SiO$_2$ EMBEDDED NANO-COMPOSITE COPOLYMERIC MEMBRANES OF POLY (VINYL ALCOHOL)-G-POLYACRYLIC ACID FOR PERVAPORATION SEPARATION OF BINARY ORGANIC/ORGANIC MIXTURES

Mallikarjunagouda B. Patil[a*], Amshumali M. K.[b] and Shridhar N. 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 Engineering Physics, K.L.E Institute of Technology, Hubballi, 580027, Karnataka, India*

Abstract: The Copolymers were prepared by grafting reaction using acrylic acid (AA) and poly (vinyl alcohol) (PVA) and to this SiO$_2$ nanoparticles were incorporated gravimetrically (w/w). The membranes of SiO$_2$ embedded poly(vinyl alcohol)–g-polyacrylic acid (PVA-g-PAA) and cross-linked with glutaraldehyde. The prepared membranes were tested for their suitability in separation of methyl tert-bytyl ether (MTBE) and methanol binary mixtures by using pervaporation (PV) technique. The feed composition was constant and nanoparticles loading on PV separation performance were examined. Sorption studies were performed in MTBE-methanol feed mixtures to assess the extent of interaction between membranes and feed components. Pervaporation separation index (PSI) was performed and is in accordance with PV reading. Addition of filler particles reduced the extent of sorption with improved membrane performance. In MTBE/methanol systems, total permeate flux attained with pristine PVA-g-PAA based membranes is 1.4 where as PVA-g-PAA, 20wt. SiO$_2$ loaded membrane shows   0.421 kg/m^2 h, respectively, over the respective feed methanol

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[*] Mallikarjunagouda B. Patil, *email:* mallupatil04@gmail.com

concentration ranges of 10–90% (v/v). A trade-off between separation and permeate flux was apparent from the decrease in permeation flux with increasing separation factor. Selectivity ranged from 431 to 1433 to plain graft membrane to 20 wt. % SiO_2 loaded membrane respectively.

Keywords: Nanocomposite,   poly(vinyl   alcohol),   Organic-Organic   Separation, pervaporation

Introduction

Membrane-based pervaporation (PV) separation is an outstanding technique compared to conventional distillation for specific separations involving azeotropic and closely boiling liquid mixtures.[1-4] Over the past years, PV has been used commercially for dehydrating alcohols using high permselective poly(vinyl alcohol)/polyacrylonitrile (PVA/PAN) thin film composite membranes, under the trade name of GFT. In recent years, with the development of novel type of membranes, many research groups have employed this technique for organic dehydration.[5-8] The key to the success in PV dehydration is the development of a suitable polymer membrane that offers high selectivity, flux and long-term stability, along with favorable mechanical strength to withstand the operating conditions.[9] However, optimizing these characteristics is a formidable task. Recently, research trends have shifted from the use of nascent membranes[10] to developing filler-reinforced mixed matrix membranes, in which nano-sized inorganic fillers have been used.[11] Membrane performance in such cases depends on filler loading, matrix/filler adhesion, level of dispersion of filler particles in the polymer matrix in addition to their physico-chemical characteristics.[11-12] However, the mechanical strength properties of such membranes depend on the combination of fillers and polymers that are usually prepared by *in situ* mixing of fillers with cross-linking agent to cast the membranes.[13-14]

Separation of organic–organic mixtures by membrane based separation techniques is being investigated widely due to its great importance in chemical and petrochemical industries. In the present investigation an effort was made to improve the organic-organic liquid separation by pervaporation. A new generation nanocomposite copolymeric membranes were synthesized and tested it for their efficiency in separation processes. 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. Graft membranes of PVA and Acrylic acid were synthesized and while synthesizing insitu addition of SiO$_2$ nanoparticles were incorporated. Further membranes were characterized by FTIR, TEM and SEM, techniques. The membranes were used in pervaporation separation of organic-organic mixture. The effects of SiO$_2$ nanoparticle content on pervaporation properties of the adsorbent membranes for the separation of organic-organic mixture were systematically studied. The reversal of tradeoff effect was actually found and tentatively elucidated.

