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Pervaporation Separation of Toluene-Heptane Mixtures with Polyvinyl chloride/ Alumina/ Activated Carbon Membranes

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This paper explores the fabrication of high performance & low-cost Membrane by incorporation of alumina and activated carbon in Polyvinyl Chloride (PVC) matrix using phase inversion technique. This study examined the various effects of the alumina (Al_2O_3) and activated carbon (C) on the PVC matrix by several analytical techniques such as scanning electron microscope (SEM), Thermogravimetric Analysis (TGA), and contact angle. The synthesized membranes were used to separation of toluene from toluene-heptane mixtures using pervaporation technique and analysed the mass fraction of toluene in the permeate collected in the pervaporation setup using refractive index method. The results showed that the PVC/ 50% activated carbon/ 50% alumina membrane would be a promising alternative for separation of toluene from heptane-toluene solution. As an outcome, PVC/activated carbon/alumina-based membrane has given better separation of toluene from heptane-toluene solution as compared to other synthesized membrane.

Keywords: Membrane, Phase inversion, PVC, Refractive index

Introduction

In modern era, azeotropic and extractive distillation techniques are the preferable choice for the separation of aromatic-aliphatic mixtures.[1] However, these techniques have process complexity due to the requirement of heavy machinery or higher energy consumption. So these methods are not efficient for the separation of heptane-toluene mixtures. Among all separation techniques, pervaporation is a new and reliable method, has several advantages as compared to other methods. It has less environmental impact, is simple to operate, and is a low-cost separation technique. Thus, the pervaporation method is an eye-opener for researchers in the field of separation techniques.[2]

Pervaporation is a membrane separation process, which uses the polymeric membrane for selective permeation of one or more components from a liquid mixture.[3,4] The Membrane acts as a selective barrier between the two phases: the liquid-phase feed and the vapour-phase permeate. It allows the desired component(s) of the liquid feed to transfer through it by vaporization.[5] Separation of components is based on a difference in transport rate of individual components through the Membrane. Pervaporation used in many industrial applications like dehydration of alcohol, control of ethanol concentration in the fermenter, recovery of methanol from methanol and methyl tert-butyl ether mixture, separation of ethylene glycol and water mixtures, recovery of flavor and fragrance, removal of a volatile organic compound.

Polyvinyl chloride (PVC) is a low cost, durable and long lasting polymer that is widely used for several applications like building, construction and pervaporation applications. Several study stated that PVC membrane had high affinities for aromatic structures with less affinities for aliphatic structures. This characteristics of PVC membrane made selective for aromatic-aliphatic separation.[6]

Das *et al.* prepared polyvinyl chloride/ bentonite clay based membranes using dioctyl phthalate as a plasticizer and demonstrated the permeability and diffusion coefficient of tetrahydrofuran from mixture.[7] Aouinti *et al.* prepared PVC/ activated carbon based membrane and observed the selective separation of toluene from mixtures.[8] An *et al.* synthesized PVC/ ethylene-co vinyl-acetate copolymer membranes and determined the possible separation of benzene from benzene/cyclohexane mixture.[9] In this study, a novel hybrid membrane was prepared from rhodium loaded or zeolite loaded and PVC. Authors of this paper investigated the effective separation of benzene from benzene/ cyclohexane mixture using pervaporation

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technique.[1] Aouinti *et al.* examined the separation of toluene from heptane using clay incorporated hybrid PVC membrane pervaporation method.[10] Authors of this paper used commercial polymeric thin film and determined the separation coefficient for acetone-water, acetonitrile-water and ethanol-water.[11] Gongping *et al.* prepared polydimethyl siloxane/ ceramic composite membrane for the separation of butanol-water mixtures.[12] Yuna *et al.* synthesized zeolite membrane for separation of xylene isomers using pervaporation method.[13]

In this paper, PVC membrane was prepared using phase inversion technique. Activated carbon and alumina particles as fillers were incorporated in PVC membrane and observed the effect of fillers for effective separation of toluene from heptane. The synthesized membranes were also characterized using various analytical techniques such as Scanning Electron Microscope (SEM), Thermogravimetric Analysis (TGA), contact angle. The effects of activated carbon and alumina content weight fractions, and toluene weight fractions in the feed were carefully examined using pervaporation technique.

Materials and Method

Raw Material

Solvents (N-Methyl-2-pyrrolidone (NMP), Polyvinyl pyrrolidone (PVP)), Polyvinylchloride (PVC), fillers (Activated carbon, Nanosized alumina), Toluene, *n*-Heptane were procured from Sigma-Aldrich, USA.

