



## Removal of Dichlorinated Volatile Organic Compounds from Aqueous Solutions Using Polydimethylsiloxane Membranes Cured with Different Cross-Linking Reagents

K. Pattabhi Ramaiah<sup>1</sup>, M. Veera Narayana Reddy<sup>1</sup>, S. Sridhar<sup>2</sup>, A. Krishnaiah<sup>1\*</sup>

<sup>1</sup>Department of Chemistry, Sri Venkateswara University, Tirupati - 517 502, Andhra Pradesh, India. <sup>2</sup>Membrane Separation Group, Chemical Engineering Division, Indian Institute of Chemical Technology, Hyderabad - 500 007, Andhra Pradesh, India.

Received: 07<sup>th</sup> October 2015; Revised: 16<sup>th</sup> November 2015; Accepted: 26<sup>th</sup> November 2015

### ABSTRACT

Hydrophobic polymer possesses significant potential for selective separation of volatile organic compounds (VOCs) from their aqueous solutions by pervaporation. In the present study, composite membranes of polydimethylsiloxane supported on polyvinylidenefluoride substrate were synthesized and cured the membranes with various cross-linking reagents such as tetraethoxysilane (TEOS), phenyltrimethoxysilane, and octyltrimethoxysilane. The potential of the cross-linked membranes for the extraction of volatile dichlorinated hydrocarbons, such as dichloromethane and 1,2-dichloro ethane, which pose serious environment threat and health hazard, was evaluated. Cross-linking and surface morphology of the indigenously developed membranes were determined by Fourier transform infrared and scanning electron microscopy. Effect of operating parameters, such as feed composition and permeate pressure on separation performance in terms of flux and selectivity, was determined. The membranes exhibited considerable feasibility for scale-up with significant potential for removal of dichlorinated VOCs from aqueous solutions.

**Key words:** Pervaporation, Cross-linking, Polydimethylsiloxane, Volatile organic compounds removal, Perm selectivity.

### 1. INTRODUCTION

Chlorinated volatile organic compounds (VOCs) such as chloro methanes, chloroethanes, and chloroethylenes, frequently contaminate ground water and soil. These VOCs, released from various industries, are potential carcinogens and are a threat to living beings. Hence, there is a need to prevent the remove these compounds from water bodies [1-3]. Separation of organic compounds from aqueous media through conventional methods, such as distillation, adsorption, and liquid-liquid extraction, is energy intensive. In addition, complete removal cannot be achieved by distillation or any other conventional method [4].

Pervaporation (PV) is a promising membrane-based separation technique for dehydration as well as extraction of VOCs [5-7]. For the separation of low concentration VOCs, the organophilic rubbery polymer membrane is preferred, because it is more permeable to VOCs [8]. There is a variety of organic compounds that maybe potentially separated by PV.

These compounds are of different chemical nature and their interactions with the membranes can be affected by the process variables and contribute to the feasibility of the process. At present, there are limited potential polymers for hydrophobic PV process. Silicone-containing polymers generally exhibit good organophilicity and silicone rubber (mainly polydimethylsiloxane [PDMS]) based membranes have been most investigated for organic aqueous solutions such as alcohols, ketone, phenol, and chlorohydrocarbons [9,10]. PDMS has poor film-forming properties and unsatisfied PV performance. To avoid this PDMS was cross-linked with various silicalite reagents [11].

In the present paper, PDMS/polyvinylidenefluoride (PVDF) composite membranes were synthesized and cured with three kinds of cross-linking reagents with typical functional groups cast onto porous PVDF substrate. Octyltrimethoxysilane (OTMOS) and phenyltrimethoxysilane (PTMOS) were typical hydrophilic, organicphilic, and rigid compounds,

\*Corresponding Author:

E-mail: abburikrishnaiah@gmail.com  
Phone: +91-9393621986

respectively, due to the octyl and phenyl-groups, and tetraethoxysilane (TEOS) was a typical tetra-functional reagent. The distinct differences of functional groups in the three kinds of cross-linking reagents may be of great influence on the surface properties and structures of cross-linked PDMS. The surface properties and structures of cross-linked PDMS may play an important role in PV properties. The obtained PDMS/PVDF composite membranes were used for the separation of VOCs/water mixtures by PV process. Besides, the relationship between PV performance and the cross-linking density, surface properties of PDMS membranes cured with different cross-linking reagents was investigated in detail. Effect of operating parameters, such as feed composition and permeate pressure on membrane performance, has been studied. Structural properties of the indigenously synthesized membranes were characterized by scanning electron microscopy (SEM) and Fourier transform infrared (FTIR) spectroscopy.

