ACTA CHEMICA IASI, **28_1**, 47 - 62 (2020)
DOI: 10.2478/achi-2020-0004

POLY(VINYL ALCOHOL) AND MCM-41 MIXED MATRIX MEMBRANES FOR PERVAPORATION DEHYDRATION OF ISOPROPANOL AT THEIR AZEOTROPIC POINT

M. B. Patil[a*], M. K. Amshumali[b], S. N. M. Mathad[c]

[a]*Bharat Ratna Prof.C.N.R Rao Research Centre, P. G. Department of Chemistry, Basaveshwar Science College, Bagalkot-587101, India*
[b]*Department of Chemistry, Vijayanagara Sri Krishnadevaraya University, Ballari, Karnataka, India*
[c]*Department of physics, KLE Institute of Technology, Hubballai, 580030Karnataka, India*

Abstract: The present study focuses on the development of mixed matrix membranes of poly(vinyl alcohol) (PVA) mixed with MCM-41 mesoporous silica, with different loading from 2-10 wt. % with respect to the polymer and on their use for the dehydration of isopropanol by pervaporation (PV) at the azeotropic point, from aqueous mixtures of 12.3 wt.% water, at 30°C. The membranes were crosslinked with tetraethyl ortho silicate (TEOS) and the ion exchange capacity (IEC) was determined. The membranes were analyzed by Fourier-Transform Infrared Spectroscopy (FTIR) to confirm the crosslinking occurrence. The morphology of the membranes was studied by scanning electron microscopy (SEM). The extent of interaction and degree of sorption were measured by sorption studies. PV results showed that the flux and selectivity were enhanced with increasing loading of MCM-41 particles in the PVA matrix, due to increasing of PVA membrane hydrophilicity. In the case of mixed matrix membrane containing 10 wt. % of MCM-41, the selectivity for water was 1430 and a flux of 0.356 kg cm^{-2} h^{-1} was achieved, due to joint effects of molecular adhesion between mesoporous material particle surfaces and PVA matrix. Higher selectivity value found for mixed matrix membranes in comparison with the plain PVA membrane.

***Keywords*:** Mixed matrix membranes; azeotropic point; poly(vinyl alcohol); MCM-41

---

[*] Corresponding author: *mallupatil04@gmail.com*

Introduction

The separation procedures are to a great degree utilized for contaminant removal from raw materials, primary product recovery in the chemical industries production and contaminant elimination from effluent water and air streams. In the membrane-based separation processes, the separation of the components from a liquid or a gas mixture takes place on the basis of their respective permeation rates through the membrane material. In the recent years, the membranes and membrane processes gained a very important role in the industrial production of substantial technical significance, being involved in a wide range of applications, as producing potable water from seawater, industrial effluent water treatment, hydrogen recovery from off-gases or to fractionate, advanced concentration and purification of solutions in the pharmaceutical and chemical industry. Membranes became key elements in artificial kidneys and controlled drug delivery systems. Pervaporation is a newer technique used to separate the mixtures, a very economical and effective technique for the separation of water from organic solvents and different solvents. This technique has been emerged as a novel liquid separation process in the recent years, which may eventually compete the conventional distillation for the final dehydration stages of organic-organic liquid mixtures, removal of dissolved organic contaminants from aqueous streams, ethanol production and continuous removal of bio-solvents with inhibitory effects on the production rate from fermentation broths.[1]

