Pervaporation dehydration of bio-fuel (n-butanol) by dry thermal treatment membrane

Sohelia Manshad¹,², Arun M Isloor¹,², Mohd Ghazali Mohd Nawawi¹, Inamuddin³,⁴,⁵, Imran Khan⁴ and Hadi M Marwani³

¹ Department of Polymer Engineering, Universiti Teknologi Malaysia, 81310 Johor Bahru, Malaysia
² Membrane and Separation Technology Laboratory, Department of Chemistry, National Institute of Technology Karnataka, Surathkal, Mangalore, India
³ Chemistry Department, Faculty of Science, King Abdulaziz University, Jeddah 21589, Saudi Arabia
⁴ Applied Science and Humanities Section, University Polytechnic, Faculty of Engineering and Technology, Aligarh Muslim University, Aligarh 202 002, India
⁵ Authors to whom any correspondence should be addressed. E-mail: smanshad12@yahoo.com, isloor@yahoo.com and inamuddin@zhcet.ac.in

Keywords: pervaporation, graphene oxide, polyetherimide, dry-thermal treatment technique, flat-sheet membranes

Abstract
In the present investigation, laboratory synthesized graphene oxide (GO) as a nano-filler was used in polyetherimide (PEI) flat-sheet membranes (PM). The PEI flat-sheet membrane was fabricated through a dry-thermal treatment (DTT) method. The effects of fabrication method were investigated on polyetherimide-GO membrane prepared by dry-thermal treatment (PMDTT). The morphological structure was investigated via different characterization; Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), X-ray diffraction (XRD), transmission electron microscopy (TEM), contact angle measurement and Raman spectra. The results indicated that, the hybrid PMDTT membrane displayed reasonably better pervaporation separation performance in comparison to neat PMDTT membranes. The concentrations of water at the permeate side of hybrid and neat PMDTT membrane were 99.3 and 90.9 wt.%, respectively. Hybrid membranes showed a 78.3% enhanced permeation rate. Enhancement of pervaporation property of hybrid PMDTT membrane could be ascribed mainly due to the presence of graphene oxide in the dense top layer. Overall, the blending of graphene oxide in hybrid PMDTT membranes could be a promising approach for enhancing the pervaporation properties of the membranes.

Introduction
Pervaporation (PV) is a membrane separation process, which is utilized for liquid phase, especially for the constant boiling point and close boiling mixtures [1]. Membrane based PV separation is a practical and economically viable process to the prevalent separation processes of reverse osmosis, distillation and ultrafiltration. Meanwhile, a hybrid separation system like PV membrane combined with distillation process can be more frugal. Minimum operating costs and energy consumption are the other remarkable features of the PV process [2]. The PV membrane is a dense membrane (non–porous) or a very finely–porous ceramic membrane. The fabricated membrane has an affinity towards organic or inorganic components. The PV process is carried out in three steps: Selective sorption on the influent-side of the membrane; selective diffusion through the membrane; desorption in the gas phase on the permeate-side. The major PV application is for the removal of water from organic mixtures (hydrophilic membrane) and the separation of organic mixture present in water (hydrophobic membrane) [3–5]. Membrane morphology, cost effectiveness and simplicity in fabrication are the major concerns for industrial applications. Improvement of morphological structure and developing better fabrication techniques are the major challenges. Researchers across the globe are working hard to develop cost-effective and efficient ways for membrane fabrication [6, 7].
Due to the green house effect on environment and nonrenewable unstable source, in recent years biofuels have received more attention due to their eco-friendly and cost consideration. In this paper the focus is on n-butanol, which is a biofuel, which can be produced from fossil fuel and bio-sources. However, from both sources, chemical compounds of similar properties as that of butanol are also produced. The n-butanol indicates a higher potential than low carbon containing alcohol such as methanol and ethanol. N-butanol, which has four carbon atoms offers a higher calorific value and about 25% more energy than ethanol. Therefore, a higher number of carbon atom containing fuel can reduce the fuel consumption. Moreover, n-butanol exhibits many advantages over ethanol such as, lower volatility and less ignition problems [8]. The chemical properties of n-butanol could make this alcohol as a future biofuel to substitute gasoline. The low vapor pressure point and higher flash point make n-butanol safer as a fuel for high temperature utilization [9, 10]. Butanol contained more hydrogen and carbon atoms as compared with that of ethanol and methanol. Hence, this alcohol is a better blending substance into diesel and gasoline fuel than low carbon (methanol, propanol and ethanol) alcohols. Meanwhile, the viscosity of n-butanol is slightly higher than a smaller carbon chain alcohols, which were listed above. Furthermore, butanol holds lesser heat of vaporization property than ethanol. Hence, this property leads to low ignition point and easier to use in cold temperature too [11].