## 2. EXPERIMENTAL

### 2.1. Materials

The hydroxyl-terminated PDMS base polymer, with an average molecular weight of 4200, was supplied by Alfa Aesar, Ward Hill, MA, USA. PVDF polymer was supplied by Zhuzhou Hongda Polymer Materials Co. Ltd., China.

n-Heptane, dimethylformamide (DMF), dichloromethane (DCM), and 1, 2-dichloroethane were supplied by S.D. Fine Chemicals, Mumbai, India. OTMOS, PTMOS, TEOS, and dibutyltindilaurate (DBTDL) that were used as cross-linking agents and catalyst, respectively, were purchased from Aldrich Chemical Co., Milwaukee, WI, USA and Himedia Laboratories Pvt. Ltd., Mumbai, India. The chemical structures of PDMS, PVDF, and the cross-linking reagents are shown in Figure 1. Deionized water used throughout the experiments was prepared in the laboratory using a pilot scale reverse osmosis plant.

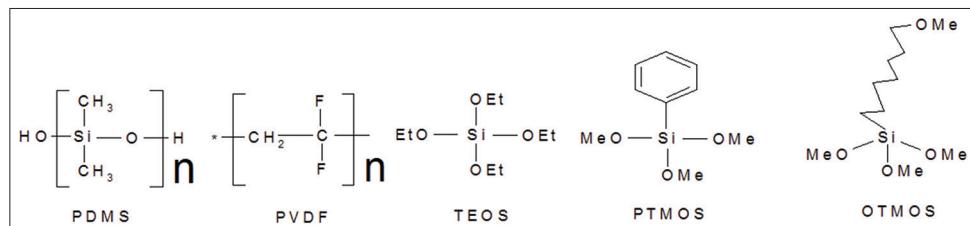
### 2.2. Preparation of PDMS Composite Membranes

PVDF porous support layer was prepared by dissolving 13 g of PVDF in 87 ml of DMF to form a 13% w/v solution with constant stirring for about 8 h at room temperature until a homogeneous mixture

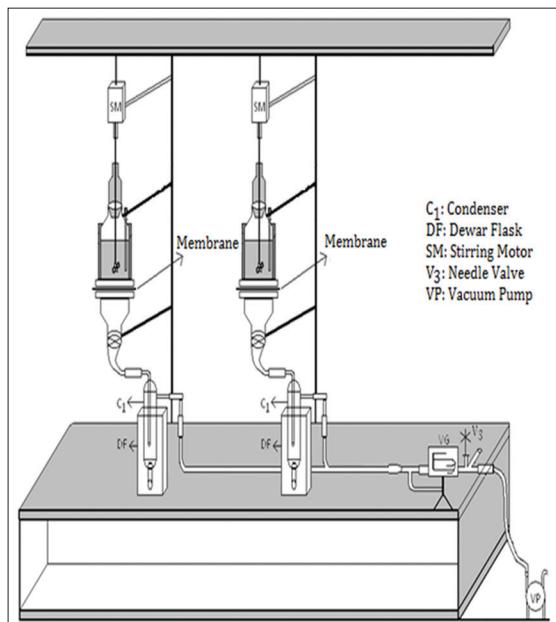
was obtained, and the bubble free PVDF solution was cast on a non-woven fabric support fixed on a glass plate with the aid of a glass rod. The glass plate was immersed in water (non-solvent) bath to get an ultraporous substrate. The thickness of PVDF layers was controlled in the range of 40-50  $\mu\text{m}$ . PDMS solution in n-heptane was prepared by adding the polymer, solvent, cross-linking reagent, and DBTDL in the ratio 30:70:2.5:0.5 by weight [11] with continuous stirring at room temperature. This bubble free solution was cast on the ultraporous PVDF support and dried at room temperature for 5 h and then placed in an oven at 120°C for 48 h to remove residual solvent. The thickness of PDMS layers was controlled in the range of 10-50  $\mu\text{m}$ . The cross-linking reagents used in the present study are TEOS, PTMOS, and OTMOS, and the resulted PDMS composite membranes were referred as T-PDMS, P-PDMS, and O-PDMS, respectively.