In the recent years, PV has been extensively used commercially for dehydrating alcohols using high permselective poly(vinyl alcohol)/polyacrylonitrile (PVA/PAN) film composite membranes with commercial name of GFT. In the recent years, many researchers attempted to develop new generations of membranes for organics dehydration.[2-5] The development of a suitable polymer membrane is the key to success in PV dehydration, bringing high selectivity, flux, stability and mechanical strength to withstand the operating conditions.[6] However, scrutinizing these parameters is a difficult task. Recently, research interests moved from the use of simple membranes[7-8] to developing compatible filler-reinforced mixed matrix membranes, in which nano-sized inorganic fillers have been included.[9-18] The performance of the membrane exclusively depends on the level of filler particles dispersion in the polymer matrix, filler loading, matrix/filler adhesion, in addition to their physico-chemical characteristics.[19-20] However, the mechanical strength of such membranes depends on the compatibility between fillers and polymers, usually prepared by *in situ* mixing of fillers along with cross-linking agent to cast the membranes.[21]

In continuation of our previous research work,[22] we now extend the expansion of nanocomposite membranes of PVA filled with PAN-coated TiO_2, as well as TiO_2 nanoparticles for PV dehydration of aqueous mixtures of tetrahydrofuran (THF) and 1,4-dioxane. The PV dehydration of 1,4-dioxane and tetrahydrofuran have also been studied before.[7,8,15] In the present research work, we explore the possible utilization of PVA–PAN-coated TiO_2 nanocomposite membranes[22] for PV dehydration of 1,4-dioxane and THF. We have widely studied and reported these membranes in our earlier report.[22]

The purpose of this study to find a strategy for achieving parallel enhancement of flux and selectivity and thus the establishment of the methodology for the fabrication of mixed matrix pervaporation membrane and process development. PVA-MCM-41 mixed matric membranes were prepared and characterized by FTIR, SEM, DSC and TGA techniques. The effects of MCM-41 particle content on pervaporation properties of the adsorbent membranes for the separation of isopropanol/water mixture at azeotropic composition were systematically studied. The reversal of tradeoff effect was actually found and tentatively elucidated.

Experimental

Materials and methods

Poly(vinyl alcohol) with molecular weight 125 000 and hydrochloric acid was purchased from s.d. Fine chemicals, India. Tetra ethyl orthosilicate (TEOS) (98 % pure) was purchased from Acros Organics, India. Deionized water, with conductivity of 5.5 μS/cm, was obtained in the laboratory using a double distillation unit. All reagents used for the work are used without further purification.

Particle size measurement of MCM-41

The particle size of completely dried MCM-41 was measured by Zetasizer (Model 3000HS, Malvern, U.K), by wet sample technique using a sample adapter. Particles were dispersed in water, placed on cuvette holder and zeta average diameter was measured. Soon after completion of the measurement, the sample cuvette was washed thoroughly to avoid contamination. Particle size was analysed in triplicate and the average value was taken in data analysis.

Membrane fabrication

VA TEOS Hybrid membrane

6 g of PVA was dissolved in 80 mL of double distilled water at 60°C. In the PVA solution, 2 wt. % of TEOS referring to weight of PVA (0.12 g of TEOS) was poured, then 1 mL of HCl was added as a hydrolysis-condensation. The reaction mixture was stirred for 12h at 60°C. A sol–gel

type reaction occurred. The final mixture was cast onto a glass plate, dried at room temperature and once dried peeled off from the glass plate.

Mixed Matrix membrane

For the preparation of MCM-41 containing membranes, the corresponding amounts of MCM-41 mesoporous silica, to form 2, 4, 6, 8 and 10 wt % with respect to total weight of the polymer were added to the prepared crosslinked slurry of PVA (the hybrid PVA TEOS solution prepared as described in section 2.3.1). Prior to be used in the mixture above, the MCM-4 was preconditioned by drying in vacuum oven at 250°C, dispersed in 5 mL of water and sonicated (sonicator model VC 50, Sonics & Materials Inc.) for 2 h. The resultant mixture was stirred for 5 h to get homogeneous slurry, casted as membranes by pouring onto a clean and dry glass plate, dried, peeled off and stored properly. The mixed matrix membranes were labeled as PVA-MCM-41/2, PVA-MCM-41/4, PVA-MCM-41/6, PVA-MCM-41/8 and PVA-MCM-41/10, respectively, indicating the percent content of MCM-41. The thickness of the films was measured using a dial micrometer (AMES, model 56212). For each film, 10 measurements at different points were measured and the average thickness was calculated (around 65 ± 0.2 μm, standard deviation less than 1.5μm).

