an acceptable mechanical strength must be developed for the per-

vaporation process to be effective [3]. To tackle these parameters and enhance the efficiency of pervaporation membranes, inclusion of halloysite nanotubes [4], metal-organic frameworks [5] and inorganic nanofillers [6] has been investigated in membranes by physical mixing.

In current study, the authors are more specifically interested in preparing the hydrophilic composite membranes for dehydration of isopropanol by using the PV technique. Sodium carboxymethyl cellulose (NaCMC) is a chemically modified derivative of cellulose, a natural polysaccharide found in plant cell walls and fibers. In NaCMC, the hydroxyl groups of cellulose are partially substituted with carboxymethyl groups (-CH$_2$-COONa), making it water-soluble and highly versatile [7]. It is widely used as a stabilizer, thickener and film-forming agent due to its excellent hydrophilic nature [8-10]. On the other hand, poly(vinylpyrrolidone-*co*-vinyl acetate) [P(VP-*co*-VAc)] is a

non-ionic amphiphilic copolymer composed of vinylpyrrolidone (VP) and vinyl acetate (VAc) units. It is characterized by its solubility in both hydrophilic liquids, such as water and hydrophobic solvents, which is attributed to its amphiphilic nature [11,12].

Besides polymers silicotungstic acid (STA), a Keggin-type heteropoly acid (HPA), is widely recognized due to their favourable properties such as strong acidity, catalytic nature and high hydrophilicity, employed as fillers to improve the membrane barrier properties [13]. The presence of such HPAs in the polymer matrix enable the polymer to effectively interact with the solvent molecules especially water because of the presence of hydrated protons [14]. The synthesis of blend membranes composed of NaCMC/P(VP-*co*-VAc) containing hydrophilic groups promote the swelling, thereby improving flux and selectivity in the membrane. However, the swelling degree of blend membrane can be lowered through crosslinking the polymer matrix with cross-linking agents including glutaraldehyde and therefore, blend membranes has been enhanced for applications in the dehydration of aqueous organic mixtures [15]. Incorporating HPA molecules into the blend membrane fills the voids within the membrane, thereby enhancing the affinity of water molecules for the blend membrane compared to organic solvents [16]. In present work, the STA-loaded composite membranes for dehydration of isopropanol (IPA) are developed. The investigation also explores the impact of water concentration in the feed mixture on the properties of membrane flux and selectivity. Furthermore, techniques such as FTIR, XRD, DSC and TGA are utilized to explore the compatibility between the STA and the polymer matrix, while sorption studies are conducted to clarify the results related to pervaporation (PV) performance.

EXPERIMENTAL

Sodium carboxymethyl cellulose, poly(vinylpyrrolidone-*co*-vinyl acetate) and silicotungstic acid were procured from Merck, Mumbai, India. Glutaraldehyde, hydrochloric acid (35%) and isopropanol were purchased from Sd Fine Chemicals. Deionized water was used throughout the study to ensure purity and consistency in the experiments.

Preparation of composite membranes: Briefly, 2 g NaCMC and 2 g P(VP-*co*-VAc) dissolved separately in 100 mL of water and stirred overnight to form a homogenous solution. The resultant solutions were mixed thoroughly and stirred until the formation of a homogenous blend solution. Afterward, the solution was transferred into a petri dish, dried at 35 ℃ in an oven. The obtained membranes were collected from the petri dish, crosslinked with crosslinking solution (30:70 water-acetone mixture), 2.5 mL glutaraldehyde (crosslinking agent) and 1 mL conc. HCl (catalyst). The membranes were left in the cross-linking bath for 2 h. To remove the unreacted glutaraldehyde, the membranes were repeatedly washed with water and methanol after crosslinking. The obtained membrane is designated as MSTA0.

Briefly, 2 g NaCMC and 2 g P(VP-*co*-VAc) dissolved separately in 90 mL of water and stirred overnight to form a homogenous solution. The resultant solutions were mixed thoroughly and stirred until the formation of a homogenous blend solution.

In a spate flask, 200 mg of STA was dissolved in 20 mL of water and stirred until it formed a clear solution. Then the STA solution was transferred into the above polymer blend solution and stirred to obtain a homogenous solution. Afterward, the solution was transferred into a petri dish and dried at 35 ℃ in an oven. The obtained membranes were peeled off from the petri dish and crosslinked with crosslinking solution containing a water-acetone mixture (30:70), 2.5 mL glutaraldehyde (crosslinking agent) and 1 mL conc. HCl (catalyst). The membranes were left in the crosslinking bath for 2 h. After crosslinking, the membranes were repeatedly rinsed with water and methanol to remove unreacted glutaraldehyde. The obtained composite membrane is named MSTA5. The same procedure was adopted to generate composite membranes containing different amounts of STA (10 and 15 wt.%). The generated composite membranes were designated as MSTA10 and MSTA15, respectively.