Experimental

Materials and methods

Poly(vinyl alcohol) with molecular weight 1,25,000, Acrylic acid, ceric ammonium nitrate, glutaraldehyde and hydrochloric acid was purchased from s.d. Fine chemicals, 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.

Synthesis of copolymers

The PVA-g-AA copolymers were prepared by the free radical polymerization. Free radical polymerization has three basic steps, (i)

initiation, (ii) propagation and (iii) termination. *Initiation*, involves the creation of radicals by means of the radical's reaction with a vinyl monomer, *propagation* is the fast and growing addition of monomers to the advancing polymer chain without altering the active centre and the last step *termination* is the obliteration of the growth active center, usually by *combination or coupling* of the radicals of two growing polymer chains or by *disproportionation.*[15] The gravimetric amount of PVA i.e. 6 gm (w/v) was made dissolved in water at 80 °C under constant stirring for 7 hrs. After this, 1 gm of aqueous solution of AA (in 20 mL) mixed with PVA solution, under the same temperature and stirring rate. To this solution 0.1 gm of ceric ammonium nitrate is added as free radical initiator.[16] The solution was kept under stirring for 6 hours. The resulting solutions were precipitated in methanol and obtained solid product was dried in oven at 80°C for 05 hours and stored properly. The reaction scheme between PVA and AA is shown in the reaction scheme 1.
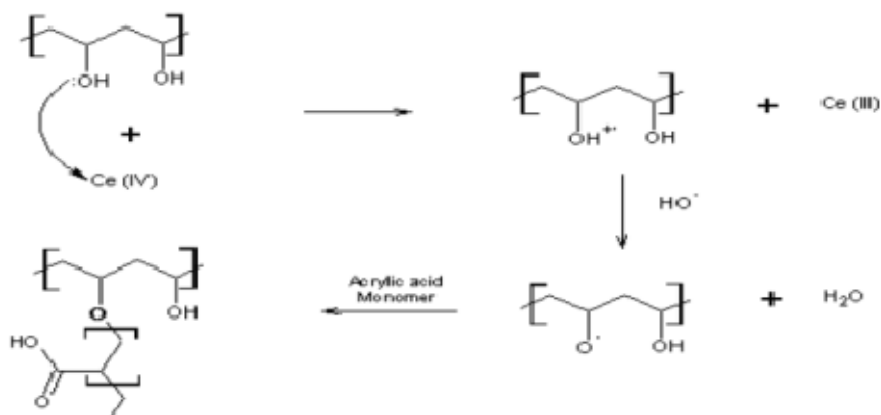
Scheme 1. Reaction mechanism of polymerization of poly acrylic acid.

Membrane fabrication

    Gravimetric weight of copolymer (w/v) product (6 gm) was dissolved in 80 mL of water at 60°C. Once homogeneous solution was

obtained, the solution after attaining room temperature was casted on to the clean and dry glass plate. Once the solution was dried, the membranes were peeled off from the glass plate and stored properly.

Nanocomposite membrane Fabrication

For the preparation of SiO$_2$ containing membranes, the corresponding amounts of nano silica, to form 2.5, 5, 7.5 and 10 wt % with respect to total weight of the polymer were added to the prepared PVA-g-AA solution as above procedure.. Before adding SiO$_2$ nanoparticles on to the solution, it is necessary to condition the nanoparticles, the SiO$_2$ nanoparticles were dried in vacuum oven at 250 °C for 2 hours and dispersed in 5 mL of water and sonicated (sonicator model VC 50, Sonics & Materials Inc.) for 2 h. Once nanoparticles were conditioned than the aqoues solution of this was added into the solution mixture and stirred for 5 h to get homogeneous viscous solution. Than casted as membranes by pouring onto a clean and dry glass plate, dried, peeled off and stored properly. The nanocomposite membranes were fabricated by employing the solution casting followed by solvent evaporation method. The four variant of SiO$_2$ nanocomposite copolymeric membranes were fabricated with varying 2.5 to 10 wt. % (w/w) of SiO$_2$ nanoparticles. The membranes were named as M-2.5, M-5. M-70 and M-10 with their SiO$_2$ content i.e. 2.5, 5, 7.5 and 10 wt. % respectively. 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 $72 \pm 0.2\ \mu$m, standard deviation less than 1.5μm).