In industries, initial purification of n-butanol is performed via increasing the concentration by distillation to 80 wt%, then further purification would continue with the pervaporation membrane process to increase concentration more than 99.5 wt%. For the recovery of n-butanol, membranes having different morphologies are used. Thus, the development of an appropriate and efficient membrane is a real challenge for n-butanol dehydration by pervaporation process. Many polymeric membranes displayed reasonable performance of pervaporation [12]. Meanwhile, many of the reported membranes exhibited some defects at high temperatures such as decreasing diffusion due to swelling and shorter life of the membrane during a short time of pervaporation [13]. Few of the membranes exhibit acceptable permeation performance, however these membranes are highly expensive and have complex fabrication method. Membrane and material researchers have applied a wide range of various materials and fabrication techniques to overcome the defects of the current membranes. Some of the fabrication techniques are physical or chemical. Physical modification occurs by mixing two or more polymers (blending) [14, 15]. The grafting method provides covalent bonding to the polymer chain. By chemical modification, less dense polymer chains are strengthened by cross-linking [16] onto the monomer or polymer, unlike this grafting method, curing is more simplified for practical application because, grafting can occur in a minute, while curing can take a second. The combination of an efficient method and material improves the performance of the separation process [17–19]. Polyetherimide (PEI) has remarkable properties such as excellent film forming property, tolerant to mechanical strength, chemical resistance and high solvent resistance. Moreover, PEI membranes have less swelling property, which is resulting in higher separation performance. The low swelling PEI properties make it a possible candidate for dehydration process [20, 21]. PEI indicates low permeation versus higher separation factor, equilibrium of the PEI separation performance is required to modify by a filler like nano graphene oxide. Graphene has received wide attention by the researchers’ because of its derivative graphene oxide (GO). GO enhances the permeation factor of PEI polymer due to hydrophilic properties of the filler [22–26] like the presence of rich oxygen groups such as hydroxyl, carboxyl, carbonyl and epoxide groups. These rich oxygen groups exhibit polar properties [27, 28]. The functional groups’ of GO enhances the interface interaction with PEI polymer [29, 30]. The GO contains polar groups which can easily interact with water molecules and it increases the hydrophilicity of the membrane and diffusion rate of permeate side [31, 32]. The water selectivity is improved via the presence of the GO functional groups [33–36].

Modification of most of the inorganic materials have a low separation factor, however nano-GO offers a higher separation performance. GO application is dependent on the presence of hydroxyl groups. Presence of GO hydroxyl groups results in properties such as large surface area, superior flexibility, enhanced optical transmittance, mechanical stiffness, exceptionally high thermal electronic conductivities and permeability to gas and water. These properties have made it a miracle material [36, 37] in membrane and material research. Figure 1 shows the schematic diagram of the chemical structure of GO.

The primary aim of the present research is to furnish a simple and an efficient means of fabrication of flat sheet asymmetric membrane for the dehydration of n-butanol/biofuel mixture. Here, we have prepared polyetherimide membrane containing graphene oxide as an additive and the membrane was prepared by dry thermal treatment method (Hybrid PMDTT). The present research helps in overcoming the defects of the prior art and leads to the production of nano-hybrid asymmetric membrane with single step fabrication technique. The simplified asymmetric manufacturing is a new fabrication method for a two-layer morphology membrane without using a third element for fabrication like the support layer.
Materials & methods

Polyetherimide (PEI) 15 (wt%) was procured from Saudi Arabia (SABIC Company), solvent N-methyl-2-pyrrolidone (NMP) was procured from the United States (J.T. Baker). SONOREX ultrasonicator was used for the solvent degassing.

Fabrication of asymmetric membrane

Graphene oxide was synthesized by a modified Hummers method [38]. The detailed procedures can be found in our previous article [44]. Required polymer solution was prepared by dissolving polyetherimide (PEI) 15 wt% into N-methyl-2-pyrrolidone (NMP as a solvent) and further graphene oxide 0.5 wt% was added portion wise into polymer solution. To avoid any unwanted morphological structure and to make homogenous solution, ultrasonication was performed for 90–120 s. The polymer solution was mechanically stirred (REMI 2MLH) for 24 h. Further, polymer solution was cast on the glass plate using Doctor’s blade (MTI corporation EQ-Se-KTQ-250), then kept in the oven (between 38 –40 °C) for 240 min. The glass plate was removed from the oven and kept at room temperature for 30 min. This duration leads to a stable solvent formation on the glass plate. Finally, glass plate was kept in the oven between 55 to 60 °C for another 120 min. This step has enhanced a dense top layer and spongy bottom layer. Graphene oxide displays a one-atom thick with two dimensions and honeycomb lattice form that has attracted scientist’s’ attention for its notable electrical, physical and mechanical properties. In the experiment, higher proportion of the grapheme oxide was also attempted, however which has resulted in nonhomogenous solution. Hence, 0.5% was the optimum amount of graphene oxide.