Synthesis of Membrane

The polymer was dissolved in using Polyvinylpyrrolidone (PVP) and N-Methyl-2-pyrrolidone solvents at room temperature using phase inversion technique. Further, activated carbon and alumina were added in the polymer solution and stirred for 2 hours at room temperature. At last, the prepared solution was casted on a glass plate. Subsequently, same solution was placed in a coagulation bath for solvent evaporation and got the thin film of polymeric membrane. Various polymeric membranes have been prepared using phase inversion technique (Table 1).

Pervaporation Experiment

A mixture of Toluene and n-heptane was placed in the feed tank. The solution was preheated around 65–75°C temperature with the help of a water bath before being sent to the membrane module (Fig. 1). There were three components of the membrane module; the first was the upper side, the second was the middle side, and the third was the lower side. The area of membrane module was 122.65 cm^2. The upper side part was then feed inlet part from where the feed enters the module. The second part was used to bypass the liquid retentate, and the third part was used to exert pressure using vacuum pump technique. For high driving force, pressure may be applied through the pressure port module. There was a permeate collected in the outlet part of the module. To keep downstream pressure below 5 mm Hg, the vacuum pump was linked to the downstream side. A chiller was used to condense the permeate vapours into liquid. Pervaporation separation of toluene and n-heptane mixture was carried out with the synthesized membranes. The Membrane was cut in the required shape and clamped within the membrane module. Membrane module was connected with the permeate collector, which was kept in a chiller to ensure the vapours are condensed. Feed mixture was preheated at a temperature of 75°C. Using a vacuum pump, the permeate pressure was kept below 5 mm Hg. Initially, 50 wt.% toluene/ 50 wt.% heptane mixture was prepared. With the help of a chiller, the vapour permeates through the membrane was condensed in a

Table 1 — Compositional analyses for various types of synthesized polymeric membranes

Sample	NMP (wt. %)	Al_2O_3 (wt. %)	AC (wt. %)	PVP (wt. %)	PVC (wt. %)
Pure PVC (M4)	74	0	0	6	20
PVC+C (M3)	65	0	9	6	20
PVC+Alumin a (M2)	65	9	0	6	20
PVC+C+Alu mina (M1)	65	4.5	4.5	6	20

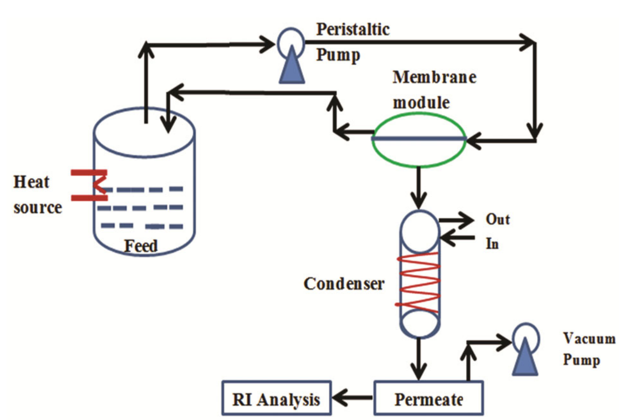

Fig. 1 — Schematic Diagram for pervaporation experiment

condenser and collected in the permeate collector. The experiment was repeated with various synthesized membranes in order to get the best membrane, which gives the maximum separation of toluene from n-heptane/toluene feed mixture. As an outcome, the permeate was brought to ambient temperature. Moreover, the percentage of toluene in the permeate was determined using the Refractive Index technique.[14]

Results and Discussion

In this section, results of different characterization parameters of fabricated PVC membrane have been discussed. Based on the type of fillers, following prepared membranes were listed as below:

(1) Alumina doped PVC membrane
(2) Carbon /Alumina doped PVC membrane
(3) Carbon-doped PVC membrane
(4) Pure PVC membrane

The characterization techniques such as SEM, EDX, TGA, contact angle and refractive index that have been adopted for comparative analysis of PVC membranes.