### 2.3. PV Experiment

PV experiments were conducted by using a bench scale setup developed indigenously with feed batch volume of 70-100 ml (Figure 2) using various PDMS cross-linked membranes. The feed temperature was 30 $\pm$ 2°C (ambient) and vacuum at permeate side was in the range 2-10 mm Hg. The effective membrane area in the PV cell assembly was approximately 20  $\text{cm}^2$ . After attaining the required vacuum without any discrepancies, 100 ml of the feed was poured into the feed chamber of the PV manifold after attaining the vacuum condition, followed by introducing an overhead mechanical stirrer with a speed of 200 rpm during the process. PV experiment was then begun using different feed compounds and compositions. Aqueous solutions of 0.79-1.33 wt% DCM and 0.36-0.84 wt% 1,2-dichloro ethane (DCE) in water were used separately as feed solutions. Permeate was collected in vapor form and condensed using liquid nitrogen (-195.79°C) for a duration of 6-8 h in a glass condenser trap. The experiments were repeated twice using fresh feed solution to ensure reproducibility. The collected permeate was weighed after allowing it to attain room temperature in a Sartorius electronic balance to determine the flux and then analyzed by gas chromatography (GC) to evaluate membrane selectivity.



**Figure 1:** Chemical structure of the polydimethylsiloxane, polyvinylidenefluoride, tetraethoxysilane, phenyltrimethoxysilane, and phenyltrimethoxysilane.



**Figure 2:** Laboratory pervaporation set-up.

#### 2.4. Flux ( $J_i$ ) and Selectivity ( $\alpha$ )

PV characteristics are presented in terms of flux ( $J_i$ ) and selectivity ( $\alpha$ ) defined as follows:

In PV, the flux ( $J_i$ ) of a given species, say faster permeating component "I" of a binary liquid mixture comprising of DCM, DCE, and water is given by:

$$J_i = \frac{W_i}{A * t} \quad (1)$$

Where,  $W_i$  represents the weight of organic compound collected in permeate (kg),  $A$  represents the membrane area ( $m^2$ ), and  $t$  represents the PV time (h).

Membrane selectivity,  $\alpha$  is the ratio of concentrations of organic and water in permeate with respect to that in the feed and was calculated from the respective concentrations in feed ( $x$ ) and permeate ( $y$ ) side using the equation:

$$\alpha = \frac{y(1-x)}{x(1-y)} \quad (2)$$

#### 2.5. Analytical Procedure

The feed and permeate samples were analyzed using a Nucon GC (Model 5765) installed with thermal conductivity detector and packed column of 10% diethylenglycol sebacate on 80/100 Supelcoport of 1/8" ID and 2 m length. The oven temperature was maintained at 70°C (isothermal) while the injector and detector temperatures were maintained at 150°C each. The sample injection size was 1  $\mu$ l, and pure H<sub>2</sub> was used as the carrier gas at a pressure of 1 kg/cm<sup>2</sup>.

The GC response was calibrated for this particular column and conditions with known compositions of VOC/water mixtures, and the calibration factors were fed into the software to obtain correct analysis for unknown samples.

#### 2.6. Membrane Characterization

FTIR spectra of the PDMS composite membranes taken in KBr pellets were scanned in the range between 4000 and 400  $cm^{-1}$  on a Nicolet-740, Perkin-Elmer-283B FTIR spectrophotometer.

The surface and cross-sectional morphology of the PDMS composite membranes were studied by SEM using a Hitachi S2150 microscope (Ibaraki, Japan). To obtain smooth cross-section, the samples were cut in liquid nitrogen medium.