Scanning electron microscopy

SEM micrographs of the pristine PVA and PVA-MCM-41/2 membranes were chosen to study the morphology. The membranes were sputtered with gold coating to make them conductive and placed on a copper stub. The scanning was carried out using JEOL model JSM-840A, Japan. The thickness of the gold layer accomplished by gold sputtering was approximately 15 nm.

FTIR

Pristine PVA membrane and PVA-MCM-41 membranes well-grounded with KBr to make thin pellets using a hydraulic pressure of 400-450 kg/cm^2 were used to trace the FTIR spectra, using a Shimadzu FTIR spectrophotometer.

Pervaporation experiments

The pervaporation (PV) experiments were carried out in a 100 mL batch process reactor containing indigenously built glass manifold and operated at vacuum (0.05 mmHg in the permeate stream). The effective membrane area of the reactor is 20 cm^2 and the weight of the feed mixture taken in the PV cell was 70 g. In the feed mixture chamber, the temperature was kept constant by a thermostatic water jacket. Before starting the PV run, the test membrane was equilibrated for about 3 h with the feed mixture. After reaching the equilibrium, the permeate vapors were collected in cold traps immersed in liquid nitrogen for up to 2 h. The permeate weight was measured using a Mettler Balance (model B 204-S, Greifensee, Switzerland, accuracy 10^{-4} g)l. The weight flux of permeated liquids J (kg.m^{-2}h^{-1}) was calculated as the ratio between the weight of liquids subjected to separation W (kg) and the effective membrane area, A (m^2) multiplied with the measurement time, t (h) as:

$$J = \frac{W}{At} \tag{1}$$

The analysis of feed and permeate samples was done using Nucon Gas Chromatograph (model 5765, Mumbai, India) equipped with a thermal conductivity detector (*TCD*) and DEGS or Tenax packed column of 1/8" ID of 2 m in length. The oven temperature was maintained constant at 70°C, while injector and detector temperatures were 150°C. The sample injection volume was 1 μL. Pure hydrogen was used as the carrier gas at 0.75 kg cm^{-2} flow. The GC response was calibrated for column and for the known compositions of water with ethanol mixture. Calibration factors were fed into GC software to obtain the analysis for the unknown samples. The selectivity, α and separation index, *PSI*, were calculated as:

$$\alpha = \left(\frac{P_{\mathrm{A}}}{1-P_{\mathrm{A}}}\right)\left(\frac{1-F_{\mathrm{A}}}{F_{\mathrm{A}}}\right) \quad (2)$$

$$PSI = J\,(\alpha - 1) \quad (3)$$

where F_{A} is weight % of water in feed and P_{A} is weight % of water in permeate. A minimum of three independent readings on flux and α were taken under similar conditions of temperature and feed compositions to confirm steady-state pervaporation.

% Degree of Sorption (% DS)

The sorption or water uptake behavior of the membranes was carried out by cutting the membranes in a 2.5 cm diameter in circular and drying them in an oven. Once the membranes were dried, the dry membranes were weighted on a single-pan digital microbalance (model AE 240, Mettler, Switzerland) with an accuracy of ± 0.01 mg and readings are noted down as initial weight. These membranes were soaked inside specially designed airtight test bottles containing 30 cm^3 by volume in different water alcohol mixture i.e. 10, 20 and 30 wt. % water-containing mixtures with isopropanol, Test bottles were transferred to oven maintained at constant desired temperature i.e. at 30°C [22]. The soaked membranes were weighed after 48 Hrs and are noted as final weight.

