

Effect of Graphite on The Pervaporation Performance of Silicone Rubber Membranes

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Abstract: Pervaporation process is a membrane based separation process. Polymer membranes were widely used for separating liquid mixtures using pervaporation process. In this study, composite membranes were prepared by mixing natural graphite (NG) and silicone rubber (QM) using two roll mill. Synthesized composite membrane was used for the separation process. The composite membrane reveals the impressive separation performance of methanol – toluene mixtures with preferential selectivity towards methanol. 10 phr (parts per hundred) natural graphite filled membrane obtained best flux and 15 phr membrane showed better selectivity. Optimal separation performance with the permeation flux of 386% and separation factor 1.5 times compared to QM control membrane is obtained. The study confirmed that increasing toluene feed concentration improved the selectivity of membranes.

Keywords: Pervaporation, Graphite, Silicone rubber, Methanol, Toluene.

1. INTRODUCTION

Pervaporation (PV) has been used as an effective membrane technique for separating azeotropic mixtures, heat sensitive compounds and close boiling point liquids. This method used for the separation of water from organic solvents and their mixtures and separation of liquid organic mixtures [1-3]. The advantages of PV are, it can be carried out at low temperature and the reuse of membrane with minimum environmental emission of the treated chemicals. Thus, in terms of energy and material consumption as well as environmental emission, PV is an ideal example of process intensification. This technique mainly used for the dehydration of organics using hydrophilic membrane or from the removal of organic using organophilic membranes [4-5]. However, for the separation of organic-organic mixtures neither of these membranes can be used. It requires suitable membrane selectivity based on the closeness of solubility parameter value of the permeate with membrane material [6]. It is the only membrane process in which a phase transition occurs during transport through a dense or microporous matrix. The phase transition occurs due to the vacuum at the permeate side. Selectivity is obtained by selective dissolution of components from a liquid mixture in the

membrane material and the differences in diffusion through the membrane. This allows separation of solvents on the basis of their affinity for the membrane material, in contrast to classical distillation where separation occurs as a result of differences in volatility. Thus, azeotropic mixtures and mixtures with a relative volatility close to one can be separated by pervaporation, on condition that they have a clear difference in properties determining their transport through pervaporation membranes. Silicon rubber coated on different membranes improved their separation efficiency and selectivity [7-8]. Addition of solid filler on polymer can remarkably improve the solubility property through the preferential adsorption, which results in the increase of separation factor and decrease of permeation flux [9].

Graphite filler is suitable for the separation of toluene-methanol mixtures because of the hexagonal arrangement of carbon atoms similar to that of benzene ring and the π – π bonds interaction between the planes allowing interaction with electron clouds of toluene. Lopez *et al.* [10]. Investigated the specific interactions between aromatic electrons of organic compounds and graphite surfaces as detected by immersion calorimetry.

The pervaporation separation of methanol/toluene and ethanol/toluene mixtures investigated by Park *et al.* [11-12] using the blend membranes of poly(acrylic acid)

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(PAA) and poly(vinyl alcohol) (PVA). It was found that alcohols permeated preferentially through these membranes. The flux decreased gradually as the PVA content of the blend increased, whereas selectivity increased. Literature shows that in most of the organic–organic separations glassy membranes have been used. Duval *et al.* [13] investigated separation of toluene/ethanol mixtures by pervaporation, using adsorbent-filled membranes by various activated carbons. For all the carbons tested, total flux through the membrane decreased drastically with the addition of the active carbon particles; however, the porous structure of carbon seemed to have no effect on selectivity. The rubbery membranes gives high flux but poor selectivity due to its amorphous structures and hence presence of appreciable amount of free volume in the bulk of the elastomeric chains. Natural rubber and SBR membrane has been used [14] for separation of toluene–methanol mixtures with preferential toluene permeation through these rubbery membranes. A large amount of researches had been reported about silicone rubber with or without silica [15–17], and series of silicone rubber compound membranes [18–19] had been reported for butanol recovery. Dashti *et al.* studied molecular dynamics and artificial intelligence knowledge of ANFIS to investigate water–acetic acid pervaporation (PV) separation through poly vinylalcohol (PVA)/silicone based membranes under a wide range of experimental condition [20]. Rezakazemi *et al.* studied Polydimethylsiloxane (PDMS) membranes supported on cellulose acetate (CA) and polyamide (PA) microfiltration membranes on the effects of support layer and permselective thickness on the separation performance of membranes at different operating conditions [21]. Shahverdi *et al.* studied Poly(vinyl alcohol) (PVA)/zeolite 4A mixed matrix composite membranes supported on polypropylene microfiltration membranes were prepared by solution