Scanning Electron Microscopy (SEM)

In order to elucidate the surface topography of membranes, all types of membranes have been scanned using SEM analysis. Pure PVC membrane shows very fewer pores at the surface as shown in Fig. 2(a). During coagulation process, water diffused into the membrane as nonsolvent and created some void structure. However, after doping of Al_2O_3 in the polymer matrix, wider pores have been formed in the cross sectional image of sample (Fig. 2(b)). Some void openings have been appeared after incorporation of activated carbon in PVC matrix in Fig. 2(c). Membrane have become more porous as compared to pure PVC membrane. Required void openings have been presented in the membrane synthesized from PVC, activated carbon and alumina (Fig. 2(d)). Due to a combination of activated carbon and Al_2O_3, the membrane becomes highly porous as compared to pure PVC membrane.[1,15–18]

EDX Analysis

The EDX spectra of PVC, activated carbon-doped PVC, aluminum nanoparticle (Al_2O_3) doped PVC, and activated carbon-aluminum nanoparticle (Al_2O_3) doped PVC are shown in Fig. 3 (a) to (d), respectively. The EDX spectra of PVC confirmed that carbon, oxygen, and chlorine are the main elements in the membrane. The weight% of carbon, oxygen, and chlorine are 51.78, 6.89, and 41.33. After carbon doping in PVC, a new nitrogen peak was observed in EDX spectra with an increase in carbon and oxygen weight percent.[19,20] The increase in the weight percentage of carbon and oxygen is due to the doping of activated carbon, which contains carbon, oxygen, and nitrogen. This result confirmed that activated carbon was successfully doped in the PVC membrane. The EDX spectra of aluminum nanoparticle (Al_2O_3) doped PVC membrane is shown in Fig. 3(c). A new peak of the aluminum element is found in EDX spectra with increasing oxygen weight percentage.

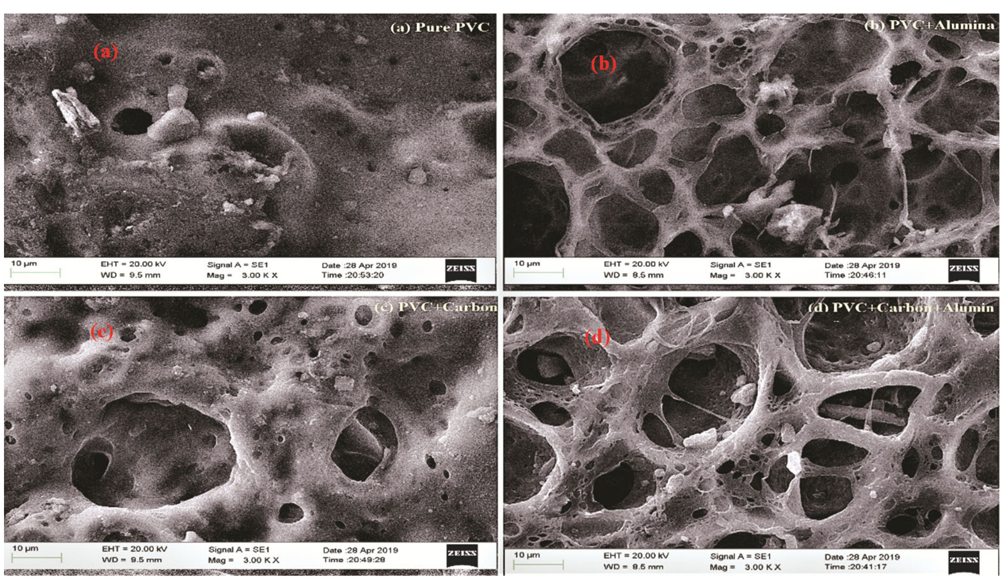

Fig. 2 — SEM images for all polymeric membranes (a) Pure PVC, (b) PVC doped Al_2O_3, (c) PVC doped Carbon, (d) PVC doped Al_2O_3 and carbon