##### 2.6.1. Sorption studies

Weighed samples of circular pieces of PDMS/PVDF composite membranes were soaked in pure water, DCM, and DCE until equilibrium were established as indicated by constant weight of the soaked membrane in pure solvents. The films were taken out after different soaking periods and quickly weighed after carefully wiping out excess adhering liquid droplets and the mass sorbed by the membrane was determined using a Sartorius electronic balance (accuracy 10<sup>-4</sup> g). Degree of swelling was calculated as;

$$\text{Degree of swelling} = \frac{M_s}{M_d} \quad (3)$$

Where,  $M_s$  is mass of the swollen polymer (g), and  $M_d$  is mass of the dry polymer (g). The percent sorption was calculated using the equation;

$$\% \text{Sorption} = \left[ \frac{M_s - M_d}{M_d} \right] * 100 \quad (4)$$

### 3. RESULTS AND DISCUSSION

#### 3.1. Membrane Characterization

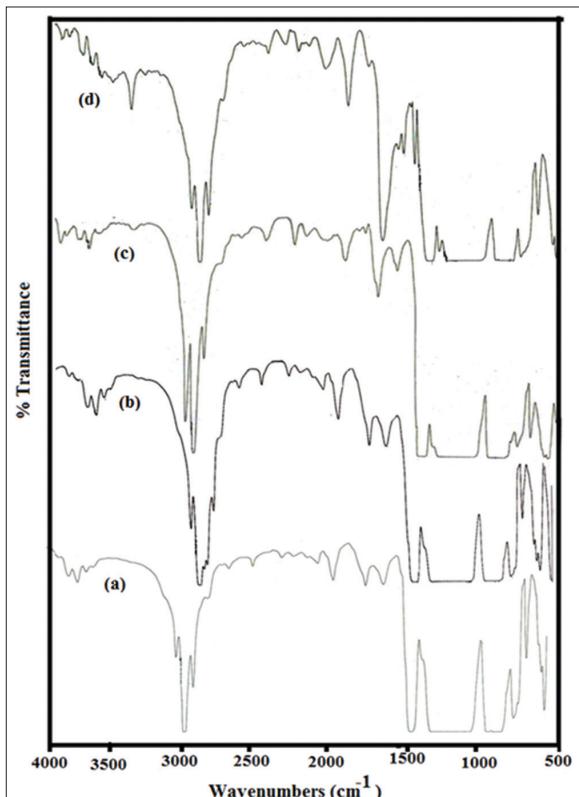
For comparison purpose, the characteristics of various PDMS layers cured with the three cross-linking reagents are listed in Table 1. The contact angle of P-PDMS is higher compared to the other membranes resulting in an increase of hydrophobicity. This may be due to the presence of the phenyl group attached to the PTMOS.

Figure 3 shows the FTIR spectra of (uncross-linked [Figure 3a], TEOS cross-linked [Figure 3b], PTMOS cross-linked [Figure 3c], and OTMOS cross-linked [Figure 3d]) PDMS composite membranes. There is a very strong peak in the region near 996  $cm^{-1}$  representing the asymmetric stretching vibration of Si-O-Si bond. The peak in the region of

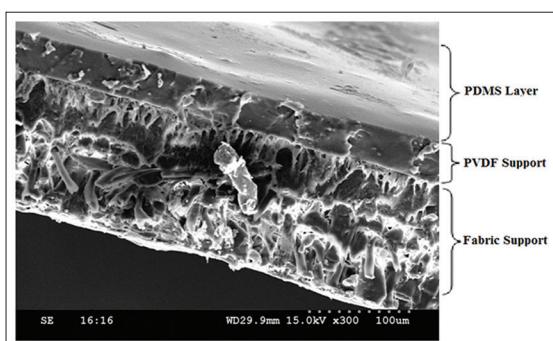
**Table 1:** Characteristics of PDMS membranes cured with different cross-linking reagents.

Membrane	Thickness ( $\mu\text{m}$ )	Contact angle ( $^{\circ}$ )
O-PDMS	15	111.1
T-PDMS	15	117.4
P-PDMS	15	118.3

PDMS=Polydimethylsiloxane



**Figure 3:** Fourier transform infrared spectra of uncross-linked, (a) tetraethoxysilane cross-linked, (b) phenyltrimethoxysilane cross-linked, (c) octyltrimethoxysilane cross-linked, and (d) polydimethylsiloxane composite membranes.



**Figure 4:** Cross-section of polydimethylsiloxane/polyvinylidenefluoride composite membrane by scanning electron microscopy.

$864\text{ cm}^{-1}$  is due to the stretching vibration of Si—C. The characteristic absorption bands of Si—OH groups

appear at  $1078\text{ cm}^{-1}$ . It is observed that the intensity of characteristic adsorption bands of Si—OH groups in cross-linked PDMS decreased notably compared with that of uncross-linked PDMS, indicating the occurrence of the cross-linking reaction. From the FTIR spectra, it can be conferred that PDMS was successfully deposited on the PVDF supports and cross-linked with different cross-linking reagents.