casting method and crosslinked with glutaraldehyde to investigate their pervaporation (PV) separation properties of water–ethylene glycol mixtures [22]. However, the selective removal of methanol from anhydrous organic liquid mixtures is required in many applications. Silicone rubber /graphite membranes were not used for the selective separation of methanol from toluene-methanol mixtures.

In this study, we developed QM- graphite membrane material with different graphitic contents and which was used for the separation of methanol from toluene-methanol mixture over the concentration range of 10–90 wt% methanol. The effects of graphite concentration and feed composition on flux and selectivity have also been estimated.

2. MATERIALS

Silicone rubber 5060-U GP-301 (HTV) (Dow Corning Co.; dimethyl, methyl vinyl siloxane dimethyl vinyl terminated (>60%), DCP (Dicumyl Peroxide) curing agent and graphite were procured from Sigma Aldrich, Bangalore, India. Other compounding ingredients and solvents were used as laboratory grade without further purification.

3. EXPERIMENTAL PART

3.1. Preparation QM/Graphite Membrane

3.2.1. Compounding of Mixes

Composite Preparation

Graphite filled Silicone rubber and unfilled membranes were prepared. The mixing was done on a laboratory scale Two roll mill. The temperature of the rolls kept constant at 28°C. First rubber was masticated for 2 minutes and then graphite and followed by DCP added one by one and the mixing was completed within

Table 1: Formulation of Mixes in Phr*

Membrane	Weight of QM	Weight of graphite	DCP
QM	100	0	1.5
QMG 5	100	5	1.5
QMG 10	100	10	1.5
QMG 15	100	15	1.5
QMG 20	100	20	1.5
QMG 30	100	30	1.5

*Parts per hundred rubber.

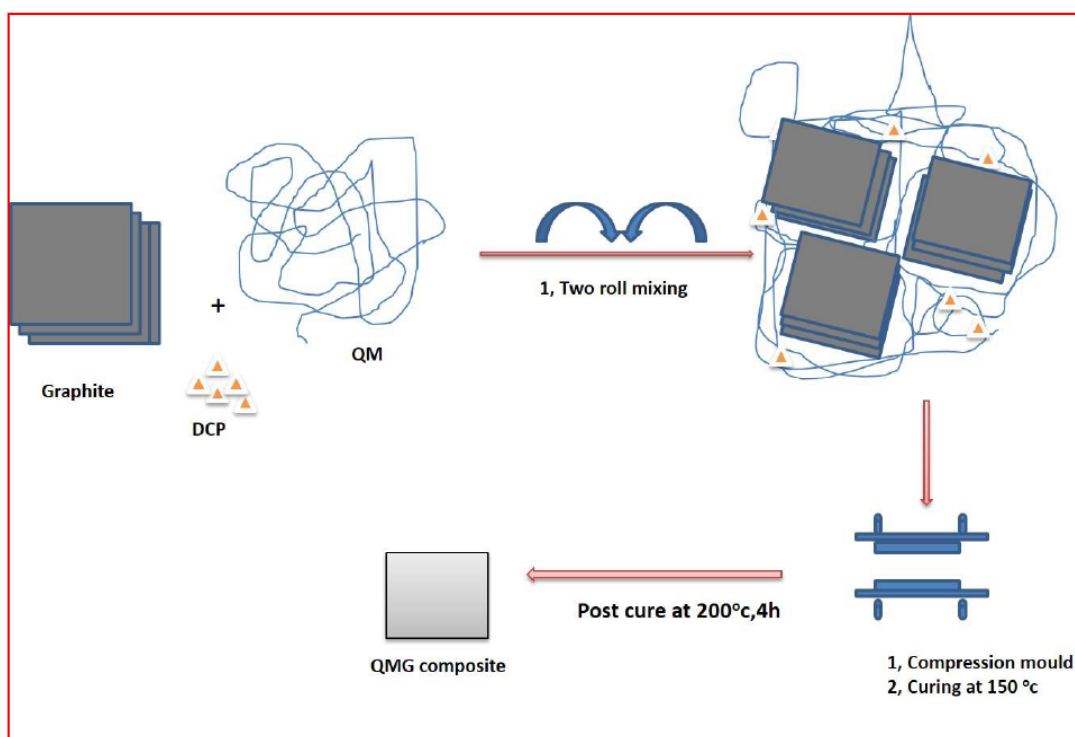


Figure 1: Schematic representation of preparation of QMG composite membrane.

