

New (polydimethylsiloxane/graphene oxide)/poly valerolactone pervaporation composite membrane: preparation, characterization and ethylene dichloride/water separation evaluation

Samira Safaei Nasab¹, Ali Arasteh Nodeh¹, Susan Khosroyar^{1*},
Mahmod Reza Khadangi Mahrod¹, Vahid Hakimzadeh²

¹Department of Chemical Engineering, Quchan Branch, Islamic Azad University, Quchan, Iran.

²Department of Food Science and technology, Quchan Branch, Islamic Azad University, Quchan, Iran.

*Corresponding author: susankhosroyar@yahoo.com

Original Research

Abstract:

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In this research, a novel type of pervaporation membrane was developed by (polydimethylsiloxane(PDMS)/graphene oxide(GO))/poly valerolactone (PVL) composite membrane. This prepared membrane was used to separate ethylene dichloride from water. The electrospinning method was used to nanofiber PVL preparation as a support layer for the composite membrane. To increase the selectivity of the optimized PVL nanofiber membrane and increase the affinity with ethylene dichloride; the membrane was coated with a dense PDMS/GO layer. The membranes were characterized by SEM, FTIR, contact angle and swelling measurements. Also the membrane performance in ethylene dichloride separation and its separation factors versus temperature (30 – 70° C) was evaluated. Results show that with increasing temperature up to 70° C, the total flux and the separation factor of (PDMS/GO)/PVL simultaneously increase from about 113 to 191 g/(m²h) and from 3.4 to 11.65, respectively.

Keywords: Electrospinning; Poly valerolactone; Polydimethylsiloxane; Selectivity

1. Introduction

1,2-dichloroethane is a volatile hydrocarbon and one of its applications is the synthesis of vinyl chloride monomer and other chlorinated solvents, as an additive to leaded gasoline as a lead scavenger [1–3]. The effects of exposure to ethylene dichloride include nervous system weakness, nausea and vomiting. This compound has little potential for bioaccumulation, and inhalation in air is likely to be the main source of human exposure [4]. The results of research on experimental animals showed that 1,2-dichloroethane has relatively acute toxic effects on them, such that the liver and kidneys are damaged due to exposure to EDC [5]. The lowest reported effect levels were 49 to 82 mg/kg body weight per day for ingestion and inhalation respectively (increased liver weight in rats exposed for 13 weeks) and

202 mg/m³ (effects on liver and kidney function in rats which were exposed for 12 months) [6]. According to these data, 1,2-dichloroethane is considered a possible human carcinogen, so exposure should be controlled. With these explanations the new approach is required to removing EDC. Green technology [7], membrane filtration [8], Advanced oxidation processes (AOPs) [9], adsorption and other conventional water treatment technologies [10–12] were used to EDC removal. Some of these methods have the disadvantages of economical environmental protection, high input costs, a long duration and requirements for equipment and space [13]. Therefore, to separate EDC from wastewater, a cost-effective, efficient and EDC recyclable technology is necessary. Recently, pervaporation (PV) has been used as one of the most promising areas of membrane technologies, in the separation of heat-sensitive biomaterials, boiling or

azeotropic liquid mixtures and water or organic materials from their mixtures due to advantages in economy, environmental aspects and process safety [14, 15]. In pervaporation process, the membrane has the main effect on process. Many materials such as polymeric, inorganic and hybrid have been used as the PV membrane material [16]. Recently, polymers are used in PV membrane construction due to easy processing, controlled and adjustable transport properties, satisfactory mechanical stability and low cost [17]. Despite the stated capabilities for polymeric membranes used in pervaporation process, these membranes have disadvantages such as low chemical and thermal stability, poor resistance to hazardous environments, and especially the inherent trade-off between permeability and selectivity [18]. Among the membranes that used in the PV process, there is a unique type of membrane, known as mixed matrix membrane, which can be made using two or more different materials in order to improve membrane performance [19]. The problem with most membranes in PV separation is the lack of simultaneous increase in permeability and selectivity. The use of some additives in the membrane structure can solve this problem [20]. Graphene oxide (GO) is one of material that used as an additive to modify polymeric membrane properties due to its hydrophilic functional groups [21].