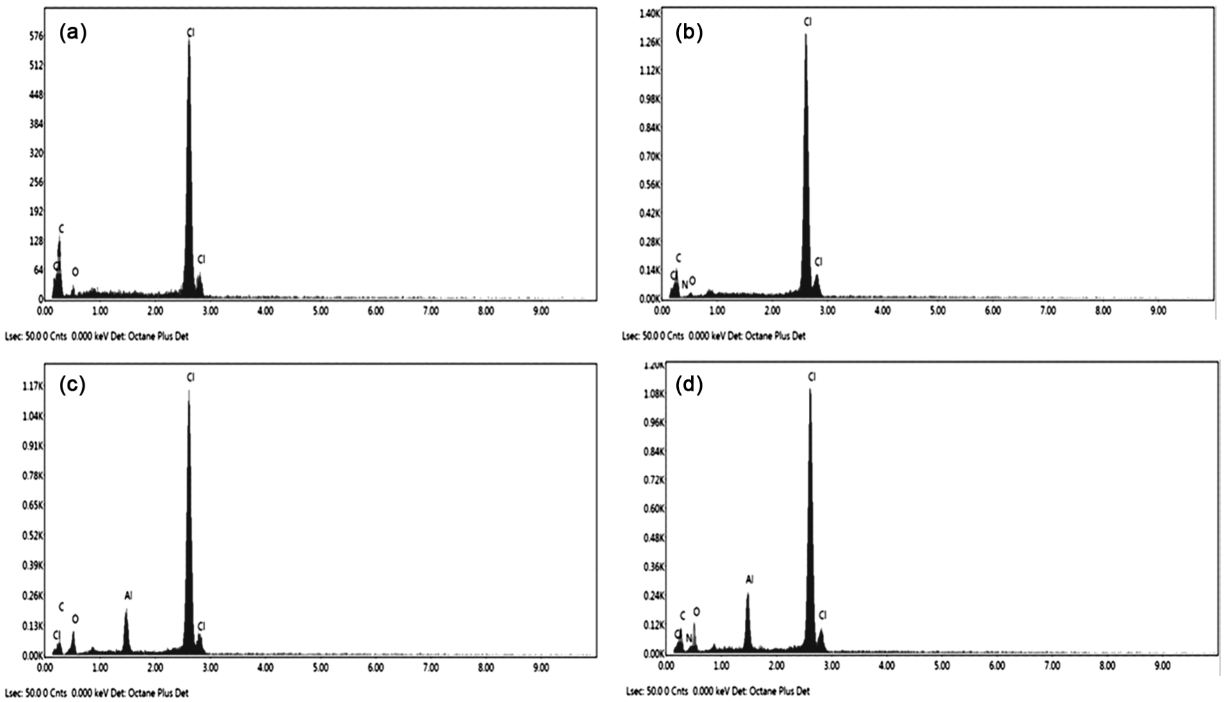

Fig. 3 — EDXanalysis for all polymeric membranes (a) Pure PVC, (b) PVC doped Carbon, (c) PVC dopedAl_2O_3, (d) PVC doped Al_2O_3 and carbon

The EDX results hints that carbon and oxygen weight percentage was decreased and increased, respectively, due to the doping of aluminum nanoparticles (Al_2O_3). The activated carbon-aluminum nanoparticle (Al_2O_3) doped PVC EDX spectra are shown in Fig. 3(d). The result confirmed that all elements were well distributed on the PVC membrane surface. The weight percentage of carbon and chlorine decreased in EDX spectra of activated carbon- aluminum nanoparticle (Al_2O_3) doped PVC with increased weight percentage oxygen and aluminum. The conclusion of all EDX spectra was that activated carbon, and aluminum nanoparticles (Al_2O_3) were well distributed on the surface of PVC.

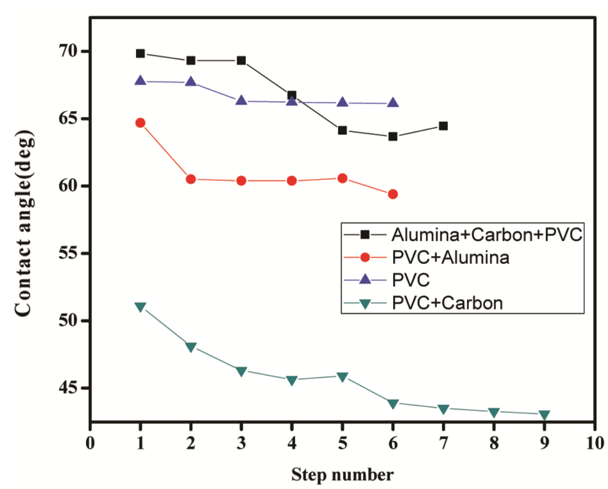

Fig. 4 — Contact angle measurements for all polymeric membranes (a) Pure PVC, (b) PVC doped Al_2O_3, (c) PVC doped Carbon, (d) PVC doped Al_2O_3 and carbon

Contact Angle Analysis

The hydrophilicity of the Membrane is a critical element influencing membrane performance when organic molecules are separated from water solutions. Therefore, to explore the connection between membrane efficiency and its surface properties, it is essential to determine the membrane hydrophilicity.