The morphology of the composite PDMS/PVDF membrane prepared in this study is presented in Figure 4. There is no difference for PDMS layers cured with different cross-linking reagents in SEM images, and the three kinds of PDMS layers were cast onto the PVDF porous substrate tightly.

### 3.2. Sorption Studies

Table 2 represents the % sorption of composite membranes in pure water and pure VOCs. As the number of chlorine atoms increases in a moiety with a given number of carbon atoms and/or the number of carbon atoms increases in an organic with a given number of chlorine atoms, its molar volume increases and its solubility in water decreases [12]. Thus, when the organic compound has more chlorine or carbon atoms, it becomes more hydrophobic, and the % sorption of the chlorinated hydrocarbons in an organophilic polymer such as PDMS increases. The data in Table 2 are in agreement with this observation.

### 3.3. Effect of Feed Concentration

The variation in PV performance over a wide range of feed compositions of DCM and DEC at  $30^{\circ}\text{C}$  and permeate pressure of 2 mm Hg was investigated using PDMS membranes cured with different cross-linking reagents. It is observed that with increasing in the feed composition performance of membrane enhanced. Effect of feed concentrations of the VOCs on organic flux and selectivity are shown in Figure 5a-d. A rise in the feed composition of DCM (0.79-1.33 wt%) and DCE (0.36-0.84 wt%) resulted in enhancement of flux and selectivity. Mass transport through the PDMS layer occurs by solution-diffusion mechanism [13]. Compared with O-PDMS and T-PDMS, the significant enhancement of both total flux and separation factor of P-PDMS was obtained over the whole range of VOCs concentration tested. This may be attributed to its low cross-linking density and strong swelling resistance. P-PDMS membranes exhibited a higher VOCs perm-selectivity with the VOCs concentrations in feed pertaining to the maximum solubility limit of VOCs in water due to its high hydrophobicity of membrane surface.

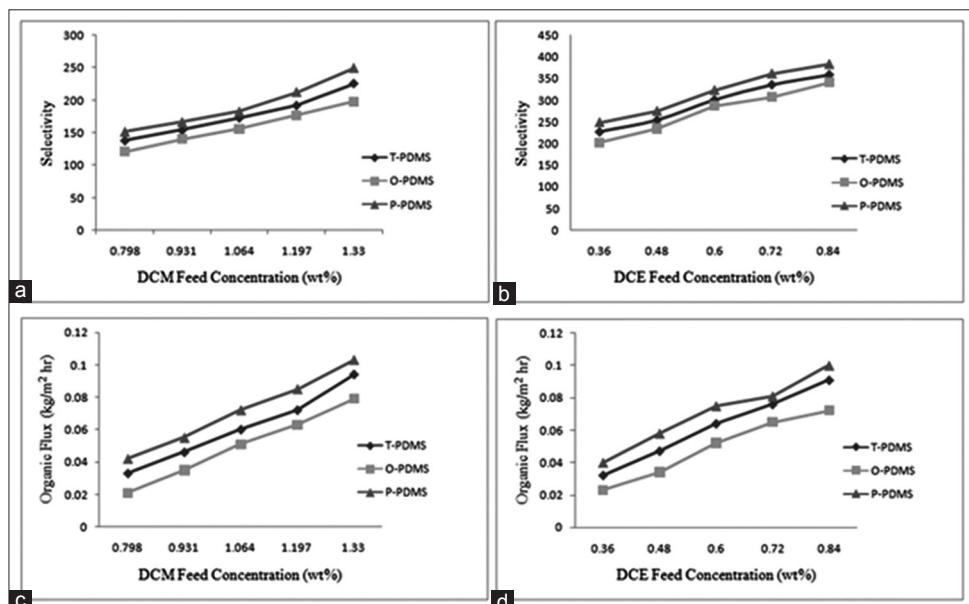
### 3.4. Effect of Permeate Pressure

PV of feed pertaining to the maximum solubility limit of VOCs in water through various PDMS composite membranes was performed, and the results are presented in Figure 6. As the pressure increased