Characterization of prepared membrane

Membrane morphological structure was determined via scanning electron microscopy (SEM, JEOL 2100) for the surface and cross-section images. The Fourier transform infrared spectroscopy (FTIR, Bruker Alpha) was employed to display the functional groups by identifying chemical bonds of the components (PEI and GO) in the membrane. As a consequence, the presence of the functional groups influenced the separation factor and the permeation rate. Raman spectra was utilized to identify the disorder in the sp² carbon of the molecule like a fingerprint (Horiba scientific, LabRAM HR). X-ray diffraction (Rigaku Miniflex tabletop) verifies the interstitial space between elements in the membrane. Membrane surface roughness was characterized via atomic force microscopy (AFM, Bruker dimension icon). The degree of hydrophilicity of the membrane was measured by the contact angle water drop.

Pervaporation experiment

The pervaporation performance of asymmetric membrane was exhibited by the permeation rate and separation factor using equations (1) and (2). Feed mixture (n-butanol/water) was pumped across the membrane surface. The membrane cell has 78 cm² of effective area. A vacuum pump was set at 0.05 bar pressure. The permeated vapor was collected in a liquid nitrogen bottle trap. The permeation rate (J, g m⁻² h⁻¹) was obtained according to the equation (1), the separation factor was analysed by the refractometer index. The analysis result was calculated from equation (1) and (2).

\[
J = \frac{Q}{AT}
\]  
(1)

Figure 1. Schematic diagram of the graphene oxide structure.
\[
\alpha = \frac{Y_2}{X_2} \frac{Y_1}{X_1}
\]

where \( J \) and \( Q \) are the flux and the mass permeated over time \( h \) with the surface membrane area \( A \) \((\text{m}^2)\), respectively. \( X_2 \) and \( X_1 \) are the mole fractions of the water and alcohol in the feed side, respectively. While, \( Y_2 \) and \( Y_1 \) indicate the weight fractions of the water and alcohol in the permeate side, respectively.

**Results and discussion**

**Characterization analysis of the nano- graphene oxide**

Figure 1 indicates the schematic diagram of the graphene oxide. The FTIR, TEM and zeta potential results are illustrated in figures 2(a), (b) and Table 1, respectively. FTIR results of GO showed that, oxidation was successful as illustrated by the peak at 1725 cm\(^{-1}\) that displayed a stretching vibration and broad peaks around 3363 cm\(^{-1}\). Peak at 1302 cm\(^{-1}\) corresponds to the stretching vibration and deformation vibration of O–H. The peaks at 1625 and 1218 cm\(^{-1}\) were assigned to C=C and C–O–C. These data proved the formation of carboxylic acid groups on the surface of the graphene.