20 minutes. Cure characteristics of the samples were determined using a Moving Die rheometer at a temperature of 150°C. Thin films of the pervaporation samples moulded using an electrically heated hydraulic press under a pressure of 150 bars at 150°C. Different contents (0, 5, 10, 15, 20, 30) of graphite filled membranes were prepared and these membranes are represented as QM, QMG 5, QMG 10, QMG 15, QMG 20, QMG 30. Schematic representation of preparation of composite membranes are shown in Figure 1.

3.2.2. Pervaporation Studies

The pervaporation experiments were performed with the effective area of the membrane in contact with feed solution was 16.61 cm². The membrane was first swelled in the organic mixture to be separated and then mounted in the cell. The vacuum was then pumped out on the downstream side. Feed solution is introduced into the upper part of membrane which is maintained at atmospheric pressure. The membrane was kept in the pervaporation cell for about 1 h in each run to reach equilibrium conditions before collecting the permeate. Once steady state was reached permeate was collected in traps immersed in liquid nitrogen. The flux was calculated by weighing permeate on a digital microbalance Mettler Toledo (JB1603-C/FACT) with an accuracy ±0.0001 g. The feed and permeate

compositions of all of the mixtures were determined by measuring their refractive indices with a refractometer. All the experiments were carried out at room temperature and were repeated to obtain reproducible results and the errors inherent in the pervaporation measurements were less than 1.0%. Separation performances of the membranes can be evaluated on the basis of total flux (J) and separation factor (α). Schematic representation of pervaporation setup is given in Figure 2.

The pervaporation performance of the QMG membranes were evaluated by the separation factor (α), and the separation flux (J) by the following expressions

$$\alpha = \left(\frac{Y_a}{Y_b} \right) / \left(\frac{X_a}{X_b} \right) \quad (1)$$

Y_a and Y_b represent the composition of the more permeating component (methanol) and less permeating component (toluene) in the permeate and X_a and X_b are those of more permeating component and less permeating component in the feed respectively.

$$J = Q / At \quad (2)$$

J is the molar flux of the membrane in kg m⁻² h⁻¹, Q is the quantity of permeate in kilograms, A is the

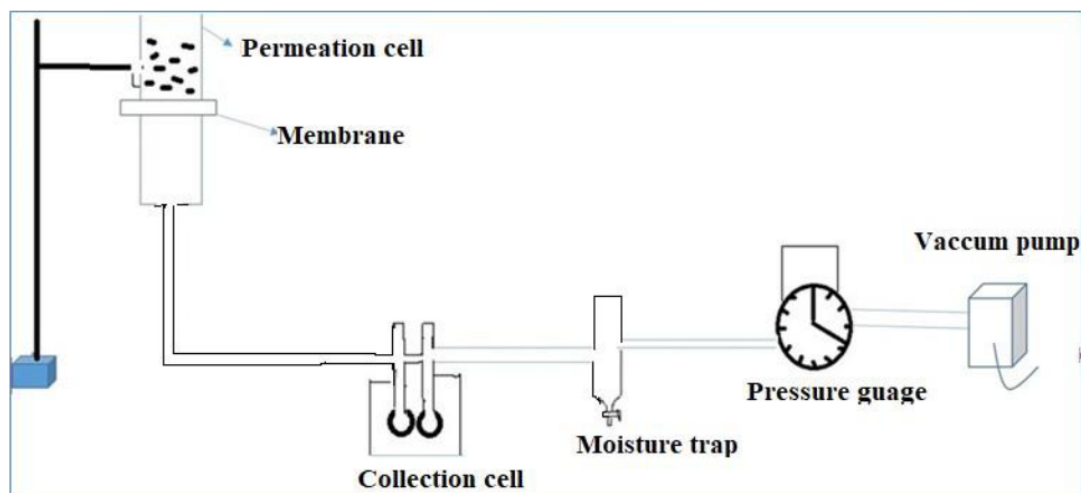


Figure 2: Schematic representation of pervaporation experiment.

effective area of the membrane in m^2 used for separation, t is time in hours.