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.

Scanning electron microscopy

SEM micrographs of the pristine PVA-g-AA and M-5 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.

Transmission Electron Microscopy (TEM)

Transmission electron microscopy (TEM) of the free standing nanocomposite membrane of PVA-g-AA SiO$_2$ was conducted. An electron transparent thin foil specimen from the SiO2embedded polymer sample was prepared by ultra-microtomy (Leica model Ultracut UCT). TEM studies were conducted using a JEOL JEM 2100 operated at 200 kV. Wherein bright field images and selected area diffraction patterns were obtained and analyzed.

Mechanical Property study

Tensile strength and ultimate elongation were measured for all the prepared membranes. Tensile tests were performed with a universal testing machine (UTM) (Lloyd, UK) according to the test method ASTM D 412 by using 5.0 N load cell with cross head speed of 100 mm/min. Average of 5 tests for each polymer membrane sample were considered. The readings obtained from the machine are tabulated in Table 1.

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^{-1}). 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:

$$J = \frac{W}{At}$$
(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:

$$\alpha = \left(\frac{P_A}{1 - P_A} \right) \left(\frac{1 - F_A}{F_A} \right)$$
(2)

$$PSI = J\,(\alpha - 1)$$
(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.
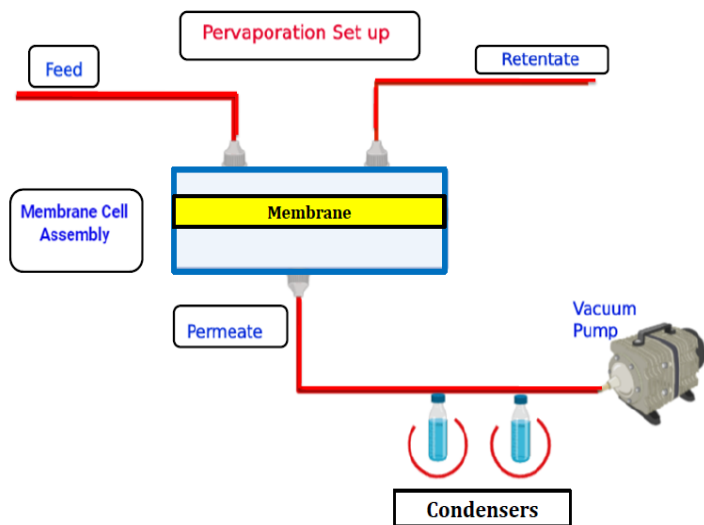
% Degree of Sorption (% DS)

Figure 1. Schematics of pervaporation set up.

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 $\pm$ 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:

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

where W_∞ and W_0 are the weights of swollen (final weight) and dry membranes (initial weight), respectively. The schematic of pervaporation unit is shown in figure 1. The image graphics were designed by using BioRender software.

Results and Discussion

Fourier transforms infrared spectroscopy Study
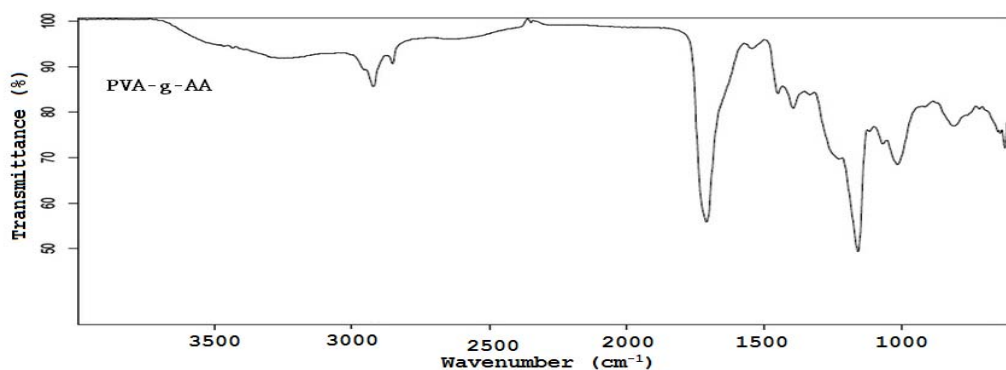
Figure 2. IR spectra of grafted copolymer of PVA-g-AA.