Pervaporation studies: The methodology employed in pervaporation was elucidated in previous research [17]. Two bell-shaped B-24-size glass column reducers/couplers of identical size were clamped together by means of external padded flanges and tie rods to assure a vacuum-tight configuration in the pervaporation cell. The feed chamber was provided by the upper portion. The liquid mixture in the permeate was determined by measuring the refractive index (RI) value of liquid and comparing it to the established RI *vs*. liquid mixture composition graph. After collecting the permeate in liquid N_2 for 8 h, the compositions of the feed and permeate were analyzed at 35 ℃ using an Abbe Refractometer (Atago, Model: DR-A1, USA) and compared to a standard graph of refractive index *vs*. mixture composition. Based on the pervaporation data, the flux (J_i) was determined as stated below:

$$J_i = \frac{\text{Mass of water in permeate (kg)}}{\text{Membrane area (m}^2) \times \text{Permeation time (h)}}$$

Characterization: The dispersion and interaction of silicotungstic acid (STA) with NaCMC/P(VP-*co*-VAc) blend composite membranes were analyzed using FTIR spectroscopy (Bomem MB-3000 FTIR, Canada). To assess the thermal stability and degradation behaviour of NaCMC, P(VP-*co*-VAc), STA and STA-loaded blend composite membranes, thermal analysis were performed using thermal analyzer (Model-SDT Q600, USA). The thermal curves were recorded from 30-600 ℃ at a heating rate of 10 ℃/min in a N_2 atmosphere. To understand the crystalline nature and molecular dispersion of STA in polymer composite membranes, XRD (Panalytical X-ray diffractometer, model-X'pert Pro) analysis were performed at a scanning rate of 10°/min with Cu*K*α radiation (λ = 1.54060 Å). To investigate the morphological structure of composite membranes SEM (JOEL Model JSM 840A) analysis was performed. Swelling experiments, refractive index (RI) and membrane selectivity (α) analyses were performed as per reported studies [18,19].

RESULTS AND DISCUSSION

FTIR studies: The FTIR spectra of P(VP-*co*-VAc), NaCMC, STA, MSTA0 and MSTA10 are illustrated in Fig. 1. The FTIR spectra of P(VP-*co*-VAc) show a band at 1734 cm⁻¹ attributed to the C=O stretching vibration of poly(vinyl acetate) (PVAc)

component [20]. The band at 1658 cm⁻¹ is attributed to the C=O stretching vibration of the poly(vinyl pyrrolidone) component. The bands at 1242 and 1026 cm⁻¹ correspond to the C–N and C–O–C stretching vibrations, respectively [21]. The FTIR spectra of NaCMC bands at 3425 and 2923 cm⁻¹ correspond to the O-H and C-H stretching vibrations, respectively. The bands at 1604 cm⁻¹ and 1388 cm⁻¹ correspond to asymmetric and symmetric stretching vibrations of the carboxylate group (-COO). The band at 1018 cm⁻¹ corresponds to the C–O–C stretching vibration [22]. The FTIR spectra of STA show a band at 1388 cm⁻¹ that corresponds to the symmetric stretching vibration (ν_s) of the W-O bonds in the Keggin structure. The band at 980 cm⁻¹ represents the asymmetric stretching vibration (ν_{as}) of the W-O bonds. The band at 925 cm⁻¹ is attributed to the asymmetric stretching vibration (ν_{as}) of the Si-O bonds in the Keggin unit. The band at 786 cm⁻¹ corresponds to the asymmetric stretching vibration (ν_{as}) of the W-O-W bonds, which are part of the central polyoxometalate structure [17]. The FTIR spectra of MSTA0 show bands at 1388, 1606 and 3403 cm⁻¹ that correspond to C–O–C, C=O and O-H stretching vibrations, respectively. The FTIR spectra of MSTA10 also show similar bands to that of MSTA0 with slight variations. Additionally, new bands observed at 989 and 789 cm⁻¹ are due to the presence of STA particles in the polymer matrix, which indicates that STA particles are successfully incorporated into the composite membranes.
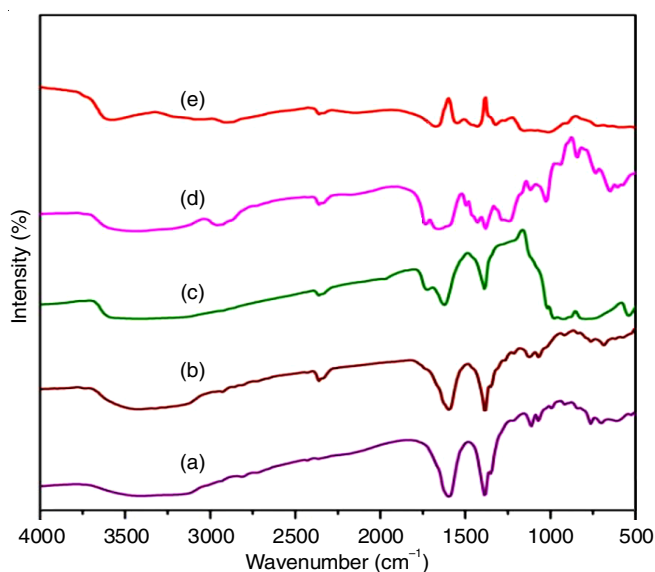