The TEM results showed a transparent layer of graphene oxide that indicates the complete exfoliation of the graphite. As tabulated in Table 1, the GO contains a negative charge which results in an easier interaction with water molecules and enhances water diffusivity of the membrane. The SEM images display the surface and cross-section images of PMDTT with and without GO present in the membranes. As illustrated in Figures 3(b) and (d), PMDTT membrane contains two-layers; dense top layer and spongy substructure, which is due to thermal fluctuations during drying time. Maintaining the optimum drying period and optimum temperature are the important parameters while fabricating an asymmetric membrane. Figure 3 shows the membrane containing GO, which has comparatively a wider morphological structure. The functional groups on the edge of nanoplate produce negative/positive force so they spread inside the membrane with the minimum overlapping on each other \([38, 39]\). Therefore, the membrane containing GO could provide faster diffusion and water penetration through the membrane, unlike other current techniques which use interfacial polymerization or applying support-layer to provide a two-layer membrane.
FTIR peaks, shown in Figure 4, provide data regarding effects of functional groups in the PMDTT membrane. Figure 4, Polyether-imide and graphene oxide’s FTIR shows different peaks for each material; blue plot shows PEI polymer, the red plot shows PMDT membrane and black plot represents the GO functional group. The fabricated PMDTT membrane presents similar characteristics in its peaks, hence implying that physical changes occurred between the PEI and the GO. The peaks at 2800–3800 cm$^{-1}$ were assigned to a stretching hydroxyl group and intercalated water molecules. The nature of such a broad peak can be explained by the hydroxyl groups attached to the carbon basal plane in different forms, such as tertiary and secondary alcohols, enols, phenols and carboxylic groups. There is a smaller peak at 1713 cm$^{-1}$, which was assigned to the carbonyl groups present in ketones and carboxylic acids located at the edge of the basal plane. The peak at 1625 cm$^{-1}$ originates from non-oxidized aromatic regions in the structure. The peak at 1218 cm$^{-1}$ was assigned to the C–O–C. The fingerprint region was composed of C–C and C–O bonds [37]. The GO and PMDTT absorption bands are observed between 3050 to 3450 cm$^{-1}$ (hydroxyl bonds of GO), while C–H and C = O stretchings were at 2960, 2850 and 1650 cm$^{-1}$, respectively. C–N stretching appeared at 1364 cm$^{-1}$ and C–O stretching is appeared at 1050 cm$^{-1}$, respectively. These results confirmed chemical properties of the membrane components. FTIR results determined two peaks around 1716, and 1364 cm$^{-1}$, these peaks are identified as imide groups in the sample structures [38, 40]. The hydroxyl groups (OH) of the GO interacts with the polar groups of the membrane components via hydrogen bonds. The hydrogen bonds of graphene oxide shifted from 3290 cm$^{-1}$ to 3350 cm$^{-1}$ in the composite (PEI-GO) membrane. The broad band changes indicated OH groups
of the GO surface. This will diminish the hydrogenic bond because of the deposition of PEI polymer in the membrane [38, 41].

Raman spectra presented in figure 5 shows two consecutive peaks in both samples (GO- PMDTT and GO). These consecutive peaks indicate ‘D’ and ‘G’ bands at 1358 and 1598 cm$^{-1}$, respectively. The ‘D’ and ‘G’ bands corresponds to the defective carbon atoms (D band) in a layer of the GO structure and vibrating tangential of carbon in the structure (G band). Therefore, GO presence is confirmed in the GO-PMDTT membrane component. A peak at the ‘G’ band (1598.59 cm$^{-1}$) demonstrates the carbon-carbon bond in the GO-PMDTT membrane like GO sample, this bond can be provided through the PEI polymer and graphene oxide bonds [42].

X-ray diffraction peaks in Figure 6 presents the interlayer crystal inter atomic spacing (d-spacing) of GO powder, PEI and PMDTT membrane. Figure 6 demonstrates the peaks of synthesized GO, which were repeated in the fabricated membrane. The d-spacing value of 9.0 Å of GO has not been changed in PEI and PMDTT. Hence, the polyetherimide structure did not change the inter atomic spacing between the graphene oxide platelets kept almost the same peaks in the GO- PMDTT membrane structure. The free volume of polymer is influenced by the temperature. Increasing the temperature reduces the free volume of the PEI (polymer) structure. Moreover, the temperature has similar effects between inter atomic spacing of the graphene oxide. Temperature plays an important role in maintain the free volume and inter atomic spacing. Hence, pervaporation behavior impacted directly via two main factors: free volume and inter atomic spacing. To dehydrate n-butanol, it is essential to reduce the free space between the PEI and GO molecules. Accordingly, water diffusion increased through the GO-PMDTT membrane and n-butanol molecules are easily trapped and they blocked the inner and outer region of the membrane. So, the separation factor increased based on water channel formation into the membrane components (PEI free volume and GO d-space).

Figure 7 presents the surface roughness and peak valley of membrane by atomic force microscopy. The PMDTT membrane value was different in the top-layer and substructure surface. The AFM results showed that, neat membrane had a higher roughness as compared with the PMDTT with nano-GO which verify the effects of platelets on physical structure. However, this difference is not very impressive.

Table 2 represents the root mean square (RMS) roughness value, which increased with the surface density structure of membranes. Dense surface of PMDTTT membrane had a higher roughness value than the
sponge-like structure of substructure-layer of the membrane. The temperature variation in fabrication techniques affects the maximum peak valley and RMS values. Since the different temperature (high/low) effects on the morphological structure and polymer chain formation in membrane structure. Therefore, RMS value for surface structure of the membrane depends on the membrane fabrication temperature. On the other hand, RMS and the maximum peak valley had a direct connection with temperature and drying time for the fabricated membrane.