4. RESULTS AND DISCUSSIONS

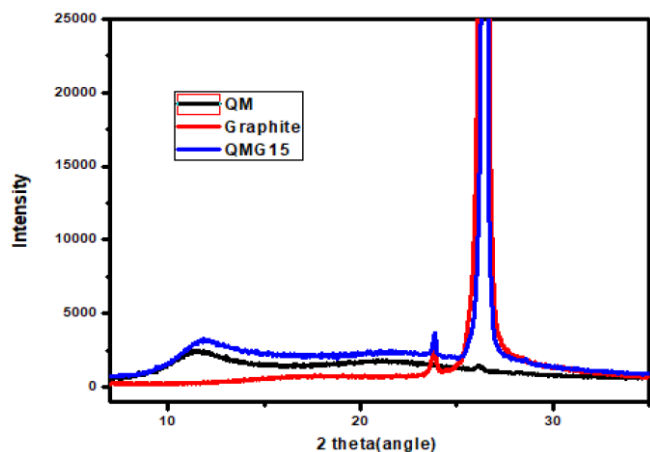


Figure 3: XRD spectrum of QM, graphite and QMG15.

X-ray diffraction patterns of the membranes are shown in Figure 3. It is interesting to note that

crystalline peak of graphite is observed at $2\theta = 26.4^\circ$ but there is no significant change in this peak. The pure QM membrane exhibits an amorphous peak at $2\theta = 11.28^\circ$ and peak become broader with the introduction of graphite in the silicone matrix. This implied that silicone polymer chains are enter into the graphite layers and thereby there is better interaction between graphite and silicone rubber chains.

4.1. Pervaporation

4.1.1. Effect of Filler Loading

In the present study, a novel membrane based on silicone rubber and graphite is used for separating Toluene/Methanol mixture (10/90 wt %).

Table 2 shows the effect of graphite concentration on the pervaporation characteristics of QM/Graphite composites. The affinity of membrane towards toluene is the major factor for the separation of methanol and toluene. With increasing the graphite content, flux increases and reaches a maximum at 10 phr of graphite (QMG 10) and then decreases. The variation

Table 2: Variation of Flux, Separation Factor, and Component flux with Graphite Loading

Membrane	Permeate Composition	Flux (J)	Separation Factor (α)	PSI J($\alpha-1$)	$J_{Toluene}$	$J_{Methanol}$
QM	8.5/91.5	0.00373	1.1960	0.0007	0.0317	0.3413
QMG 5	6.1/93.9	0.0075	1.7103	0.0053	0.0458	0.7042
QMG 10	7.9/92.1	0.0144	1.2953	0.0043	0.1138	1.3262
QMG 15	5.8/94.2	0.00400	1.8045	0.0032	0.0232	0.3768
QMG 20	7.9/92.1	0.00355	1.2953	0.0010	0.0280	0.3269
QMG 30	9.1/90.9	0.00801	1.1098	0.0009	0.0729	0.7281

of flux with increase in concentration of graphite is illustrated in Figure 4. The flux of pure silicone rubber membrane is $0.00373\text{kg/m}^2\text{h}$. Thus QM with 10 wt % graphite membrane shows a maximum enhancement for flux compared to other composite membranes (0.0144).

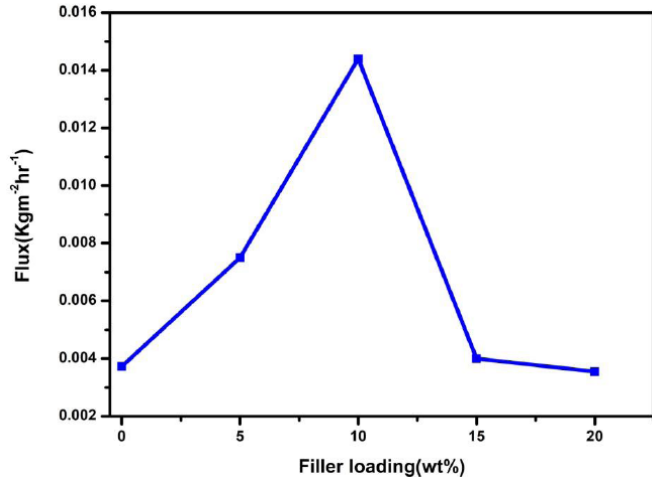


Figure 4: Effect of concentration of graphite on flux.