The degree of swelling *DS,* (%) was calculated as:

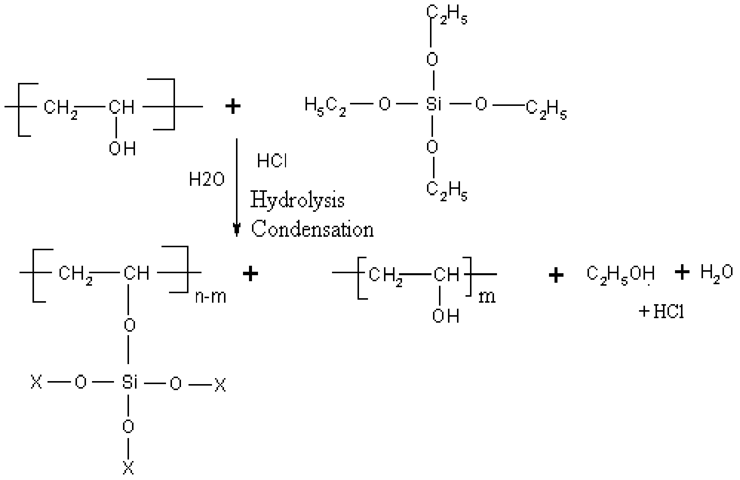
$$\%\,DS = \left(\frac{W_\infty - W_0}{W_0}\right)\times 100 \quad (4)$$

where W_∞ and W_0 are the weights of swollen (final weight) and dry membranes (initial weight), respectively.

Results and Discussion

Reaction of PVA and TEOS

PVA was crosslinked with TEOS and the reaction scheme was shown in the Scheme 1; the polycondensation reaction was carried out as explained below.[23] During the fabrication of the PVA/TEOS hybrid membranes, TEOS easily hydrolyzed in the presence of HCl, generating silanol groups. These groups form siloxane bonds by the elimination of ethanol, with the participation of available ethoxy groups during the reaction. This kind of reactions led to a cohesive interaction between hydroxyl and siloxane groups of PVA.



Scheme 1. Reaction scheme of poly(vinyl alcohol) and tetraethoxysilane.

Scanning Electron Microscopy (SEM)

The SEM image of the pristine PVA and PVA-MCM-41/2 mixed matrix membranes are displayed in Figure 1. The particles of MCM-41 are scattered uniformly on the surface of PVA matrix.

Particle size and distribution Analysis (PSD)

The Particle Size Distribution analysis (PSD) estimates and provides information about the size and range of particles of a material. The histogram of particle size distribution is shown in Figure 2. MCM-41 particles vary in the size between 7 and 25 μm. The average particle size of the particles found 15 μm.

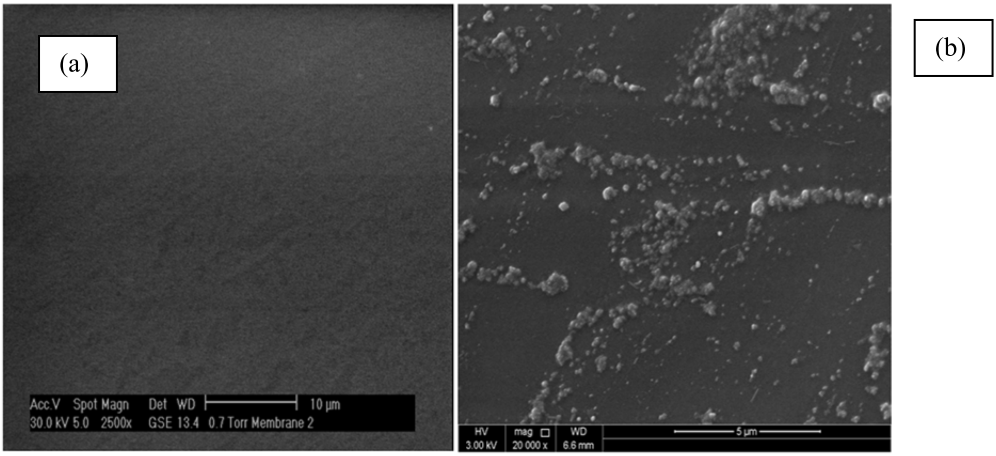


Figure 1. SEM images of (a) pristine PVA and (b) PVA-MCM-41/2 % .