Fig. 1.   FTIR spectra of MSTA10 (a), MSTA0 (b), STA (c), P(VP-*co*-VAc) (d) and NaCMC (e)

Thermal studies: Differential scanning calorimetry (DSC) was used to examine the crystalline nature and glass transition temperature (T$_g$) of the developed films. The DSC curves of [P(VP-*co*-VAc)] and NaCMC showed an exothermic peaks at 100 °C and 110 °C respectively (Fig. 2). Whereas the melting temperature was increased in case of MSTA0, which suggested that an interaction takes place between NaCMC and [P(VP-*co*-VAc)]. The DSC curve of STA exhibited an exothermic peak at 500 °C, indicating the transition from an amorphous

to a crystalline state. The absence of that peak in the STA loaded film (MSTA10) can be attributed to the thermally stable polymeric blend matrix that envelops the STA, thereby shielding it from any further transitions up to 600 °C.

The thermal degradation behaviour of STA, MSTA10, MSTA0, P(VP-*co*-VAc) and NaCMC are presented in Fig. 3. The TGA curve of STA displayed ~50% weight loss occurred between 37 and 100 °C due to loss of adsorbed water molecules. Furthermore ~18% weight loss was found between 100 to 200 °C due to loss of water molecules. The loss of water molecules are generated from the oxygen atoms of Keggin unit of STA alongside with acidic protons of STA [17]. The TGA curve of MSTA0 exhibit a gradual degradation rate with a weight loss of ~50 % at 600 °C. The TGA curve of STA-loaded composite membrane (MSTA10) showed ~42% of weight loss at 600 °C. These results suggested that after the incorporation of STA into polymer matrix, the thermal behaviour has improved compared to MSTA0.

XRD studies: Fig. 4 shows the X-ray diffraction (XRD) patterns of STA, MSTA0 and MSTA10 samples. The XRD spectrum of STA (Fig. 4c) exhibits sharp diffraction peaks between 15º to 40º indicating its high crystalline phase. These characteristic peaks confirm the well-defined crystalline structure of STA particles. In MSTA0 (Fig. 4b), the broad diffraction peak signifying its predominantly amorphous nature. The XRD pattern of MSTA10 shows a broad peak similar to MSTA0. The polymers crystallinity plays a crucial role in the regulation of molecular transport properties that occur during pervaporation. The crystalline phase of polymer tends to slow down the components' ability to penetrate and separate [23]. In this study, STA-loaded composite membrane (MSTA10) does not exhibit any STA related XRD peaks, indicating that the STA has dispersed uniformly in the polymer matrix without disturbing the morphology of the membranes.

Morphological studies: To understand the surface morphology of MSTA0 and MSTA10 membranes, SEM analysis was performed and displayed in Fig. 5. The SEM image of MSTA0 (Fig. 5a & c) indicate less roughness on the surface, indicating a proper interaction developed between the two different polymer materials. The SEM image of MSTA10 shows a rough surface with some porous nature due to the incorporation of STA molecules. This suggests that the incorporation of STA greatly changes the configurations of the membranes, possibly offering more free volumes to the polymer chains and, in turn, creating more space for water moles to permeate through the composite membranes.