Separation factor is also increases with increase in graphite content and reaches a maximum at 15 phr of graphite (QMG15) and then decreases [Table 2]. Thus QMG15 composite membrane shows the highest separation factor and QMG10 membrane obtained highest flux. From the table it is clear that there is an optimum concentration of graphite where membrane separation and flux maximum.

Scanning electron micrographs of cryogenically fractured cross sections of QM and QMG15 membranes were obtained and are shown in Figure 5. A uniform surface morphology is observed for silicone rubber as in Figure 5(a). Even distribution of graphite flakes are observed in QMG15 membrane as in Figure 5(b). Silicone rubber chains are enter into the expanded graphite flakes and dispersed surface morphology is formed. This helps in the selective movement of methanol through the composite membrane.

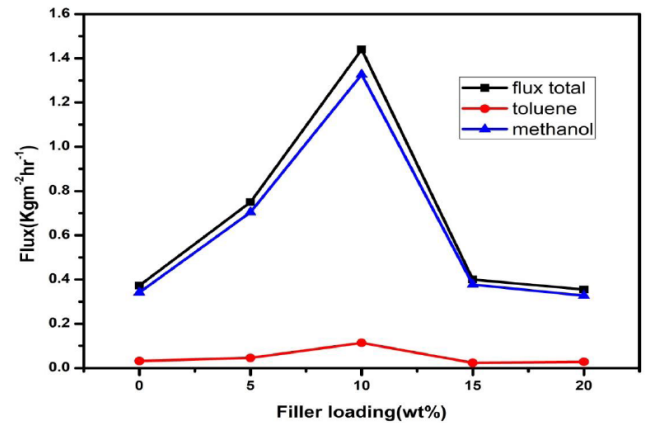


Figure 6: Variation of component flux with filler loading.

Figure 6 shows the variation of component flux with graphite concentration. It is evident from the graph that methanol flux is higher than toluene flux and both exhibit the maximum at 10 phr of graphite loading. So methanol flux is actually contributing towards the total