In this research, a composite membrane for EDC pervaporation process fabricated and evaluated in terms of properties and structure. Poly valerolactone (PVL) was used as the substrate of the composite membrane in the regard of its better mechanical strength. Polydimethyl siloxane (PDMS) was used as a constituent material of the selector layer. In order to increase the affinity of PDMS to ethylene dichloride and to increase the separation factor of ethylene dichloride to water, a hydrophilic graphene oxide (GO) nanoparticle was used. The performance of (PDMS/GO)/PVL composite membrane on separation was evaluated and the effect of temperature on membrane flux and EDC/water separation factor was systematically studied.

2. Materials and methods

2.1 Materials

The poly (valerolactone) (PVL) (MW = 4500 g/gmol), Dimethylformamide (DMF) and acetone were purchased

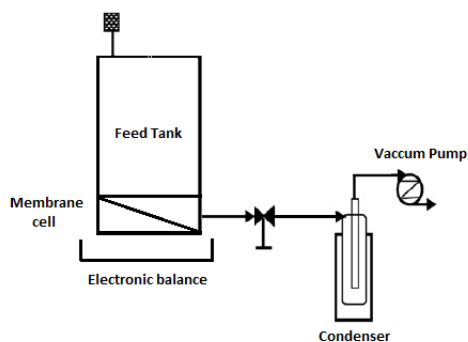


Figure 1. The schematic diagram of the experimental apparatus that used in this study.

from QRec. Silicone potting compound produced by Momentive (USA) and was used to fabricate the crosslinked PDMS membrane. Graphene oxide (GO) was supplied from Allightec (USA). Deionized (DI) water was obtained by a purification system (Millipore).

2.2 Methods

2.2.1 Membrane preparation

PVL nanofiber membranes were prepared using electrospinning method. At first, 16 wt% of PVL dissolved in the DMF solvent. 15 mL of the PVL solution was used for PVL nanofiber membrane fabrication. The solution is stirred vigorously for 2 hours, and then the glass ware of this solution is placed in silicone oil at 50° C and stirred overnight. Then the glass ware is taken out of the silicone oil bath and placed at room temperature. After that, it is the turn to add acetone to the PVL-DMF solution. After adding acetone to the above solution, it was stirred overnight at room temperature. After the solution preparation, the electrospinning process is performed. For nanofiber preparation, 15 mL of the prepared PVL solution transferred to the syringe. The syringe pump was set at a flow rate of 2 mL/h and the needle was attached to the rotor base with a wire. In order to collect the membrane on a flat surface, a piece of aluminum foil was stuck on the rotating drum. When the power supply was turned on, the solution was first pumped at a high pumping speed to reach the needle. After that, the pumping speed was adjusted to the designed value. Since the structure of electrospun PVL membrane would be vilious, so that post-treatment operation is necessary. In order to optimize the PVL nanofiber membrane, heat pressing was done. In order to form a uniform surface of the PVL membrane, the flattening process of the PVL membrane is necessary. So, the PVL membrane was firstly put in ethanol, and then washed by ultra-pure water. Before being heated up the membrane was flattened by a tissue paper and dried in the room temperature. For heat pressing process of membrane, two sides of the membrane were covered by the aluminum foil and then was put under the heating surface. After finishing the heat pressing process, the PVL membrane was wetted by ethanol. Then, the membranes were drowning in DI water. The temperature of 55° C and duration times of 30 min were tested for heat pressing process. After fabricating the membrane support, the selective dense PDMS/GO layer was coated on the optimized PVL nanofiber membrane. In order to uniformly coating a thin

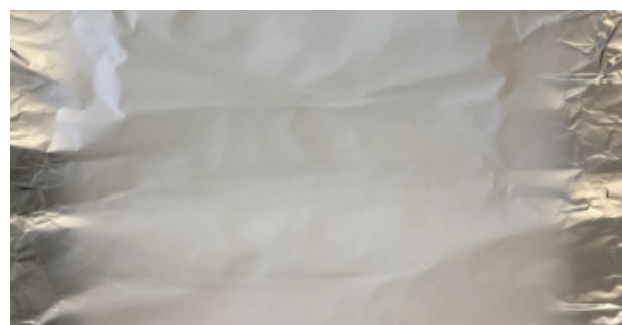


Figure 2. Electrospun PVL membrane on the aluminum foil.