Experimental pervaporation results
In order to investigate the impact of membrane morphology structure and GO incorporation on dehydration of n-butanol, experiments were conducted with different temperatures (30, 40 and 50 °C), pressures (0.05, 0.75 and 0.1 bar) and constant concentration (95% wt) variations. The asymmetric membrane pervaporation performance results were compared with the previous similar composition membrane to determine the physical impact on membrane separation performance. Figures 8 and 9 present the permeation rate of n-butanol/water mixture, increasing with pressure, for nano-hybrid and neat membrane, respectively. Separation factor of nano-hybrid PMDTT and neat PMDTT are presented in Figures 10 and 11, respectively. The pervaporation dehydration experiments were carried out in different temperature ranges from 30 to 50 °C. In previous research work, the results showed that permeation rate reduced with temperature in a spongy like membrane versus dense structure membrane [43].

This performance was dependent on drying time and temperature of membrane fabrication that influence the polymer chain in a membrane morphology structure. On the other hand, the novel asymmetric membrane contains both structured layers (sponge-like and dense morphology). Therefore, it is expected that this membrane provides a stable PV separation performance with increasing temperature. Figure 8 shows that the permeation rate of PMDTT increases slightly which verifies the asymmetric morphology structure impact on the permeation rate of n-butanol/water mixture. Theoretically, a dense layer in the membrane separation increases the chances of higher separation factor and resistance of permeation rate. However, PMDTT membrane contains a thin, dense selective layer, which exhibited a stable trend of performance versus the current membranes with dense layer. The presence of GO functional groups and the thickness of dense layer were the main success key to PMDTT performance in dehydration of n-butanol. However, the presence of GO

| Membranes          | Maximum peak-valley | RMS roughness Ra (nm) |
|--------------------|---------------------|-----------------------|
| PMDTT              | 1.7                 | 1.5                   |
| PMTT               | 3.8                 | 2.04                  |
| PMDTT (Top layer)  | 5.07                | 3.34                  |
| PMDTT (Substructure layer) | 2.61              | 2.35                  |
| Neat PEI           | 3.7                 | 3.19                  |

Figure 7. AFM images of fabricated membrane (thin dense top layer) (a), sponge-like sub-structure (b) and polyetherimide membrane (c).
with plenty of functional groups on the edge of GO sheets improved the permeation rate and specifically the separation of water molecules (Figure 9).

The functional groups of GO (epoxy, carboxy and hydroxy) improved the diffusion of feed mixture through the top dense layer and the spongy asymmetric structure of the membrane. The temperature had slight effects from 874 to 973 (mg $^{-2}$ h $^{-1}$) while other membrane temperature increases impressively as compared to the permeation of their feed mixtures. Meanwhile, the PMDTT membrane presented the physiochemical features which were affected by the pervaporation performance, hence the asymmetric structure was responsible for the success of fabricated membrane. Figure 9 shows a neat PMDTT membrane performance and the effects of presence of GO as a filler in PEI polymer. The permeation rate of neat PMDTT membrane is lower than that of hybrid PMDTT, which verified that GO improved the permeation rate of n-butanol/water mixture. The neat PMDTT permeation rate was at a high point around 623 kg $m^{-2}$ h $^{-1}$ while hybrid PMDTT indicated 1111.5 kg $m^{-2}$ h $^{-1}$.
Figures 10 and 11 shows the separation factor performance of hybrid PMDTT and neat PMDTT membranes. As expected, the separation factor of hybrid PMDTT is higher (99.3) than the neat PMDTT membrane (90.9) at 30 °C and 0.005 bar. However, neat PMDTT membrane (Figure 11) exhibited almost constant performance at 30 to 50 °C and 0.005 and 0.01 bars from 90 to 92 although, the separation factor of the hybrid PMDTT membrane shows impressive results for dehydration of n-butanol. Since the purity of n-butanol is an important factor for industrial application, the hybrid PMDTT membrane permeation performance retains the industrial standard with 99.3 purity of n-butanol permeate at lower temperature (30 °C) which is remarkable due to saving of energy at lower temperature and pressure. This phenomenon is the main attention of the industry via economical aspect and yield.
Effect of operating temperature and pressure on PV performance

Figure 10 shows the separation factor results of asymmetric membrane. The separation factor performed higher purity of permeate of water molecules at low temperature. The purity of water molecule was 99.3 wt% at the lowest temperature and pressure (0.005 bar), which is an impressive result for biofuel recovery. The separation factor performance was reduced slightly by increasing the temperature and pressure from 99.3 to 98.5 wt%, which has decreased only 0.5 wt%. Increasing the pressure and temperature, decreases the separation factor. This might be due to the changing of the driving force between n-butanol and water molecule or d-space with the increasing temperature.