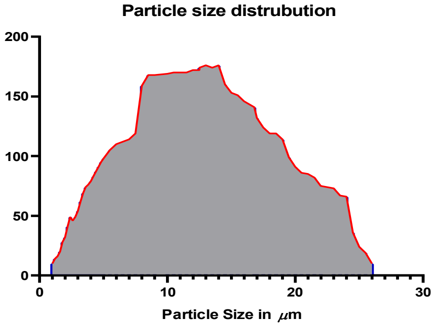


Figure 2. Particle size histogram of mesoporous MCM-41.

FTIR Studies

The FTIR of plain PVA and crosslinked (with TEOS) PVA membrane are displayed in figure 3. The crosslinking reaction of TEOS with PVA is confirmed by the FTIR spectra studies.

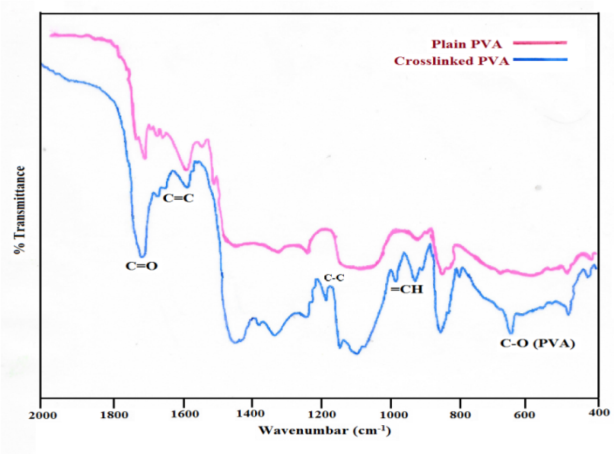


Figure 3. FTIR curves of PVA before and after crosslinking.

In the region of 1000–1100 cm^{-1}, multiple bands have appeared for plain PVA due to C-O stretching vibrations. In the case of the mixed matrix membrane, the intensity of this peak was increased, indicating the formation of Si-O-C bonds between linear alkyl chain (-CH_2-CH-) of PVA. However, -Si-O- stretching is also observed in the same region as that of C-O stretching.

% Degree of Sorption

The degree of sorption measured using equation (4) suggest that the sorption of the membrane is significant, showing its firm nature (Figure 4). The pervaporation results are greatly influenced by membrane swelling. The PVA-MCM-41 membranes swell less than the pristine PVA ones, mostly probable due to the space occupied by MCM-41 particles in the polymer matrix, which is not swelling. For PVA-MCM-41/2, a slight decrease in % DS is observed over that of plain crosslinked PVA membrane. However, for PVA-MCM-41/10 containing mixed matrix membrane, the DS of only 29 % has been recorded.

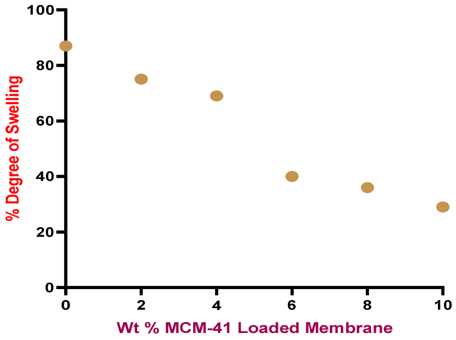


Figure 4. Degree of water sorption for the different membranes, %.