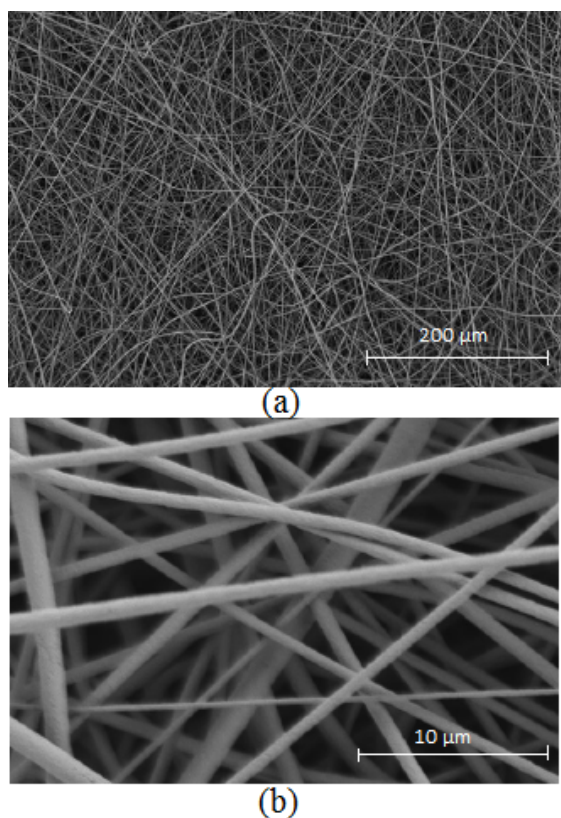


Figure 3. SEM images of the PVL nanofiber membrane (16 wt%) at (a) $500\times$ of magnification and (b): $10000\times$ of magnification.

layer of PDMS/GO on the PVL membrane, the spin coating was used. For this purpose, PDMS/GO solution should be prepared. For PDMS/GO solution preparation, the silicone elastomer, curing agent and hexane were added to a baker and well mixed. After preparation of this solution, GO nanoparticles were added to it and placed in an ultrasonic bath for 30 minutes. Then, a petri dish was fixed on the rotating disk of the spin coater and the PDMS/GO solution was dropped on the spinning petri dish. Over time 1 min, the coated dish was placed at oven and heat up to 60°C for 5 min until the PDMS on the petri dish became extremely viscous. In the next step, the PVL membrane was placed on the PDMS/GO viscose layer, and was heated in an oven at 50°C for 10 minutes until the PDMS/GO completely turned into a solid. After the petri dish cools down at room temperature, the composite membrane was separated from the petri dish for characterization.

2.2.2 Characterization

The composite membrane morphology was evaluated by a scanning electron microscope. The SEM images were made by a JSM-IT500 device with an accelerating voltage of 1.25 kV.

The contact angle measurement was measured by Acam-HSC (India) to evaluate the contact angles of 45 wt.% ethylene dichloride solution on the surface of membranes. Fourier transform infrared spectroscopy was used by a Thermo Nicolet iS10 FT-IR instrument to analyze the chemical structure of prepared membranes.

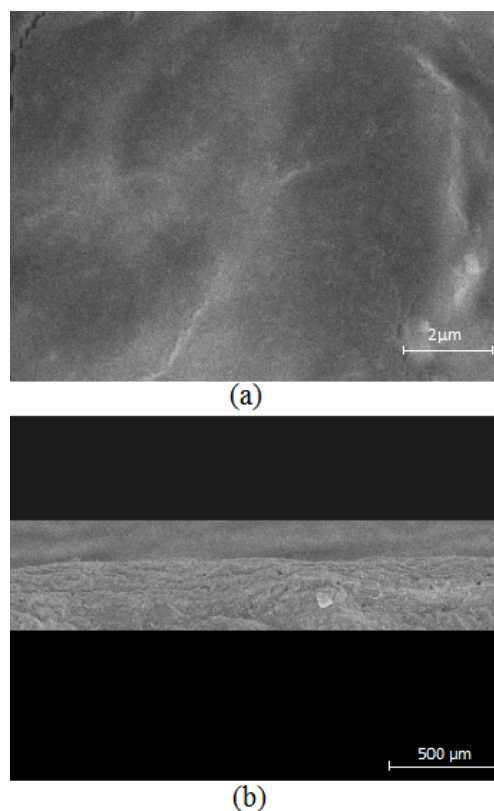


Figure 4. The surface and cross section SEM images of PVL membrane (a) Surface image, (b) Cross section.