Structure Analysis (FTIR) FT-IR spectra of the prepared membranes i.e. PVA-g-AA was shown in Figure 2. Various functional groups of graft polymer can be identified and characterized for structural moieties. FTIR spectrum showed the characteristic peaks at 2963 cm^{-1} is attributed to –CH aromatic, 1731 cm^{-1} is appeared due to >C=N and 1600 cm^{-1} represents the carbonyl groups (–C=O).The cross-linked network of PVA with acrylic acid showed a different pattern from its components. The developed graft membrane was shown a broad high intensity peak in the region 1771 cm^{-1}

which confirms the ester linkage of carbonyl groups in in the polymer network. FTIR studies confirmed the formation of grafted copolymer of PVA with acrylic acid.
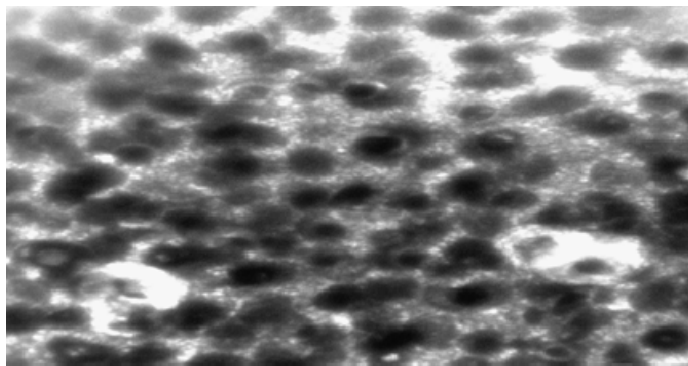
Transmission Electron Microscopy (TEM)

Figure 3. TEM images of SiO_2 nano-particle incorporated PVA-g-AA membrane.

The TEM images were exposed in the Figure 3. The 5 wt. % SiO_2 loaded PVA-g-PAA nanocomposite membrane was chosen for the study. It was observed from the image is that SiO_2 nanoparticles influenced greatly to the copolymer and has a significant effect on the morphology of nano-composite membrane. The SiO_2 nano-particles were distributed across the membrane surface uniformly exhibited eccentric SiO_2 cores, tended to have concentric homogeneous morphology.
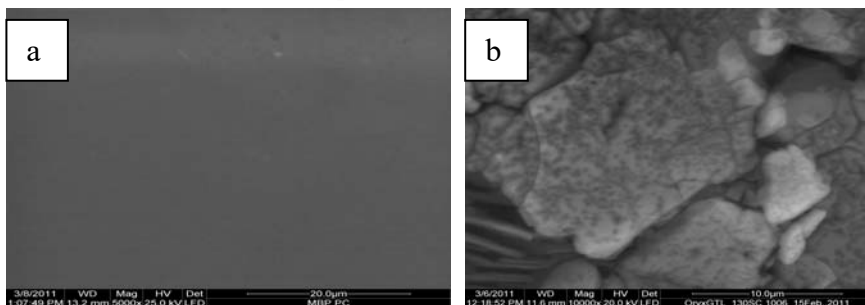
Scanning Electron Microscopy (SEM)

Figure 4. SEM images of (a) plain PVA-g-AA and (b) SiO_2 nanoparticle incorporated PVA-g-AA membrane.

Figure **4** displays the surface morphology of (a) plain PVA-g-PAA and (b) PVA-g-PAA-SiO$_2$-5 % nanocomposite membranes. From the SEM image it was revealed that the SiO$_2$ in the polymer matrix was distributed homogeneously and symmetric in shape as well in inside the membrane and no obvious defects are found at the interface. It is also observed that the prepared copolymer with nanoparticles were compatible with each other.