Pervaporation separation Index

Figure 5 shows the variation of PSI value calculated with relation (3) with the amount of MCM-41 loading in the membrane. The values of PSI increased linearly with increasing the MCM-41 content, signifying that membranes which contain filler show higher PSI value for water–isopropanol feed mixtures. The addition of MCM-41 particles into the PVA membrane not only affects the membrane hydrophilicity, but its rigidity as well. Thus, an enhanced hydrophilic–hydrophilic molecular interaction between MCM-41 and PVA enhances significantly the diffusion of water molecule through the mixed matrix membranes, by retaining the organic component on the feed side.

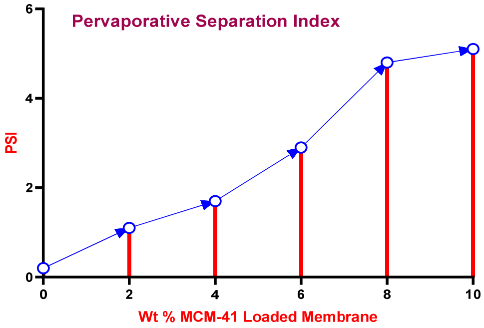


Figure 5. Pervaporation separation index.

Membrane performance

Since the transport is very sensitive to the micro level (because of the size of the molecules from the liquids), it is interesting to explore the interfacial fit between the inorganic and polymer phases. In addition to the improved mechanical strength, remarkable changes have been noticed in liquid transport phenomenon of mixed matrix membrane using MCM-41 mesoporous silica. MCM-41 is a well-known molecular sieve with a pore diameter of 2-6.5 nm with interconnected cages that is ideally suited to the binary liquid separation systems.

In the present PV experiments, the performance of the mixed matrix membrane was studied with respect to flux and selectivity. The organic component transport is hindered in the presence of large excess of water due to their hydrophilic interactions with the membrane. As seen in Figure 6, for the PVA membrane, the selectivity data for isopropanol–water is much lower than those observed for the mixed matrix membranes. The selectivity increases with the MCM-41 content for the mixed membranes, in correlation which the increased hydrophilicity with the MCM-41 content. The mixed PVA membranes are able to remove more than 97% of water at the permeate side, whereas pristine PVA was successful to separate up to 96% of isopropanol.

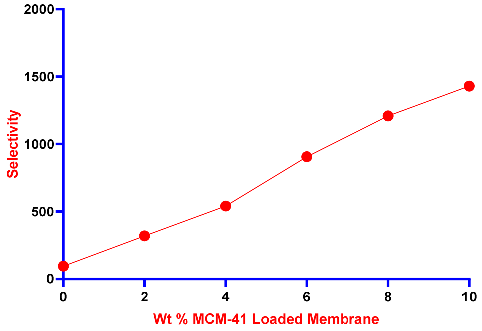


Figure 6. Selectivity results for the MCM-41 loaded PVA membrane.

The flux results are shown in figure 7 for a feed mixture containing 12.3 wt. % of water in isopropanol (azeotropic point) suggest that also flux increases accordingly as increasing MCM-41 particles ratios.

The selectivity increased from 96 (plain PVA) to 1430 (PVA-MCM-41/10), while the flux started from 0.1, (PVA) to 0.382 kg/m^2 h (PVA-MCM-41/10). This kind of increment in membrane performance clearly shows the preferential interaction of water molecules with the filled matrix membranes.

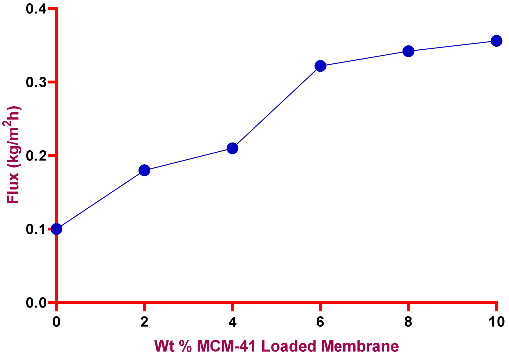


Figure 7. Total Flux with respect to MCM-41 loaded PVA membrane.