The degree of swelling was calculated by measuring the weights of the swollen sample soaked in 70 wt.% EDC aqueous solution and dry membrane and measured by following Eq. 1 [22].

$$\text{Degree of swelling} = \frac{M_s - M_d}{M_d} \quad (1)$$

where M_s and M_d denote the mass of the swollen and dry membranes (g), respectively.

A differential scanning calorimeter (DSC, 204F1, Nicolet) was used to volume-phase transition temperature (VPTT) analysis of the samples. In this analysis the temperature range between 20°C to 50°C , a constant heating rate of $1^{\circ}\text{C min}^{-1}$ under a nitrogen atmosphere and a flow rate of 50 mL min^{-1} were considered.

2.2.3 Pervaporation experiments

The schematic diagram of the experimental apparatus is shown in Figure 1. A 2% w/w aqueous solution of ethylene dichloride was pumped from a reservoir to the surface of membrane in the permeation module.

The reservoir was placed on an electronic balance to measure the weight loss of the ethylene dichloride solution. By measuring the weight loss of ethylene dichloride solution, the overall membrane flux is estimated. A negative gradient of pressure was created by a vacuum pump (model GEM-8890, Welch Vacuum Technology Inc., Skokie, Illinois). The vapor phase permeate that was exposed to vacuum, liquefied in a cold-finger condenser trap immersed in liquid nitrogen bath. The concentrations of feed and permeate

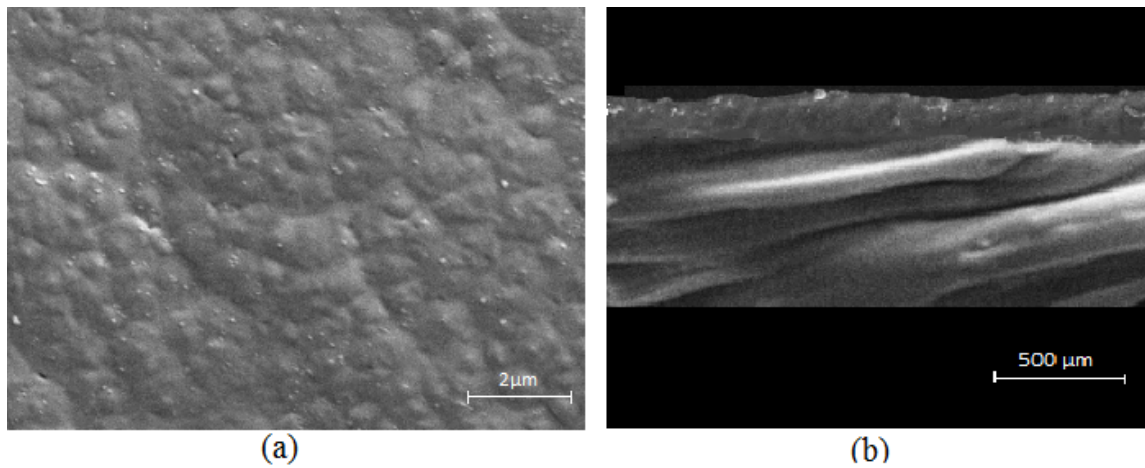


Figure 5. The SEM images of the surface and cross section structures of (PDMS/GO)/PVL composite membranes.

were also detected by the gas chromatograph (model HP 5890 with FED detector, Hewlett-Packard, Texas) equipped with a DB-WAX 20M column 30 m long and 0.25 mm diameter.

The total permeation flux is calculated via the following equation [23]:

$$J_t = \frac{m}{A \cdot t} \quad (2)$$

where m is the mass of the permeate (g), t is the permeation time (h) and A is the effective area of membrane.