Mechanical Property study

Mechanical properties were recorded for all the polymeric membranes as per ASTM D 412 and are tabulated in Table 1. Tensile strength is highest for M-10 and decreases in the order M-7.5, M-5 and M-2.5. This behaviour may be due to increased f% loading of SiO$_2$ nanoparticles in the membrane matrix. The copolymer and nanoparticles were strong bounding between each other.

The separation impact of the grafted polymer chains was apparent given that the native (unmodified) and vinylsilylated alumina membranes lacked selectivity for the MTBE/methanol system. Total permeate flux attained with the PVAc and PVP-based membranes ranged from 0.055 to 1.26 and 0.55 to 6.19 kg/m^2 h, respectively, over the respective feed methanol concentration ranges of 1–90 and 5–90% (v/v). A tradeoff between separation and permeate flux was apparent from the decrease in permeation flux with increasing separation factor.
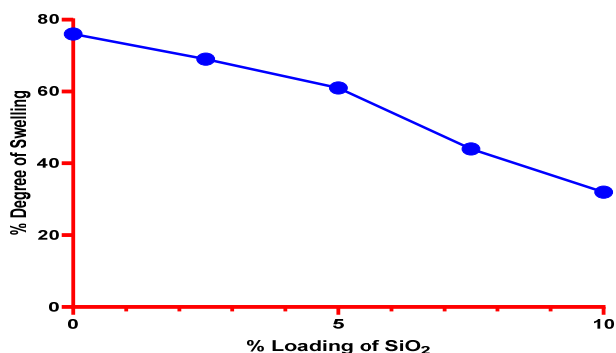
Degree of Sorption

Figure 5. Degree of water sorption for the membranes with varying % loading of SiO$_2$.

Figure 5 shows that the % degree of swelling of the prepared membranes. The % DS for the membrane were calculated using equation (4). The linear increase in the sorption of the membranes showing felicity towards methanol. The pervaporation results are greatly influenced by membrane swelling. The nanocomposite membranes swell less than the pristine PVA- g-PAA, this is probable due to the space occupied by SiO_2 particles in the polymer matrix. However, for M-20 nanocomposite membrane recorded very low as compared to other fabricated membranes. The % degree of sorption for the prepared copolymers with varying % loading of SiO_2 nanoparticles are shown in the Figure 5.

Table 1. Mechanical property of all polymeric membranes.

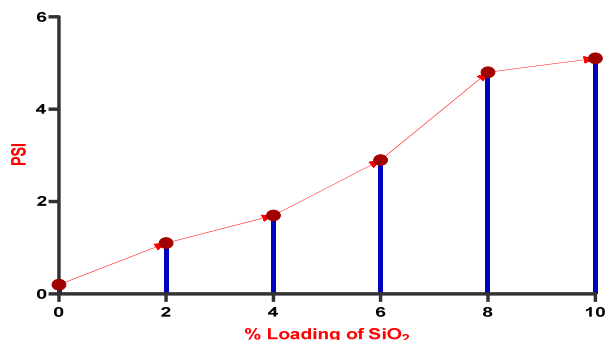| Polymeric Membrane	Tensile Strength (MPa ± S.D)
Plain PVA-co-PAA	46.6 ±0.5
M-2.5	62.0 ± 0.4
M-5	71.3 ± 0.6
M-7.5	85.4 ± 0.5
M-10	91.2 ± 0.4

Pervaporation separation Index

Figure 6. Pervaporation separation index.

Figure 6 shows the variation of PSI value calculated with relation with the amount of SiO$_2$ loading in the membrane. The values of PSI increased linearly with increasing the SiO$_2$ content, signifying that membranes which contain filler show higher PSI value for water–isopropanol feed mixtures. The addition of SiO$_2$ particles into the PVA-g-PAA membrane not only affects the membrane hydrophobicity, but its rigidity as well. Thus, an enhanced hydrophilic–hydrophilic molecular interaction between SiO$_2$ and PVA-g-PAA enhances significantly the diffusion of water molecule through the mixed matrix membranes, by retaining the organic component on the feed side.