Sorption studies: The sorption mechanism is influenced by several factors, including the penetrants affinity toward the membrane, the mutual interactions between the penetrants, the membrane microstructure. The degree of membrane swelling has a significant impact on pervaporation effectiveness [24]. Thus, determination of swelling levels is important, as it relates directly to the membrane sorption capability. Fig. 6 demonstrates the swelling behaviour of the composite membrane with respect to the amount of STA in the composite membrane. It can be observed that the swelling extent increases with rise in the amount of STA in the composite membrane. This finding
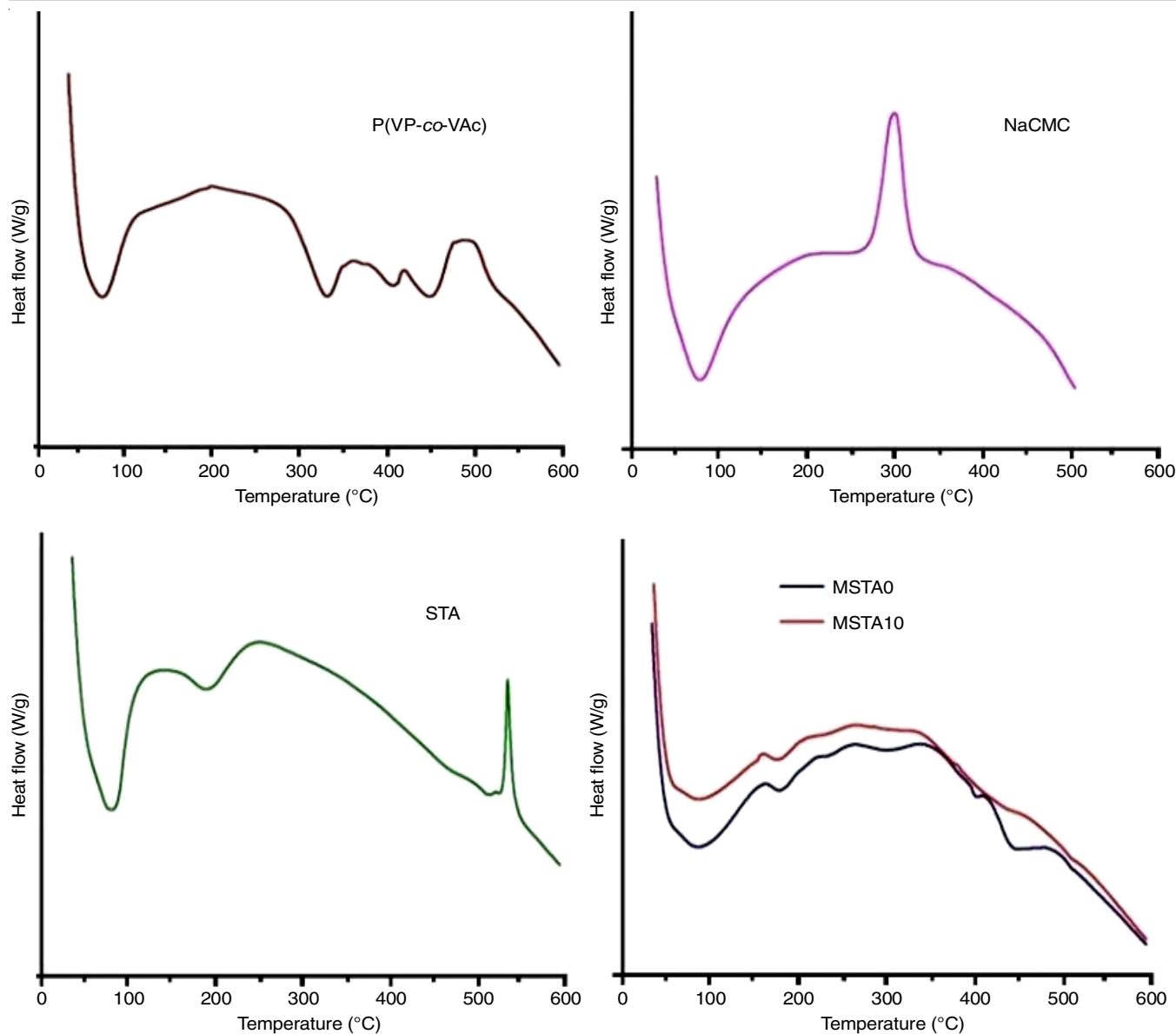
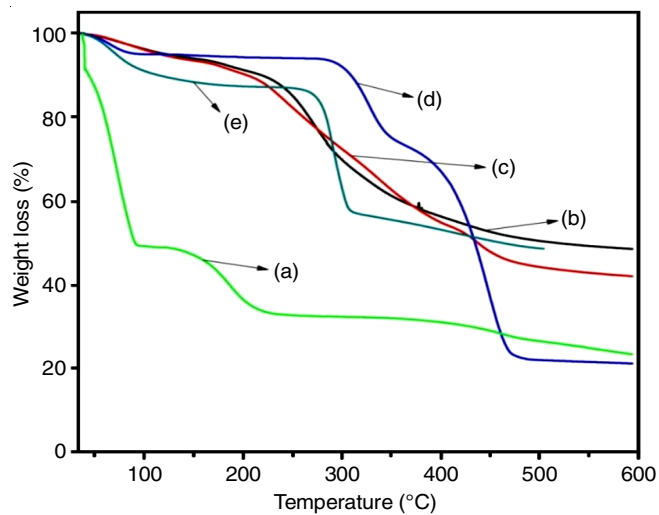Fig. 2. DSC thermograms of P(VP-*co*-VAc), NaCMC, STA, MSTA0 and MSTA10