The flux of the ethylene dichloride (J_e , $\text{g m}^{-2} \text{h}^{-1}$) was given by Eq. 3 [24]:

$$J_e = \frac{C_0 M_0 - C_t M_t}{A \cdot t} \quad (3)$$

where C_0 and C_t are the concentrations of ethylene dichloride at time 0 and time t , respectively. The water flux (J_w , g h^{-1}) was calculated using Eq. 4 [25]:

$$J_w = J - J_e \quad (4)$$

The separation factor (α), is calculated via the following equation:

$$\alpha = \frac{(Y_w/Y_e)}{(X_w/X_e)} \quad (5)$$

where X and Y are the weight fractions of component in the feed and permeate respectively, the signs of e and w refer to water and ethylene dichloride.

3. Results and discussion

3.1 SEM analysis

The electrospun PVL membrane is composed of PVL nanofibers. The resulting membrane was white and soft and fluffy without post treatment. So that it could be easily torn and after tearing the layer by layer structure was clearly visible. The whole electrospun PVL membrane on the aluminum foil is shown in Figure 2 and the structure of the membrane fibers is shown in Figure 3. Also, a relatively uniform surface was formed by electrospinning for PVL membrane (Figure 4a) and in an optimal condition; there is no beads or droplets on its structure (Figure 4b).

The SEM images of the surface and cross section structures of (PDMS/GO)/PVL composite membranes are shown in Figure 5. A uniform distribution of GO nanoparticles can be seen in the PDMS polymer matrix. According to the figure, it can be understood that the skin layer of PDMS/GO is well connected to the supported PVL membrane. The layered-like supporting layer and the thin skin layer of the

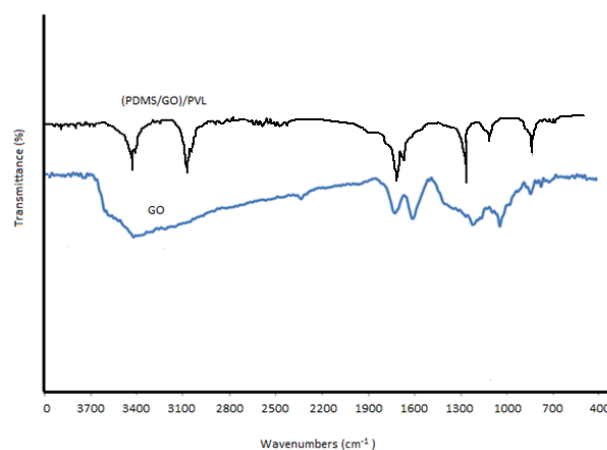


Figure 6. FTIR spectra of coated PVL membrane by (PDMS/GO).

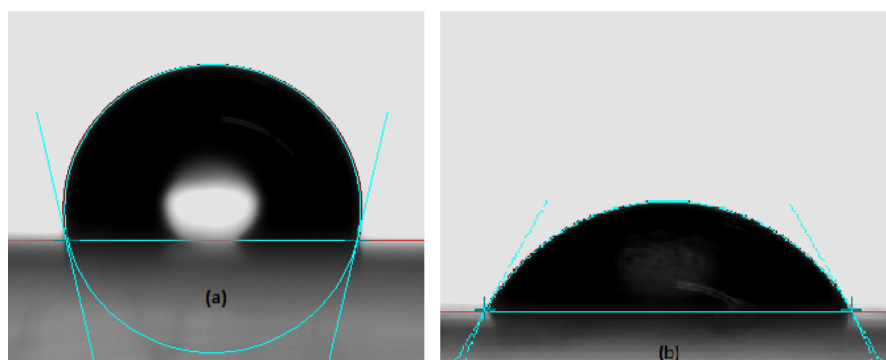


Figure 7. The contact angles of (PDMS/GO)/PVL membrane (a) 0 wt.% of GO and (b) 1.5 wt.% of GO.

composite membrane shall lead to the high selectivity and flux of the pervaporation membrane.