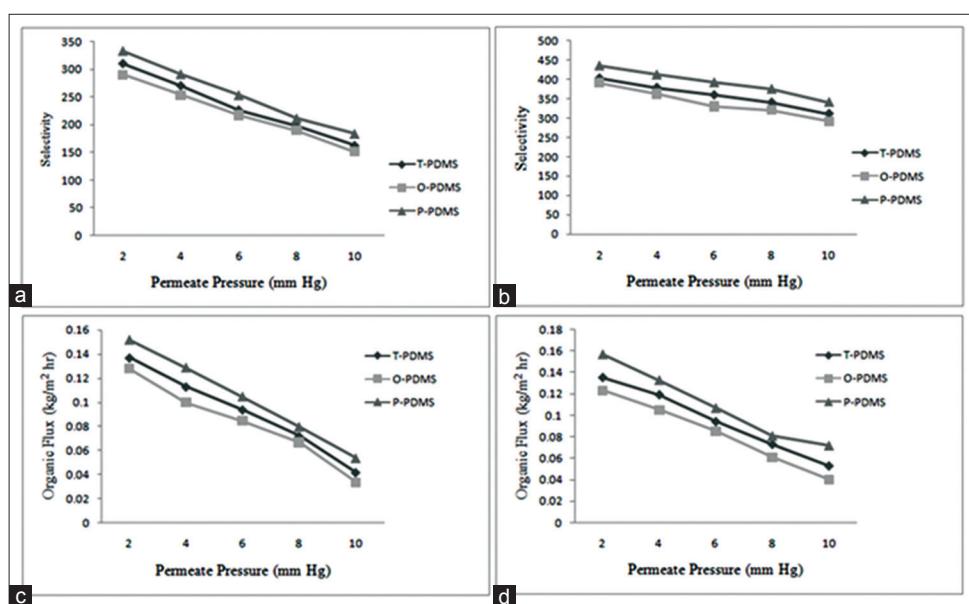
**Table 2:** Physical properties and percentage sorption of chlorinated organic compounds.

Pure compound	Molar volume ( $10^6 \text{ m}^3/\text{mol}$ )	Saturated vapor pressure at 25°C	Boiling point (°C)	Solubility in water (wt%)	% Sorption		
					O-PDMS	T-PDMS	P-PDMS
Water	18.016	23.76	100	-	1.15	1.87	2.45
DCM	64.5	430	39.6	1.33	2.23	3.70	5.28
DCE	78.8	115	84	0.84	3.06	4.36	6.13

PDMS=Polydimethylsiloxane, DCM=Dichloromethane, DCE=1,2-dichloro ethane



**Figure 5:** Effect of feed composition on flux and selectivity of polydimethylsiloxane composite membranes (dichloromethane [a and c] and 1,2-dichloro ethane [b and d]).



**Figure 6:** Effect of permeate pressure on flux and selectivity of polydimethylsiloxane composite membranes (dichloromethane [a and c] and 1,2-dichloro ethane [b and d]).

organic flux and selectivity for all the aqueous VOCs, feed mixtures reduced due to a decrease in driving force (pressure gradient). An increase in permeate pressure

from 2 to 10 mm Hg reduced the flux of DCM and DCE from 0.152 to 0.054 and 0.157 to 0.072  $\text{kg}/\text{m}^2 \text{ h}$ , respectively, and corresponding selectivity values

dropped from 333 to 183 and 435 to 341. This variation can be explained on the basis of vapor pressure gradient [14]. With decrease in a vacuum, flux would decrease due to a reduction in driving force, thus slowing desorption of the molecules.

#### 4. CONCLUSIONS

Extraction of organic solvents, such as DCM and DCE from their aqueous solutions, was studied for the first time using PDMS membranes cured with different cross-linking reagents cast on hydrophobic PVDF substrate. It was found that the surface properties and cross-linking density of PDMS membranes can be adjusted by using different cross-linking reagents, which influenced their PV performance of VOCs/water mixture. Characterization of these indigenous membranes by FTIR confirmed its chemical structure. The membrane showed adequate thermal stability to withstand industrial PV conditions. With increasing feed organic concentration, the membrane exhibited an increase in selectivity and an improvement in flux due to enhancement in chemical potential (concentration gradient) of the organic solvents and improved affinity and sorption in the organophilic membrane. The effect of operating parameters on PV performance was investigated, and P-PDMS membrane displayed remarkably high permeation flux and selectivity values toward the VOCs when compared to T-PDMS and O-PDMS composite membranes. From the experimental results, it can be concluded that the membrane exhibited considerable feasibility for scale-up with significant potential for extraction of organic solvents from aqueous solutions, due to the hydrophobic nature of the cross-linking reagents as well as the hydrophobicity of both PDMS and PVDF layers of the composite membrane.