Fig. 3. Thermograms of STA (a), MSTA10 (b), MSTA0 (c), P(VP-*co*-VAc) (d), NaCMC (e)
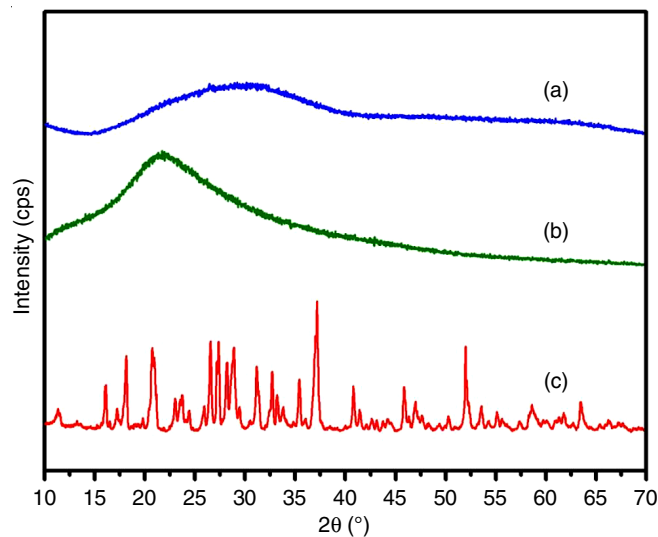

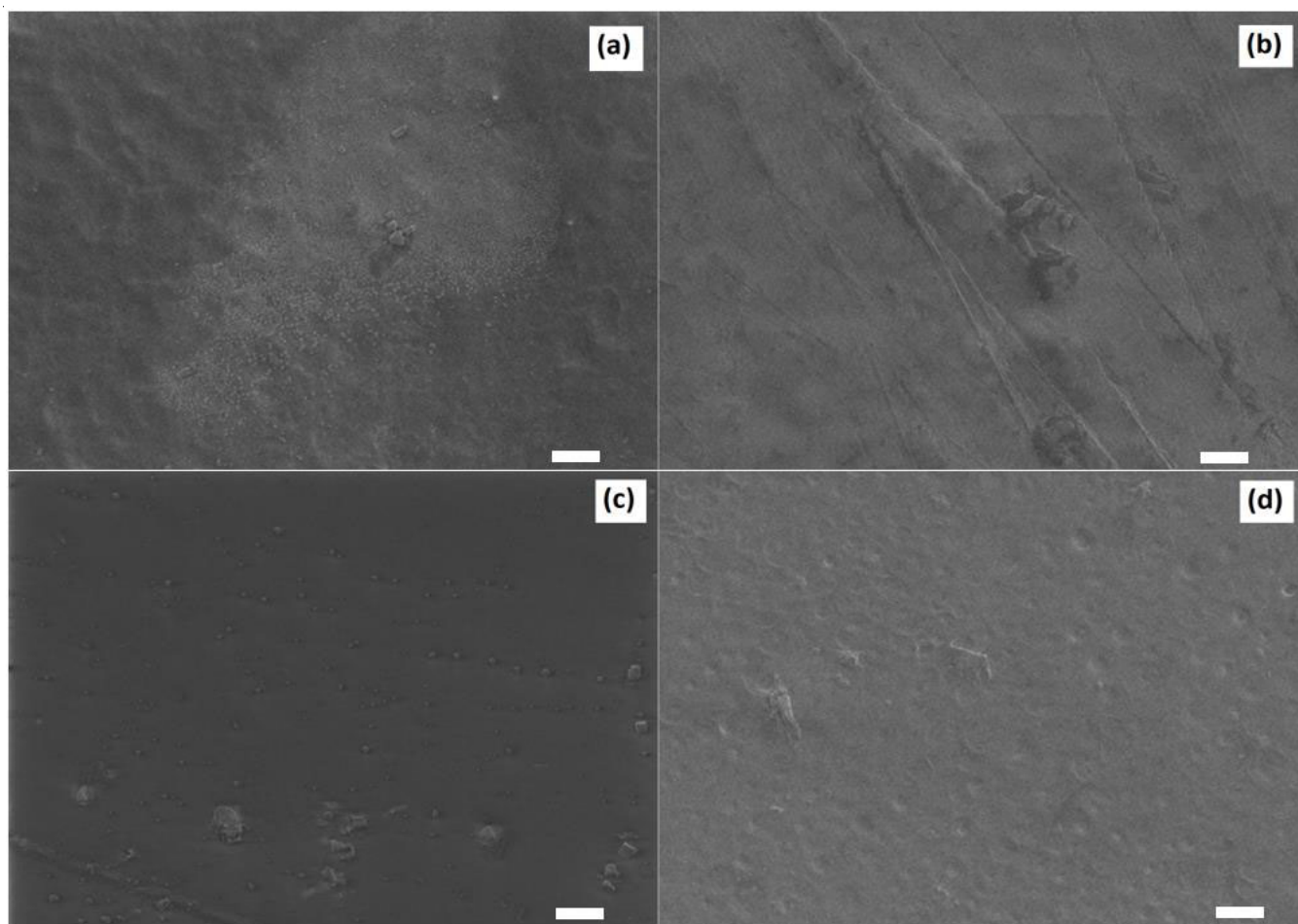Fig. 4. XRD patterns of MSTA10 (a), MSTA0 (b) and STA (c)