3.2 FTIR analysis

Figure 6 illustrates the FTIR spectrum of GO, PDMS/PVL and (PDMS/GO)/PVL membranes. For the spectrum of GO, C=O stretching vibration corresponded to peak at 1732 cm^{-1} . C-OH stretching vibration appeared at $\sim 1235\text{ cm}^{-1}$. The peaks at 1038 cm^{-1} and 3445 cm^{-1} were due to the C-O stretching vibration for the epoxy group and O-H stretching vibration respectively. Also the skeletal vibration of unoxidized graphitic domains appeared at 1623 cm^{-1} .

In the (PDMS/GO)/PVL composite membrane FTIR spectra, a wide peak at 3465 cm^{-1} represents the O-H stretching of GO, which confirms the GO existence in the composite membrane. The peaks at 1263 cm^{-1} , 1191 cm^{-1} , and 783 cm^{-1} , represent the functional groups of Si-CH₃, O-Si-O and Si-(CH₃)₂ of the PDMS molecule. Also the characteristic bands at 1732 and 1622 cm^{-1} are related to the carbonyl (C=O) of biodegradable polyester (PVL).

3.3 Contact angle measurement

The results of the water contact angle measurement are illustrated in Figure 7. As can be seen the unmodified PDMS surface is hydrophobic with a contact angle of 103° . The hydrophilicity of PDMS can be improved significantly by the addition of hydrophilic GO nanoparticles. The presence of oxygenated functional groups like epoxy, hydroxyl,

carboxyl and carbonyl groups on its structure, causes to increase the membrane hydrophilicity. The addition of GO nanoparticles (1.5 wt.%) gently improves the final membrane surface hydrophilicity and the contact angle reaches to 57° .

3.4 Swelling measurement

The equilibrium swelling ratio of (PDMS/GO)/PVL membrane in 1000 ppm ethylene dichloride solution as a function of the external temperature ($20 - 50^\circ\text{C}$) is shown in Figure 8. As can be seen, the addition of GO into PDMS surface layer causes the swelling ratio increasing. But with temperature increasing, the equilibrium swelling ratio of membranes decreases. This reduction is rapid around the Volume Phase Transition Temperature (VPTT) of PDMS polymer (32°C). In fact, the incorporation of GO into the PDMS surface membrane can change the hydrophobic/hydrophilic characteristic of the membrane. The GO nanoparticles with hydrophilic property increase the equilibrium swelling ratio of the membrane. On the other hand, at below temperature of VPTT, the hydrophilic groups on GO structure interacted strongly with water molecules and cause the swelling of the polymer to increase. At temperatures more than VPTT, the hydrophobic interactions on the surface of membrane related to PDMS between hydrophobic groups strengthened and prevent membrane swelling. Forasmuch as, high swelling ratio has a negative effect on diffusive selectively

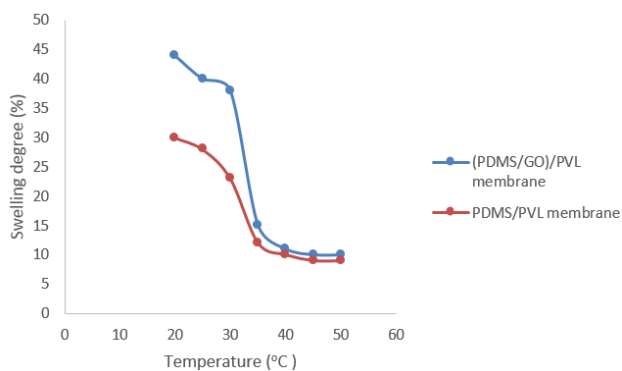


Figure 8. The equilibrium swelling ratio of prepared membranes at different temperatures.

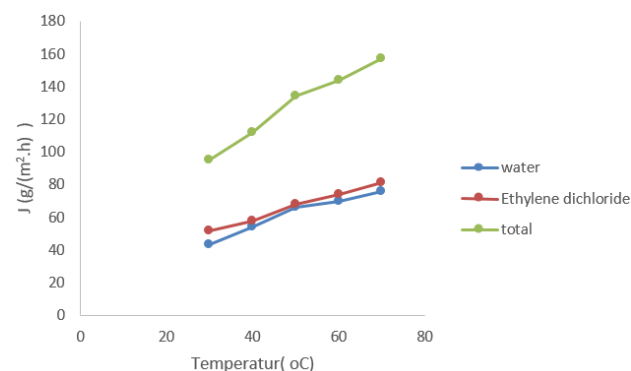


Figure 9. The flux of the PDMS/PVL composite membrane at various temperatures for ethylene dichloride solution separation in pervaporation process.