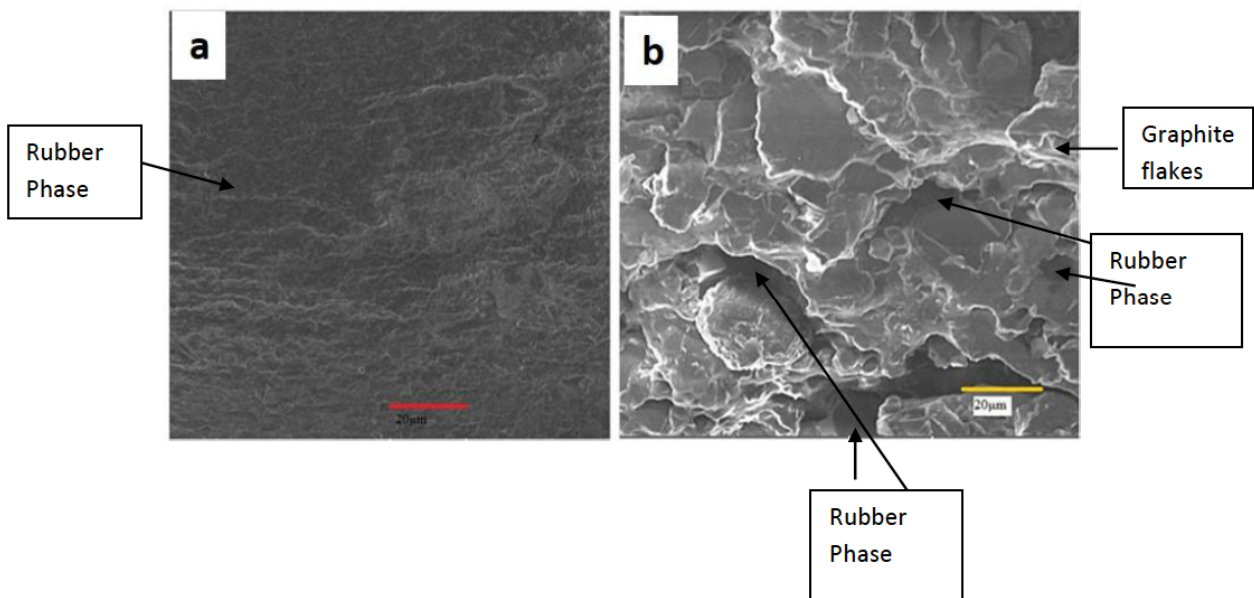


Figure 5: The SEM micrographs of (a) QM and (b) QMG15 membrane cross-section.

Table 4: Variation of Flux, Separation Factor, and Component Flux with Feed Composition

Feed Composition	Permeate Composition	Flux (J)	Separation Factor (α)	PSI	J_{Toluene}	J_{Methanol}
10/90	5.8/94.2	0.004	1.8045	0.0032	0.0232	0.3768
30/70	9.8/90.2	0.0007	3.9446	0.0022	0.0075	0.0694
50/50	8.5/91.5	0.0089	10.764	0.0869	0.0756	0.8143
70/30	9.2/90.8	0.0075	23.0289	0.1661	0.0693	0.6846
90/10	7.3/92.7	0.0089	114.287	1.0105	0.0651	0.8268

flux and hence the methanol separation is more easier compared to toluene.

4.1.2. Effect of Feed Composition

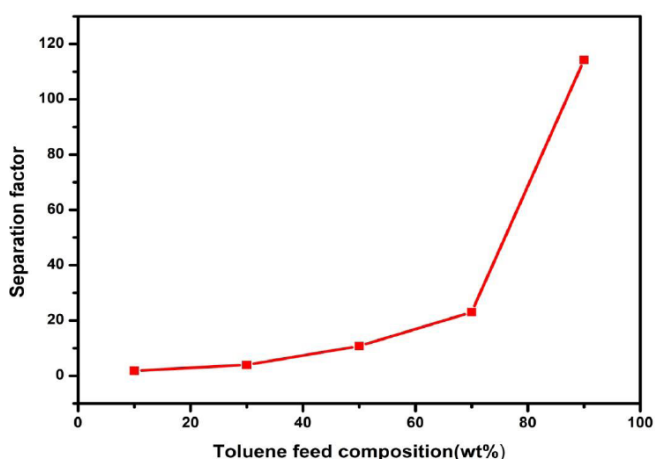


Figure 7: Variation of separation factor with toluene feed composition.

Figure 7 shows that separation factor increased with increasing toluene content in the feed. In the case of 10/90 feed composition (10% toluene and 90% methanol) the separation factor is 1.8045. But in 90/10 feed composition there is a large increase observed in separation factor i.e., 114.287. PSI shows almost an increasing tendency with increasing toluene concentration. Flux was not greatly influenced by feed concentration. The majority of total flux was for methanol than toluene. The separation factor increases with increase in concentration of toluene. As the feed contains higher concentration of toluene, the polymer membrane became more swollen, which helps in the easy passage of small methanol molecules through the membrane, thereby increasing the methanol selectivity. Flux is also gradually increasing with increasing the toluene concentration.

In order to explain how the permeant passes through the membrane during pervaporation, a model of mass transport is used in Figure 8. The most widely