Fig. 5. SEM images of NaCMC/P(VP-*co*-VAc) membrane (a & c) and MSTA10 (b & d). (scale bar = 10 μm) (magnification for a & b is x500; for c & d is x1000)
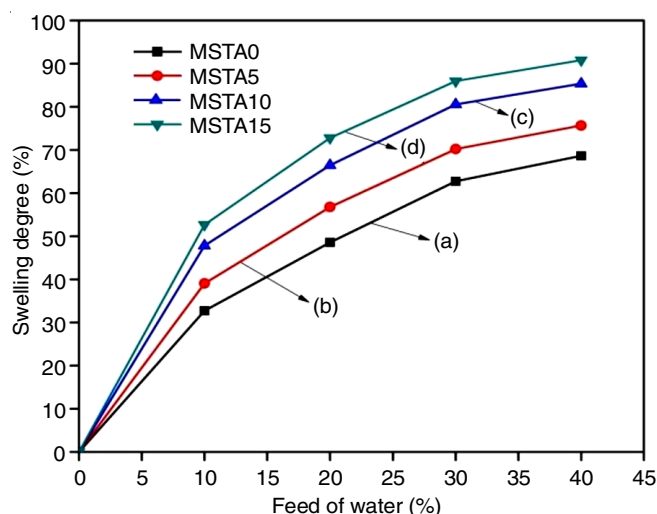

Fig. 6. Degree of swelling of MSTA0 (a) MSTA5 (b), MSTA10 (c) and MSTA15 (d)

suggests that the incorporation of STA enhances the hydrophilicity and the amorphous regions within the membrane structure, leading to improved interaction with water molecules.

Membrane performance through pervaporation (PV) studies: To assess the performance of membranes under various feed conditions, both without and with STA loading, the pervaporation studies were conducted. These experiments were carried out at 30 ºC with feed mixtures containing 10%, 20%, 30% and 40% water. The performance parameters, including selectivity, flux and pervaporation separation index (PSI), were analyzed and the results are presented in Table-1. The incorporation of STA into the blend membranes significantly influenced their PV performance. The selectivity, flux and PSI values showed prominent changes depending on the STA content and the feed mixture composition. The findings demonstrated the potential of STA-loaded composite membranes to enhance separation efficiency, likely due to increased hydrophilicity and changes in the amorphous regions, as evidenced by sorption studies.

Effect of STA on pervaporation: Table-1 shows the impact of STA content on the flux and selectivity of blend membranes of various feed mixtures. The MSTA0 had a 0.241 kg/m^2·h flux and 780.47 selectivity, removing 98.86 wt.% of water on the permeate side for a 10 wt.% water-containing feed mixture. The composite membrane with 15 wt.% STA had the maximum selectivity value of infinity at 30 ºC for all feed compositions.

The selectivity value enhanced with the enhancing amount of STA in the blend matrix and decreased with increase in water concentration in the feed mixture. The selectivity value of MSTA0 is 780.47 and after the incorporation of STA into

TABLE-1						
PERVAPORATION DATA FOR FEED MIXTURE OF WATER-ISOPROPANOL AT 30 ºC						
Feed compositions		Permeate compositions		Selectivity (α)	Flux (kg/m² h)	PSI
Water (*x*)	IPA (1-*x*)	Water (*y*)	IPA (1-*y*)			
MSTA0						
10	90	98.86	1.14	780.47	0.241	188.09
20	80	98.51	1.49	264.45	0.256	67.69
30	70	98.22	1.78	128.75	0.291	37.46
40	60	98.07	1.93	76.22	0.375	28.58
MSTA5						
10	90	99.54	0.46	1947.52	0.265	516.09
20	80	99.45	0.55	723.27	0.305	220.59
30	70	99.21	0.79	293.02	0.383	112.22
40	60	99.09	0.91	163.33	0.465	75.94
MSTA10						
10	90	99.74	0.26	3452.53	0.327	1128.97
20	80	99.53	0.47	847.06	0.375	317.64
30	70	99.37	0.63	368.03	0.432	158.98
40	60	99.24	0.76	195.86	0.493	96.55
MSTA15						
10	90	99.88	0.12	6914.07	0.387	2675.74
20	80	99.73	0.27	1477.48	0.465	687.02
30	70	99.54	0.46	504.91	0.487	245.89
40	60	99.33	0.67	222.38	0.533	118.52