Pervaporation separation index (PSI) verifies the positive impact of GO as a nano-filler into PEI polymer. Figure 12 confirms that, the PSI for nano-hybrid PMDTT membrane is much higher than expected results, therefore, GO can be used as an effective enhancer in the polymers for different purposes.

As shown in Table 3, pervaporation separation performance of nano-hybrid PMDTT is different from the neat PEI membrane at a constant concentration (95/5 wt% n-butanol/water). Permeation rate and separation factor were higher in the nano-hybrid PMDTT membrane as compared to the neat PEI membrane. Permeation rate was 897 while neat PEI membrane exhibited only 314 (g m⁻² h⁻¹). The PMDTT membrane indicated an excellent separation performance of 99.3. However, the neat PEI membrane presented 90.9 which was lower than the membrane with graphene oxide. Therefore, graphene oxide had considerable influence on n-butanol dehydration.

Conclusions

We have fabricated a novel asymmetric membrane by applying the economical methods: drying temperature and time. Comparison of hybrid PMDTT membrane with neat PMDTT membrane exhibited the effects of GO and how PEI properties improved towards hydrophilicity favor. The PMDTT membrane was characterized with TEM, SEM, FTIR, zeta potential, AFM, nanoindentation. It was confirmed that, the mechanical and thermal properties of the GO/PEI nanohybrid membranes were significantly improved after incorporating GO into the PEI matrix. The concentrations of water at the permeate side of hybrid and neat PMDTT were 99.3 and 90.9 wt.%,

| Membrane Type | Nano-hybrid PMDTT | Neat PEI membrane | Nano-hybrid PMDTT | Neat PEI membrane |
|---------------|------------------|-------------------|-------------------|-------------------|
| Temperature (°C) | Permeation rate (g m⁻² h⁻¹) | Permeation rate (g m⁻² h⁻¹) | Separation factor | Separation factor |
| 30            | 897.4            | 314.1             | 99.3              | 90.9              |
| 40            | 973.1            | 334.6             | 98.8              | 91.2              |
| 50            | 945.3            | 367.9             | 98.5              | 92.4              |

Figure 12. Pervaporation separation index of PMDTT and neat PMDTT membranes.

Table 3. Comparison of nano-hybrid membrane with neat PEI membrane.

Effect of operating temperature and pressure on PV performance

Figure 10 shows the separation factor results of asymmetric membrane. The separation factor performed higher purity of permeate of water molecules at low temperature. The purity of water molecule was 99.3 wt% at the lowest temperature and pressure (0.005 bar), which is an impressive result for biofuel recovery. The separation factor performance was reduced slightly by increasing the temperature and pressure from 99.3 to 98.5 wt%, which has decreased only 0.5 wt%. Increasing the pressure and temperature, decreases the separation factor. This might be due to the changing of the driving force between n-butanol and water molecule or d-space with the increasing temperature.

Pervaporation separation index (PSI) verifies the positive impact of GO as a nano-filler into PEI polymer. Figure 12 confirms that, the PSI for nano-hybrid PMDTT membrane is much higher than expected results, therefore, GO can be used as an effective enhancer in the polymers for different purposes.

As shown in Table 3, pervaporation separation performance of nano-hybrid PMDTT is different from the neat PEI membrane at a constant concentration (95/5 wt% n-butanol/water). Permeation rate and separation factor were higher in the nano-hybrid PMDTT membrane as compared to the neat PEI membrane. Permeation rate was 897 while neat PEI membrane exhibited only 314 (g m⁻² h⁻¹). The PMDTT membrane indicated an excellent separation performance of 99.3. However, the neat PEI membrane presented 90.9 which was lower than the membrane with graphene oxide. Therefore, graphene oxide had considerable influence on n-butanol dehydration.
respectively. Hybrid membranes showed a 78.3% enhanced permeation rate. This hybrid PMDTT membrane performance could be ascribed mainly due to the presence of graphene oxide in the dense top layer. Such membranes showed comparable properties regarding the separation process for different applications in the same categories. It was found that the incorporation of GO into PEI matrices is beneficial for the improvement of membrane selectivity. However, further research is still needed to achieve a truly molecular-level GO dispersion on the substrate surface and in turn to build upon the relationship between the separation performance and nanohybrid structure.

Acknowledgments

This project was funded by the Deanship of Scientific Research (DSR) at King Abdulaziz University, Jeddah, under grant no. KEP–54–130–38. The authors, therefore, acknowledge with thanks DSR for technical and financial support.