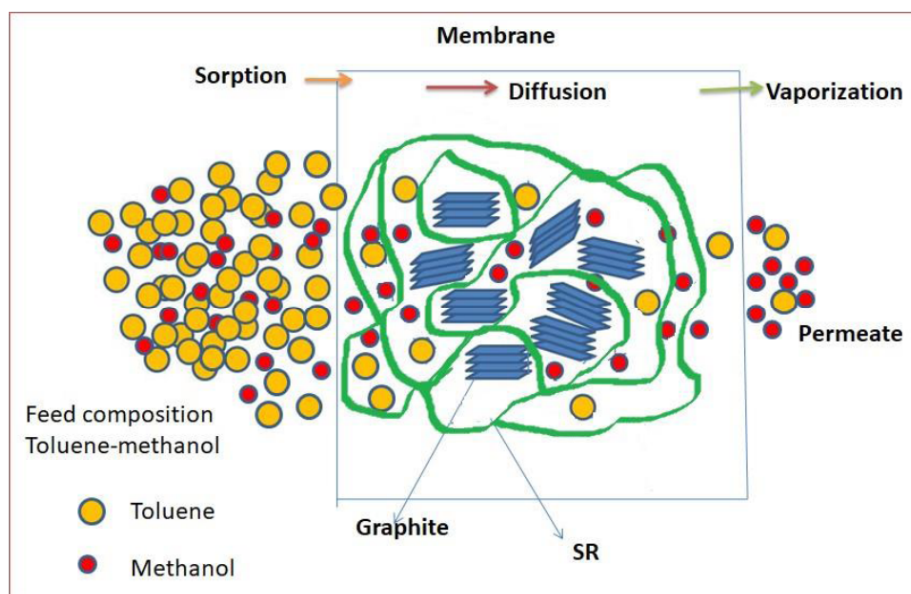


Figure 8: Schematic representation of pervaporation separation of organic mixtures through QM-graphite membrane.

accepted model is the solution-diffusion model and based on this model, the movement of permeant from the feed (liquid phase) to the permeate (vapor phase) undergoes three consecutive steps: (a) sorption of permeate from the feed liquid to the membrane, (b) diffusion of permeate through the membrane, and (c) desorption of the permeate to the vapor phase

5. CONCLUSION

Silicone rubber graphite membrane was prepared by two roll mill mixing, followed by hot pressing on a hydraulic press at 150°C. The XRD and SEM images confirmed the distribution and interaction of graphite layers and silicone rubber chains. The pervaporation result indicates that silicone rubber with 10 wt% graphite membrane showed a maximum enhancement in flux compared to neat silicone rubber membrane. But silicone rubber with 15 % graphite membrane shows better separation factor than all other membrane. Methanol flux is contributing significantly towards the total flux. Flux and separation factor are increased with increase in toluene concentration in the feed. Study confirms that synthesized QMG composite membrane can successfully use for the separation of methanol from toluene/methanol mixture.