the composite membrane, the selectivity value of MSTA increases with increase of STA in the composite membrane. MSTA5 had a selectivity of 1947.52 for 10 wt.% water in the feed mixture, while the same composite membrane exhibited 723.27 for 20% water in the feed mixture (Fig. 7a). The flux value for MSTA0 is 0.241 for 10 wt.% water in the feed mixture; upon rising the water content in the feed mixture, the flux increases (Fig. 7b). After the incorporation of STA into the composite membrane, the flux values increase as the concentration of STA increases. The flux and selectivity trends align with the swelling data indicating that the hydrophilic nature of membrane enhanced with STA loading [3]. The STA-loaded composite membranes have a higher water absorption than MSTA0, even at lower STA content, due to the hydrophilic nature of STA molecules, thus resulting in higher flux and selectivity. At higher STA loadings, the excessive water uptake caused

increased membrane swelling, resulting in a higher free volume. This facilitated the selective transport of water molecules while restricting acetic acid molecules.

Effect of feed water composition: The performance of the composition membrane for the pervaporation process depends on composition of feed; therefore, influence of composition of feed on the pervaporation performance of MSTA0 and STA-loaded composite membranes were examined and the results are presented in Table-1. The concentrations of water/IPA (10/90 to 40/60 w/w) in the feed were plotted against the water permeate composition at 30 ºC using MSTA0, MSTA5, MSTA10 and MSTA15 composite membranes (Fig. 8). The findings indicated that the separation of the water from the feed mixture is highly dependent on the water content in feed composition. For instance, the water content in permeate composition is 99.88 for 10/90 (water/IPA), which was decreased to 99.33 upon
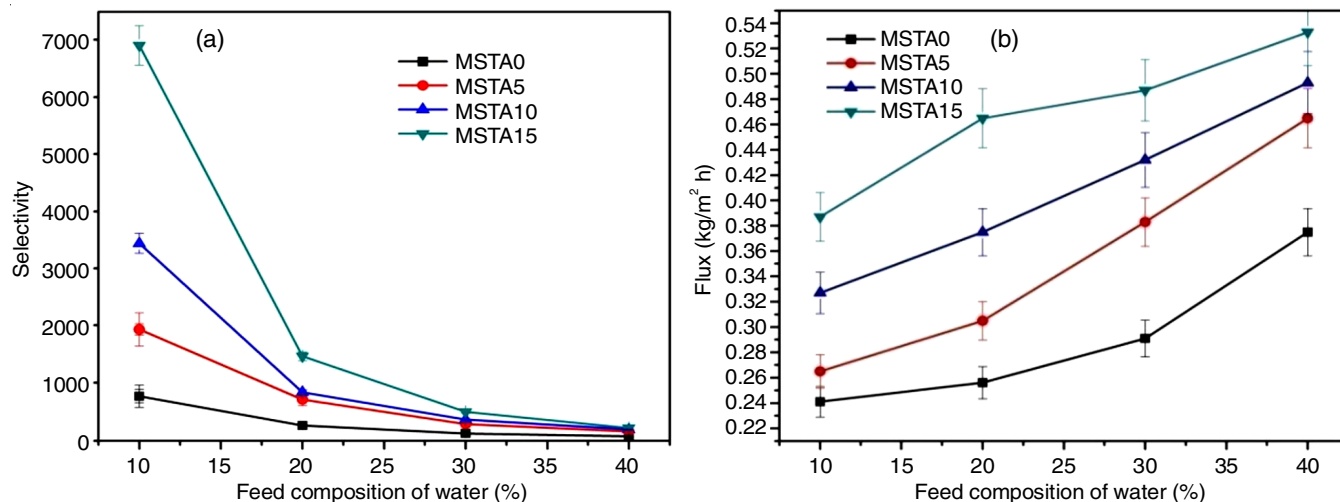