The water contact angles for all polymeric membranes are shown in Fig. 4. It is appeared that the average contact angle for PVC membrane was decreased to 60.99° from 68.13° after the incorporation of alumina in PVC matrix. Similar behavior is found in the case of activated carbon reinforced PVC matrix. The contact angle is decreased to 54.80° from 68.13° as the activated carbon was added to the PVC matrix. The contact angle for PVC/ activated carbon/ alumina is 48.57°. This value shows highly hydrophilic nature of membrane. The activated carbon and alumina particles covers the surface of the membrane and increases the hydrophilicity of the membrane. This characteristic leads to higher water absorption and lower interface energy. Ghazanfari *et al.* synthesized PVC/alumina based membrane and observed the similar result in their published article.[15,21,22] This result shows that membrane is highly hydrophilic in nature and assures its suitability for the effective separation of heptane-toluene mixture.

TGA Analysis

Thermal stability can be defined as an upper limit to the service temperature as much as the possibility of mechanical property loss. The TGA curve measured the thermal stability of membranes. The TGA curve for all preparedmembranesshown in Fig. 5. The curve shows the multistage disintegration of Membrane.

Initially, degradation of membranes were observed at around 30–420°C temperature range. Notable degradation is observed in PVC and PVC/alumina based membranes.[7,23] The second stage starts at 197°C with 5% weight loss for PVC/carbon membrane, 204°C with 4% weight loss for PVC/ carbon/ alumina membrane, 210°C with 7% weight loss for PVC/ alumina membrane, and 185°C with 10% weight loss for PVC membrane, respectively. The degradations ends at 410°C with 56% weight loss for PVC/ carbon membrane, 450°C with 60% weight loss for PVC/ carbon/ alumina membrane, 400°C with 60% weight loss for PVC/ alumina membrane and 420°C with 64% weight loss for PVC membrane, respectively. The residual amount for PVC membrane was found to be 11% at 700°C whereas for PVC/ carbon/ alumina membrane, the amount was found to be 26% at 700°C. After 500°C, the remaining residual amount is chemical inert. Moreover the thermal stability of PVC/ alumina/ activated carbon based membrane is found to be comparable with PVC/ carbon based membrane.[24,25] From the DTG curve (Fig. 6), it can be seen that the peak temperature for the degradation of pure PVC membrane, PVC doped alumina membrane, PVC doped carbon membrane and PVC doped alumina and carbon membrane was found to be 256°C, 295°C, 265°C and 323°C respectively.[26,27]

Refractive Index Test Analysis

A refractive index test was conducted to determine which membrane gave the maximum mass fraction of the permeate (Table 2). For this standard, samples were prepared with toluene and n-heptane mixture. The refractive index was noted. A reference graph for change in toluene's mass fraction with RI was plotted (Fig. 7).

RI of the permeate is obtained. Using the reference plot, the corresponding mass fraction of the permeate is obtained. The mass fraction of toluene obtained for different permeate samples are shown in Table 3.

The findings from the refractive index experiment have been verified that the PVC doped Al_2O_3 and carbon> PVC doped carbon > PVC doped Al_2O_3> Pure PVC. Hence, we can say that the PVC doped Al_2O_3 and carbon membrane is ideal for the toluene n-heptane mixture pervaporation method.[14]

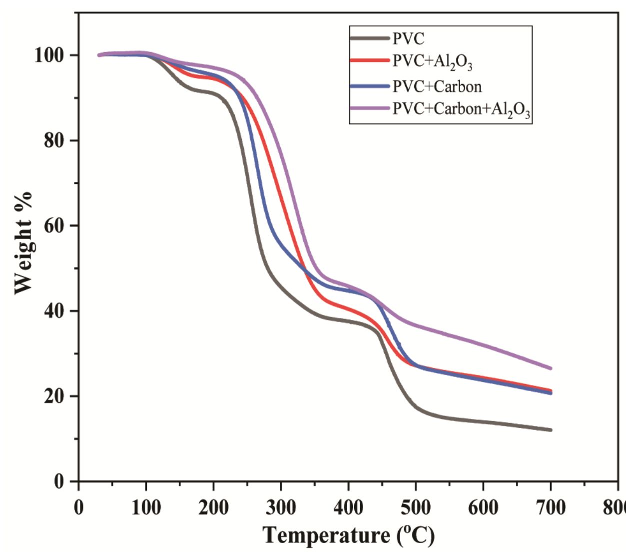

Fig. 5 — TGA analysis for all polymeric membranes (a) Pure PVC, (b) PVC doped Al_2O_3, (c) PVC doped Carbon, (d) PVC doped Al_2O_3 and carbon