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REFERENCES

- [1] Aouinti L, Denis Roizard and M. Belbachir. "PVC-activated carbon based matrices: A promising combination for pervaporation membranes useful for aromatic-alkane separations." *Separation and Purification Technology* 2015; 147: 51-61. <https://doi.org/10.1016/j.seppur.2015.04.007>
- [2] Ribeiro Cláudio P, Benny D. Freeman, Douglass S. Kalika and Sumod Kalakkunnath. "Aromatic polyimide and polybenzoxazole membranes for the fractionation of aromatic/aliphatic hydrocarbons by pervaporation." *Journal of Membrane Science* 2012; 390: 182-193. <https://doi.org/10.1016/j.memsci.2011.11.042>
- [3] Li Zhansheng, Ben Zhang, Lianxu Qu, Jizhong Ren and Yang Li. "A novel atmospheric dielectric barrier discharge (DBD) plasma graft-filling technique to fabricate the composite membranes for pervaporation of aromatic/aliphatic hydrocarbons." *Journal of Membrane Science* 2011; 371: 163-170. <https://doi.org/10.1016/j.memsci.2011.01.035>
- [4] Kujawa Joanna, Sophie Cerneaux and Wojciech Kujawski. "Highly hydrophobic ceramic membranes applied to the removal of volatile organic compounds in pervaporation." *Chemical Engineering Journal* 2015; 260: 43-54. <https://doi.org/10.1016/j.cej.2014.08.092>
- [5] Ghoreyshi Ali Asghar, Hamidreza Sadeghifar and Fereshteh Entezarian. "Efficiency assessment of air stripping packed towers for removal of VOCs (volatile organic compounds) from industrial and drinking waters." *Energy* 2014; 73: 838-843. <https://doi.org/10.1016/j.energy.2014.06.090>
- [6] Ray SK, Sawant SB, Joshi JB, Pangarkar VG. Development of new synthetic membranes for separation of benzene-cyclohexane mixture by pervaporation-a solubility parameter approach, *Ind. Eng. Chem. Res* 1997; 36: 5265-5276 <https://doi.org/10.1021/ie970351v>
- [7] Mohammadi AT, Matsuura T, Sourirajan S. Gas separation by silicone-coated dry asymmetric aromatic polyamide membranes, *Gas. Sep. Purif* 1995; 9: 181. [https://doi.org/10.1016/0950-4214\(95\)98225-A](https://doi.org/10.1016/0950-4214(95)98225-A)
- [8] Petersen J, Matsuda M, Haraya K. Capillary carbon molecular sieve membranes derived from Kapton for high temperature gas separation, *J Membr Sci* 1997; 131: 85. [https://doi.org/10.1016/S0376-7388\(97\)00041-0](https://doi.org/10.1016/S0376-7388(97)00041-0)
- [9] Ji W, Sikdar SK. Pervaporation using adsorbent-filled membranes, *Ind Eng Chem Res* 1996; 35: 1124. <https://doi.org/10.1021/ie9503609>
- [10] Lopez EC, Nevskaja DM, Muoz V, Rodriguez-Ramos I, Guerrero-Ruiz A. Specific interactions between aromatic electrons of organic compounds and graphite surfaces as detected by immersion calorimetry, *Langmuir* 2004; 20: 1013. <https://doi.org/10.1021/la035349p>
- [11] Park HC, Meertens RM, Mulder MHV, Smolders CA. *J Membr Sci* 1994; 90: 265. [https://doi.org/10.1016/0376-7388\(94\)80076-6](https://doi.org/10.1016/0376-7388(94)80076-6)
- [12] Park HC, Meertens RM, Mulder MHV. *Ind Eng Chem Res* 1998; 37: 4408. <https://doi.org/10.1021/ie980117k>
- [13] Duval JM, Folkers B, Mulder MHV, Desgrandchamps G. *CA. Sep. Sci Technol* 1994; 29: 357. <https://doi.org/10.1080/01496399408002488>
- [14] Ray S, Ray SK. Separation of organic mixtures by pervaporation using crosslinked rubber membranes, *J Membr Sci* 2006; 270: 132-145. <https://doi.org/10.1016/j.memsci.2005.06.049>
- [15] Ray S, Ray SK. Separation of organic mixtures by pervaporation using crosslinked and filled rubber membrane, *J Membr Sci* 2006; 285: 108-119. <https://doi.org/10.1016/j.memsci.2006.08.009>
- [16] Zhuang XJ, Chen XR, Su Y, et al. Improved performance of PDMS/silicalite-1 pervaporation membranes via designing new silicalite-1 particles. *J Membr Sci* 2015; 493: 37-45. <https://doi.org/10.1016/j.memsci.2015.06.043>
- [17] Ikegami T, Negishi H, Sakaki K. Selective separation of n-butanol from aqueous solutions by pervaporation using silicone rubber-coated silicalite membranes. *J Chem Technol Biotechnol* 2011; 86: 845-851. <https://doi.org/10.1002/jctb.2598>
- [18] Suhas DP, Aminabhavi TM, Raghu AV. Mixed matrix membranes of H-ZSM5-loaded poly(vinyl alcohol) used in pervaporation dehydration of alcohols: influence of silica/alumina ratio. *Polym Eng Sci* 2014; 54: 9. <https://doi.org/10.1002/pen.23717>
- [19] Dong ZY, Liu GP, Liu SN, et al. High performance ceramic hollow fiber supported PDMS composite pervaporation membrane for bio-butanol recovery. *J Membr Sci* 2014; 450: 38-47. <https://doi.org/10.1016/j.memsci.2013.08.039>
- [20] Molecular dynamics, grand canonical Monte Carlo and expert simulations and modeling of water-acetic acid pervaporation using polyvinyl alcohol/tetraethyl orthosilicates membrane, *Journal of Molecular Liquids* 2018; 265: 53-68. <https://doi.org/10.1016/j.molliq.2018.05.078>

- [21] Rezakazemi, Mashallah, Kazem Shahidi, and Toraj Mohammadi. "Synthetic PDMS composite membranes for pervaporation dehydration of ethanol." *Desalination and Water Treatment* 2015; 54: 1542-1549.
- [22] Shahverdi, Mahnaz, Bahareh Baheri, Mashallah Rezakazemi, ElaheMotaee and Toraj Mohammadi. "Pervaporation study of ethylene glycol dehydration through synthesized (PVA-4A)/polypropylene mixed matrix composite membranes." *Polymer Engineering & Science*, 2013; 53:1487-1493.
<https://doi.org/10.1002/pen.23406>

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