Fig. 7. Effect of wt.% of water in the feed on selectivity (a) and flux (b) for different blend membranes
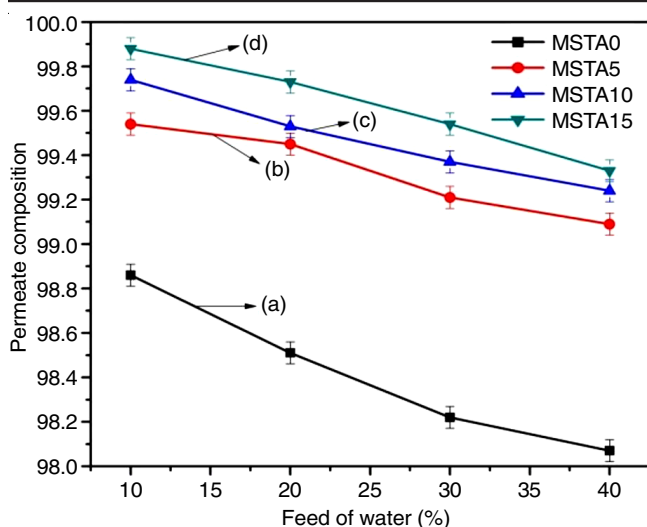
Fig. 8. Effect of wt.% of water in the feed on water permeate and its STA incorporated for different blend membranes

Fig. 9. Effect of wt.% of water in the feed on PSI and its STA incorporated for different blend membranes

increasing the water content to 40/60 (water/IPA) in permeate composition. This trend is attributed to the effect of plasticization; a feed with higher water content results in greater swelling and increased free volume within the membrane, consequently reducing its selectivity for separation. These findings suggest that the optimizing the feed composition is important to achieve improved pervaporation applications.

Effect of pervaporation separation index: The permeation separation index (PSI) represents the product of separation factor and flux, illustrating the ability of membrane to distinguish between different components. Table-1 shows that the PSI values increase with the increasing STA in the composite membrane, which implies that increasing the concentration of STA in the membrane material led to the enhancement of IPA/water separation efficiency. The addition of STA to the membrane changes its structural characteristics in along with increasing its hydrophilicity. These changes had probably a profound effect on the diffusion process and enhanced the separation efficiency of the membrane. Furthermore, it was found that increase in the water content in the feed mixture, the PSI decreases (Fig. 9). For instance, the PSI value for MSTA15 is 2675.74 for 10/90 (water/IPA), which was decreased to 687.02 upon increasing the water content to 20/80 (water/IPA) in the feed mixture. These results suggest that optimizing the feed composition and concentration of STA are crucial for enhancing pervaporation applications.

Conclusion

In this study, silicotungstic acid (STA)-loaded NaCMC/P(VP-*co*-VAc) composite membranes were prepared by varying the concentration of STA (5, 10 and 15%), crosslinked with glutaraldehyde applied for pervaporation-based dehydration of water/isopropanol mixtures. The results showed that the incorporation of STA particles into the composite membrane enhances the efficacity of separation process, achieves higher values of selectivity and flux to the water molecule. FTIR and DSC studies confirmed the incorporation of STA particles into the composite membranes. SEM study confirms the compatibi-
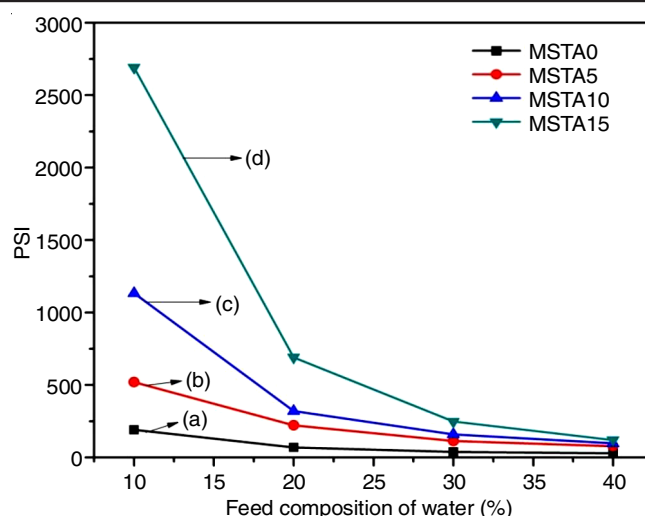
lity of polymer blend and STA-loaded composite membranes. In contrast to NaCMC/P(VP-*co*-VAc) membrane, STA-loaded composite membranes were found to be more effective for dehydrating isopropanol. Incorporation of hydrophilic STA into the polymer matrix enhances the hydrophilic nature of composite membranes to attain enhanced levels of dehydration of isopropanol. Though, the polymer matrix compatibility and hydrophilicity should be optimized since the induced plasticization effect of the overall blend membrane is observed in the presence of STA for the dehydration of isopropanol through enhancing the permeation flux and selectivity of the composite membrane. These swelling data suggest that the effect of STA on sorption shows a critical role in governing the pervaporation separation performance of the STA-incorporated composite membranes. The results indicated that the STA-loaded composite membranes are acceptable options for the pervaporation-assisted separation processes.

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CONFLICT OF INTEREST

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The authors declare that there is no conflict of interests regarding the publication of this article.

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