#### 5. ACKNOWLEDGMENTS

The authors K. Pattabhi Ramaiah and A. Krishnaiah are thankful to UGC, New Delhi for financial support in the form of UGC-BSR Fellowship and UGC-BSR Faculty fellowship, respectively.

#### 6. REFERENCES

- W. J. Parker, (1997) A multi-parameter sensitivity analysis of a model describing the fate of volatile organic compounds in trickling filters, *Journal of the Air & Waste Management Association*, **47**: 871-880.
- V. Hecht, D. Brebbermann, P. Bremer, W. D. Deckwer, (1995) Cometabolic degradation of trichloroethylene in a bubble column bioscrubber, *Biotechnology and Bioengineering*, **47**: 461-469.
- R. F. Dunn, M. M. El-Halwagi, (1994) Optimal design of multicomponent VOCs condensation systems, *Journal of Hazardous Materials*, **38**: 187-206.
- J. R. Khan, S. Muhammad, W. Ahmed, (2015) Dehydration of isopropanol and ethanol by pervaporation technique, *Pakistan Journal of Engineering and Applied Sciences*, **16**: 67-72.
- U. S. Rao, Y. Maruthi, K. V. Sekharnath, P. K. Babu, J. I. Sung, K. C. Rao, M. C. S. 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. K. Rao, C. V. Prasad, M. C. S. 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.
- K. V. Sekharnath, U. S. J. Rao, Y. Maruthi, P. K. Babu, K. C. Rao, M. C. S. 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.
- Y. I. Park, C. K. Yeom, B. S. Kim, J. K. Suh, J. S. Hong, J. M. Lee, H. J. Joo, (2008) Quantitative evaluation of concentration polarization in the permeation of VOCs/water mixtures through PDMS membrane using model equation, *Desalination*, **233**: 303-309.
- J. M. Watson, P. A. Payne, (1990) A study of organic compound pervaporation through silicone rubber, *Journal of Membrane Science*, **49**: 171-185.
- S. Q. Zhang, A. E. Fouda, T. Matsuura, (1992) A study on pervaporation of aqueous benzyl alcohol solution by polydimethylsiloxane membrane, *Journal of Membrane Science*, **70**: 249-255.
- Z. Xia, L. J. Ding, H. J. Qi, C. C. Xian, (2009) Pervaporation properties of PDMS membranes cured with different cross-linking reagents for ethanol concentration from aqueous solutions, *Chinese Journal of Polymer Science*, **27**: 533-542.
- X. Zhan, J. Li, J. Huang, C. Chen, (2010) Enhanced pervaporation performance of multi-layer PDMS/PVDF composite membrane for ethanol recovery from aqueous solution, *Applied Biochemistry and Biotechnology*, **160**: 632-642.
- J. G. Wijmans, R. W. Baker, (1995) The solution-diffusion model: A review. *Journal of Membrane Science*, **107**: 1-21.
- S. Tanaka, Y. Chao, S. Araki, Y. Miyake (2010) Pervaporation characteristics of pore-filling PDMS/PMHS membranes for recovery of ethylacetate from aqueous solution, *Journal of Membrane Science*, **348**: 383-388.

**\*Bibliographical Sketch**



*Prof. Krishnaiah Abburi has 38 years of research and teaching experience. He served S. V. University in various capacities such as Professor, Dean of Examinations, Head of the Department, and Chairman of BoS. He has been awarded prestigious UGC BSR Faculty Fellowship after his superannuation. He has published 165 papers in journals of repute and guided successfully 25 candidates for Ph. D. and 10 candidates for M. Phil. degrees. He is having one US patent entitled, "adjusting yield of a manufacturing process for energetic compounds through solubility modification" Patent No. US8002 917B2 dated August, 23, 2011 to his credit. He visited many Universities and Research Institutions around the world as Research Associate and Visiting Professor.*