ORCID iDs

Inamuddin @ https://orcid.org/0000-0003-0524-9940

References

[1] Manshad S, Nawawi M N M, Szegar M R, Hassan B H and Alamaria A M 2016 Membranes with favorable chemical materials for pervaporation process: a review Journal of Membrane Science & Technology 6 4
[2] Purkait M K, Singh R, Haldar D and Mondal P 2020 Thermal Induced Membrane Separation Processes (Amsterdam: Elsevier)
[3] Peng P, Shi B and Lan Y 2011 A review of membrane materials for ethanol recovery by pervaporation Journal Separation Science and Technology 46 234–46
[4] Smitha R, Sahanya D and Ramakrishna M 2004 Separation of organic–organic mixtures by pervaporation a review J. Membr. Sci. 241 1–21
[5] Purkait M K and Singh R 2018 Membrane Technology in Separation Science (United States of America: CRC Press, Taylor & Francis)
[6] Pham T T, Monajem I M, Mollaamin F and Dang C M 2020 Biointerface in Applied Chemistry 10 4853–63
[7] Mahmoud E, Ng L Y, Abbad M M and Mohammad A W W 2015 Novel nanohybrid polysulfone membrane embedded with silver nanoparticles on graphene oxide nanopolymers Chem. Eng. J. 277 1–10
[8] Hung M Y et al 2003 Pervaporation separation of water/ethanol mixture by TGN/PSF blending membrane Eur. Polym. J. 39 2367–74
[9] Demirbaş A 2006 Bioethanol from cellulosic materials: a renewable motor fuel from biomass Journal Energy Sources 27 327–337
[10] Huang H, Ramaswamy S, Tschirner U W and Ramarao B V 2008 A review of separation technologies in current and future biorefineries Separation and Purification Technology 62 1–28
[11] Sridhar S, Smitha B and Shaik A 2007 Pervaporation-based separation of methanol/methane mixtures a review Journal Separation & Purification Reviews 34 1–33
[12] Yang G, Xie Z, Cran M, Ng D and Gray S 2019 Enhanced desalination performance of poly (vinyl alcohol)/carbon nanotube composite pervaporation membranes via interface engineering J. Membr. Sci. 579 40–51
[13] Wang N, Ji S, Li J, Zhang R and Zhang G 2014 Poly(vinyl alcohol)–graphene oxide nanohybrid ‘pore-filling’ membrane for pervaporation of toluene/n-heptane mixtures J. Membr. Sci. 455 113–20
[14] Ibrahim G P S, Isloor A M, Inamuddin, Asiri A M, Ismail A F, Kumar R and Ahamed M I 2018 Performance intensification of the polysulfone ultrafiltration membrane by blending with copolymer encompassing novel derivative of poly (stylene-co-maleic anhydride) for heavy metal removal from wastewater Chem. Eng. J. 353 425–35
[15] Kumar R, Isloor A M and Ismail A F 2014 Reparation and evaluation of heavy metal rejection properties of polysulfone/chitosan, polysulfone/N-succinyl chitosan and polysulfone/N-propylphosphonyl chitosan blend ultrafiltration membranes Desalination 350 102–8
[16] Shenvi S, Ismail A F and Isloor A M 2014 Preparation and characterization study of PPIEES/chitosan composite membrane crosslinked with tripropylphosphate Desalination 344 90–6
[17] Ibrahim G S, Isloor A M, Inamuddin, Asiri A M, Ismail N, Ismail A F and Ashraf G M 2017 Novel, one-step synthesis of zwitterionic polymer nanoparticles via distillation–precipitation polymerization and its application for dye removal membrane Sci. Rep. 7 1–6
[18] Ibrahim G S, Isloor A M, Moslehyan A and Ismail A F 2017 Bio-inspired, fouling resistant, tannic acid functionalized halloysite nanotube reinforced polysulfone loose nanofiltration hollow fiber membranes for efficient dye and salt separation Journal of Water Process Engineering 20 138–48
[19] Ibrahim G S, Isloor A M, Yulivati E and Ismail A F 2019 Carbon-based nanocomposite membranes for water and wastewater purification Advanced Nanomaterials for Membrane Synthesis and its Applications (United States of America: Elsevier) 2 23–44
[20] Hebbar R S, Isloor A M, Anand K and Ismail A F 2016 Fabrication of polydopamine functionalized halloysite nanotube/polyetherimide membranes for heavy metal removal J. Mater. Chem. A 4 764–74
[21] Hebbar R S, Isloor A M, Prabhu B, Inamuddin, Asiri A M and Ismail A F 2018 Removal of metal ions and humic acids through polyetherimide membrane with grafted bentonite clay Sci. Rep. 8 4665