Conclusions

In order to improve the membrane performance, the present research focuses on the improvement in the membrane performance in terms of flux and selectivity. The fillers like MCM-41 mesoporous material can improve the separation properties of membranes, provided that the suitable combinations of polymer and mesoporous material are chosen. The mixed matrix membranes considered here were successful in PV dehydration of isopropanol from an azeotropic mixture with water. Even the incorporation of 2% of MCM-41 mesoporous material particles into PVA matrix has augmented the flux and selectivity to water as compared to pristine PVA membrane, while 10% MCM increased almost four times the flux and almost 15 times the selectivity. This behavior is due to the hydrophilic nature of MCM-41, acting in synergy with the hydrophilic PVA polymer.

References

1. Gudernatsch, W.; Menzel, T.; Strathmann, H. Influence of composite membrane structure on pervaporation. J. Membr. Sci. **1991**, 61, 19-30.
2. US Department of Energy, Membrane Separation Systems — A Research Need Assessment, US. DOE Report No. DE 90-011770, Department of Energy, Washington DC, 1990.
3. Baker, R. W.; Cussler, E. L.; Eykamp, W.; Koros, W. J.; Riley, R. L.; Strathmann, H. *Membrane Separation Systems: Recent Developments and Future Directions*; Noyes Data, Park Ridge, NJ, 1991.
4. Sridhar, S.; Ravindra, R.; Khan, A. A. Recovery of Monomethylhydrazine Liquid Propellant by Pervaporation Technique. *Ind. Eng. Chem. Res*. **2000**, *39*, 2485- 2490.
5. Hussain, M.; Nakahira, A.; Nishijima, S.; Niihara, K. Fracture behavior and fracture toughness of particulate filled epoxy composites. *Mater. Lett.* **1996**, *27*, 21- 25.
6. Doyen, W.; Adriansens, W.; Molenberghs, B.; Leysen, R. A comparison between polysulfone, zirconia and organo-mineral membranes for use in ultrafiltration. *J. Membr. Sci*. **1996**, *113*, 247-258.

7. Kurkuri, M. D.; Kumbar, S. G.; Aminabhavi, T. M. Synthesis and characterization of polyacrylamide-grafted sodium alginate copolymeric membranes and their use in pervaporation separation of water and tetrahydrofuran mixtures. *J. Appl. Polym. Sci.* **2002**, *86*, 272-281.

8. Aminabhavi, T. M.; Naidu, B. V. K.; Sridhar, S. Computer simulation and comparative study on the pervaporation separation characteristics of sodium alginate and its blend membranes with poly(vinyl alcohol) to separate aqueous mixtures of 1,4-dioxane or tetrahydrofuran. *J. Appl. Polym. Sci.* **2004**, *94*, 1827-1840.

9. Naidu, B. V. K.; Bhat, S. D.; Sairam, M.; Wali, A. C.; Sawant, D. P.; Halligudi, S. B.; Mallikarjuna, N. N.; Aminabhavi, T. M. Comparison of the pervaporation separation of a water–acetonitrile mixture with zeolite-filled sodium alginate and poly(vinyl alcohol)–polyaniline semi-interpenetrating polymer network membranes. *J. Appl. Polym. Sci.* **2005**, *96*, 1968-1978.

10. Bhat, S. D.; Naidu, B. V. K.; Shanbag, G. V.; Halligudi, S. B.; Aminabhavi, T. M. Mesoporous molecular sieve (MCM-41)-filled sodium alginate hybrid nanocomposite membranes for pervaporation separation of water–isopropanol mixtures. *Sep. Purif. Tech.* **2006**, *49*, 56-63.

11. Bhat, S. D.; Aminabhavi, T. M. Novel sodium alginate–Na^+ MMT hybrid composite membranes for pervaporation dehydration of isopropanol, 1, 4-dioxane and tetrahydrofuran. *Sep. Purif. Tech*. **2006**, *51,* 85-94.