Membrane performance

In the present PV experiments, the performance of the nanocomposite membrane was studied with respect to flux and selectivity. The MTBE-methanol mixture with fixed concentration i.e. 90:10 ratio was performed. As seen in Figure 7, for the PVA-g-PAA membrane, the selectivity data for MTBE-methanol is much lower than those observed for the nanocomposite
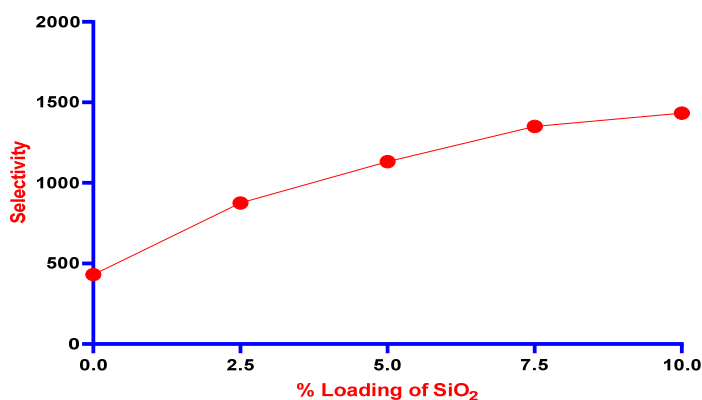

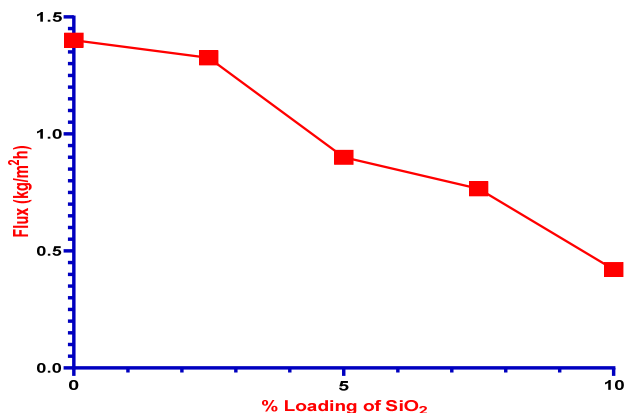**Figure 7.** Selectivity results for the Plain and Nanocomposite membranes.

Figure 8. Total Flux with respect to MCM-41 loaded PVA membrane membranes.

The selectivity increases with SiO_2 content for the mixed membranes, in correlation which the increased hydrophobicity with the SiO_2 content. The nanocomposite membranes are able to remove more than 98% of MTBE at the permeate side, whereas plain PVA-g-PAA was successful to separate up to 85 % of MTBE. The selectivity increased from 431 plain PVA-g-PAA to 1433 for M-10. The flux results are shown in Figure 8 for a feed mixture containing 90:10 ratio (v/v) of MTBE-methanol and suggest that also flux decreases accordingly as increasing SiO_2 particles ratios. The flux declined from 1.4 for pristine PVA-g-PAA to 0.421 kg/m^2 h for M-10. (This kind of decrement in membrane performance clearly shows the preferential interaction of water molecules with the filled matrix membranes.

Conclusions

Copolymers were prepared by grafting reaction using acrylic acid (AA)and poly (vinyl alcohol) (PVA) and to this SiO_2 nanoparticles were incorporated gravimetrically (w/w). The membranes of SiO_2 embedded poly(vinyl alcohol)–g-polyacrylic acid (PVA-g-PAA) and cross-linked with

glutaraldehyde. The prepared membranes were tested for their suitability in separation of methyl tert-bytyl ether (MTBE) and methanol binary mixtures by using pervaporation (PV) technique. SiO_2 loaded membrane shows 0.421 kg/m^2 h, respectively, over the respective feed methanol concentration ranges of 10–90% (v/v). A trade-off between separation and permeate flux was apparent from the decrease in permeation flux with increasing separation factor. Selectivity ranged from 431 to 1433 to plain graft membrane to 20 wt. % SiO_2 loaded membrane respectively.

Acknowledgements

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