[22] Jones T D A et al 2019 Direct metallisation of polyetherimide substrates by activation with different metals Surf. Coat. Technol. 360 285–96
[23] Zhao I et al 2013 Incorporating zwitterionic graphene oxides into sodium alginate membrane for efficient water/alcohol separation American Chemical Society 8 2097–103
[24] Chen X, Liu G, Zhang H and Fang Y 2015 Fabrication of graphene oxide composite membranes and their application for pervaporation dehydration of butanol Chin. J. Chem. Eng. 23 1102–9
[25] Ding R et al 2013 Graphene oxide–embedded nanocomposite membrane for solvent resistant nanofiltration with enhanced rejection ability Chem. Eng. Sci. 138 227–38
[26] Yang M, Zhao C, Zhang S, Li P and Hou D 2017 Preparation of graphene oxide modified poly (m-phenylene isophthalamide) nanofiltration membrane with improved water flux and antifouling property Appl. Surf. Sci. 394 149–59
[27] Dharupanedi S, Anjanapira R V, Han J M and Aminabhavi T M 2014 Functionalized graphene sheets embedded in chitosan nanocomposite membranes for ethanol and isopropanol dehydration via pervaporation American Chemical Society 53 1447–84
[28] Khayeta M, Essalhi M, Qtaishat M R and Matsuurad T 2019 Robust surface modified polyetherimine hollow fiber membrane for long-term desalination by membrane distillation Journal Desalination 466 107–17
[29] Ng L Y, Ng C Y, Mahmoudi E, Ong C B and Mohammad A W 2018 A review of the management of inflow water, wastewater and water reuse by membrane technology for a sustainable production in shrimp farming Journal of Water Process Engineering 23 27–44
[30] Chong W C et al 2017 Polyvinylidene fluoride membranes with enhanced antibacterial and low fouling properties by incorporating ZnO/rGO composites Desalin. Water Treat. 96 12–21
[31] Liu G, Jin W and Xu N 2015 Graphene-based membranes Chemical Society Review 44 5016–30
[32] Zhao J et al 2013 Fabricating graphene oxide–based ultrathin hybrid membrane for pervaporation dehydration via layer–by-layer self-assembly driven by multiple interactions J. Membr. Sci. 487 162–72
[33] Nan Q and Cao B 2016 Fabrication of positively charged nanofiltration membrane via the layer–by-layer assembly of graphene oxide and polyethylenimine for desalination Appl. Surf. Sci. 387 521–8
[34] Wang N, Ji S, Zhang G, Li J and Wang L 2012 Self-assembly of graphene oxide and polyelectrolyte complex nanohybrid membranes for nanofiltration and pervaporation Chem. Eng. J. 213 318–29
[35] Khairnar D B and Pangarkar V G 2004 Dehydration of glycerin/water mixtures by pervaporation using homo and copolymer membranes Journal of the American Oil Chemists’ Society 81 505–10
[36] Purkait M K, Mondal P and Chang C T 2019 Stimuli-Responsive Polymeric Membranes (United States of America: Academic Press (Elsevier))
[37] Ganesh B M, Isoleer A M and Ismail A F 2013 Enhanced hydrophilicity and salt rejection study of graphene oxide–polysulfone mixed matrix membrane Desalination 313 199–207
[38] Wang N, Ji S, Li J, Zhang R and Zhang G 2014 Poly(vinyl alcohol)-graphene oxide nanohybrid ‘pore-filling’ membrane for pervaporation of toluene/h- heptane mixtures J. Membr. Sci. 455 113–20
[39] Mohanty K and Purkait M K 2011 Membrane Technologies and Applications (USA: CRC Press, Taylor & Francis) Cat.: K10293,
[40] Yang M, Donald R P and Chung T S 2014 Free-standing graphene oxide thin films assembled by a pressurized ultrafiltration method for dehydration of ethanol J. Membr. Sci. 458 199–208
[41] Liang Y et al 2013 Preparation and characterization of HPEI-GO/PES ultrafiltration membrane with antifouling and antibacterial properties J. Membr. Sci. 447 452–62
[42] Thangavel S and Venugopal G 2014 Understanding the adsorption property of graphene–oxide with different degrees of oxidation levels Powder Technol. 257 141–8
[43] Lee J et al 2013 Graphene oxide nanoplatelets composite membrane with hydrophilic and antifouling properties for wastewater treatment J. Membr. Sci. 448 223–30
[44] Kumar M et al 2019 Use of cellulose acetate/polyphenyl sulfone derivatives to fabricate ultrafiltration hollow fiber membranes for the removal of arsenic from drinking water Int. J. Biol. Macromol. 129 715–27