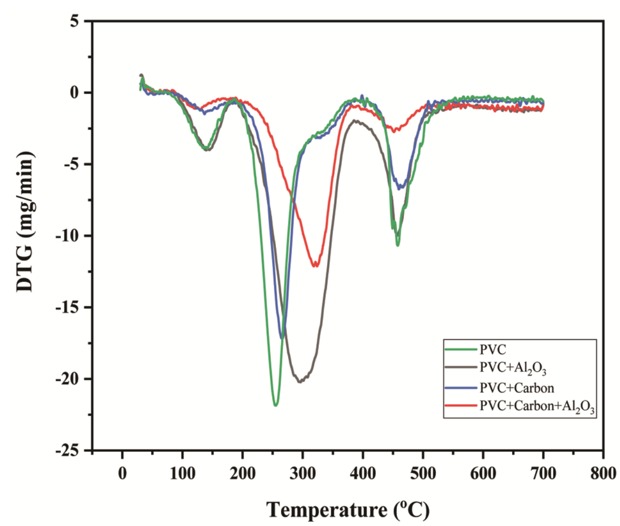

Fig. 6 — DTG analysis for all polymeric membranes (a) Pure PVC, (b) PVC doped Al_2O_3, (c) PVC doped Carbon, (d) PVC doped Al_2O_3 and carbon

Table 2 — Refractive Index of standard samples

Sr No.	Sample	Mass fraction of Toluene	Refractive index
1	Pure n-Heptane (10 ml)	0	1.381
2	Pure Toluene	1	1.494
3	1 ml Toluene + 9 ml n-Heptane	0.12	1.392
4	2 ml Toluene + 8 ml n-Heptane	0.24	1.401
5	3 ml Toluene + 7 ml n-Heptane	0.35	1.415
6	4 ml Toluene + 6 ml n-Heptane	0.45	1.428
7	5 ml Toluene + 5 ml n-Heptane	0.56	1.435
8	6 ml Toluene + 4 ml n-Heptane	0.66	1.449
9	7 ml Toluene + 3 ml n-Heptane	0.75	1.459
10	8 ml Toluene + 2 ml n-Heptane	0.84	1.473
11	9 ml Toluene + 1 ml n-Heptane	0.92	1.485

Table 3 — Variation of mass fraction of Toluene in permeate with RI

Membrane	RI	Mass fraction
Pure PVC	1.449	0.66
PVC+Alumina	1.452	0.68
PVC+C	1.465	0.79
PVC+C+Alumina	1.481	0.89

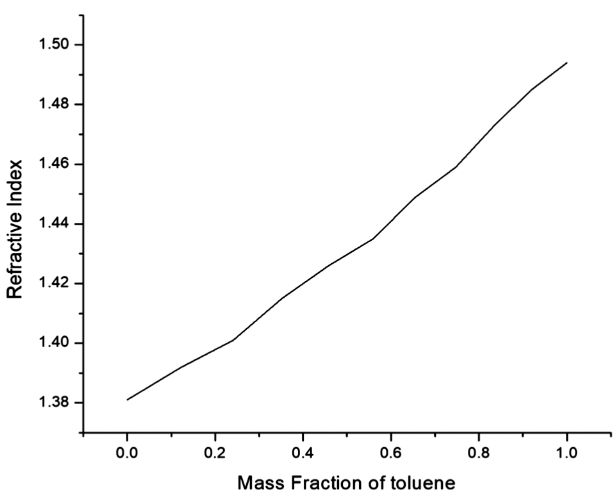

Fig. 7 — Reference graph for refractive index vs. mass fraction of toluene

Conclusions

Polyvinyl chloride membrane with doped alumina and activated carbon particles have been prepared in this work. After a complete analysis of the hybrid PVC membrane, the following conclusions can be made:

1. It can be concluded that the crystallinity and wet tability greatly influence the structural stability and porosity of the hybrid PVC membrane. This topography with better filler-polymer matrix interface adhesion results in increased permeability and stability of the membrane.
2. Scanning electron microscopy images of membranes showed the effect of doping of carbon and Al_2O_3 on pure PVC membrane structure. Due to a combination of carbon and Al_2O_3, the Membrane was found to be more porous as compared to pure PVC membrane.
3. The length and number of the macro void structure in the membrane's centre section increased after the successfully incorporation of carbon and alumina particles in the matrix.
4. Concerning the outcomes of the research of contact angle, the doping of alumina and activated carbon in PVC membrane is required for benchmark removal of toluene from heptane.

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