12. Bhat, S. D.; Mallikarjuna, N. N.; Aminabhavi, T. M. Microporous alumino-phosphate (AlPO4-5) molecular sieve-loaded novel sodium alginate composite membranes for pervaporation dehydration of aqueous–organic mixtures near their azeotropic compositions. *J. Membr. Sci.* **2006**, *282*, 473-483.

13. Bhat, S. D.; Aminabhavi, T. M. Novel sodium alginate composite membranes incorporated with SBA-15 molecular sieves for the pervaporation dehydration of aqueous mixtures of isopropanol and 1,4-dioxane at 30 °C. *Microporous Mesoporous Mater.* **2006**, *91*, 206-214.

14. Sairam, M.; Naidu, B. V. K.; Nataraj, S. K.; Sreedhar, B.; Aminabhavi, T. M. Poly (vinyl alcohol)-iron oxide nanocomposite membranes for pervaporation dehydration of isopropanol, 1, 4-dioxane and tetrahydrofuran. *J. Membr. Sci.* **2006**, *283*, 65-73.

15. Adoor, S. G.; Sairam, M.; Manjeshwar, L. S.; Raju, K. V. S. N.; Aminabhavi, T. M. Sodium montmorillonite clay loaded novel mixed matrix membranes of poly(vinyl alcohol) for pervaporation dehydration of aqueous mixtures of isopropanol and 1,4-dioxan., *J. Membr. Sci.* **2006**, *285*, 182-195.

16. Teli, S. B.; Gokavi, G. S.; Sairam, M.; Aminabhavi, T. M. Highly water selective silicotungstic acid ($H_4SiW_{12}O_{40}$) incorporated novel sodium alginate hybrid composite membranes for pervaporation dehydration of acetic acid. *Sep. Purif. Tech.* **2007**, *54*, 178-186.

17. Bhat, S. D.; Aminabhavi, T. M. Zeolite K-LTL-loaded sodium alginate mixed matrix membranes for pervaporation dehydration of aqueous–organic mixtures. *J. Membr. Sci.* **2007**, *306*, 173-185.

18. Patil, M. B.; Veerapur, R. S.; Patil, S. A.; Madhusoodana, C. D.; Aminabhavi, T. M. Preparation and characterization of filled matrix membranes of sodium alginate incorporated with aluminum-containing mesoporous silica for pervaporation dehydration of alcohols. *Sep. Pur. Tech.* **2007**, *54*, 34-43.

19. Smaihi, M.; Schrotter, J. C.; Lesimple, C.; Prevost, I.; Guizard, C. Gas separation properties of hybrid imide–siloxane copolymers with various silica contents, *J. Membr. Sci.* **1999**, *161*, 157-170.

20. Mascia, L.; Kioul, A. Influence of siloxane composition and morphology on properties of polyimide-silica hybrids, *Polymer* **1995**, *36*, 3649-3659.

21. Nunes, S. P. ; Peinemann, K. V.; Ohlrogge, K. ; Alpers, A.; Keller, M.; Pires, A. T. N. Membranes of poly (ether imide) and nanodispersed silica. *J. Membr. Sci.* **1999**, *157*, 219-226.

22. Sairam, M.; Patil, M. B.; Veerapur, R. S.; Patil, S. A.; Aminabhavi, T. M. Novel dense poly (vinyl alcohol)–TiO2 mixed matrix membranes for pervaporation separation of water–isopropanol mixtures at 30° C, *J. Membr. Sci.* **2006**, *281*, 95-102.

23. Patil, M. B.; Aminabhavi, T. M. Pervaporation separation of toluene/alcohol mixtures using silicalite zeolite embedded chitosan mixed matrix membranes. *Sep. Purif. Technol.* **2008**, *62*, 128–136.