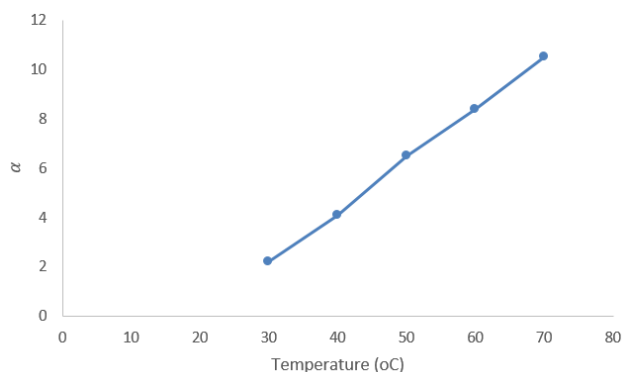


Figure 10. The separation factor of the PDMS/PVL composite membrane at various temperatures for ethylene dichloride solution separation in pervaporation process.

of membrane during pervaporation process, the highest temperature is considered for the lowest degree of swelling.

3.5 Membrane performance evaluation in pervaporation process

Flux and separation factor are the two main features of the membrane in the pervaporation process. The flux and separation factors of the PDMS/PVL composite membrane at various temperatures (30 – 70° C) for ethylene dichloride solution separation are shown in Figures. 9 and 10 respectively. It is obviously that with increasing temperature up to 70° C, the total flux and the separation factor simultaneously increase from about 95 to 157 g/(m².h) and from 2.2 to 10.5, respectively.

Also the effect of temperature on the separation properties and fluxes was investigated for (GO/PDMS)/PVL membrane in Figures. 11 and 12. As can be seen, all of fluxes including water and ethylene dichloride increase with the temperature increasing. It might be explaining by the fact that increasing the temperature has a direct effect on the penetration of the components. Moreover, as the temperature increases, the vapor pressure of the two components increases. So, the pressure difference created on both sides of the membrane due to the increase in temperature causes

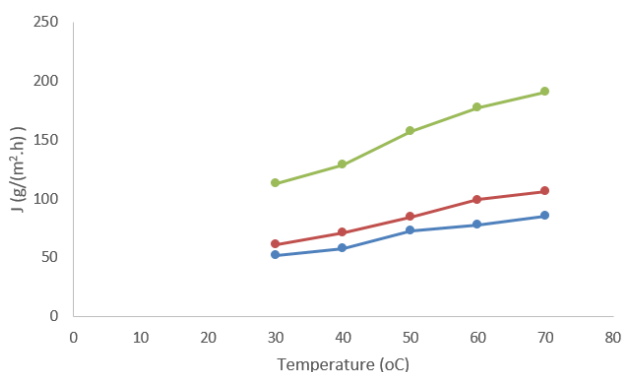


Figure 11. The flux of the (PDMS/GO)/PVL composite membrane at various temperatures for ethylene dichloride solution separation in pervaporation process.

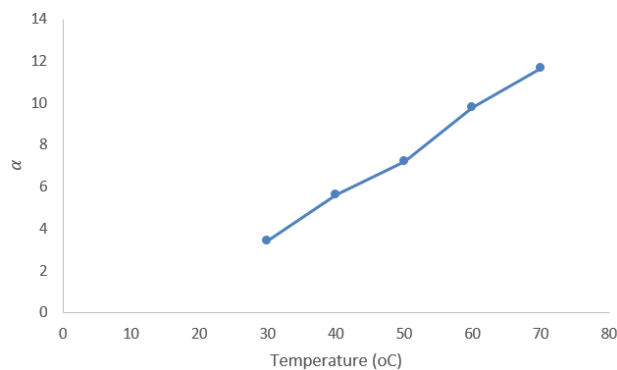


Figure 12. The separation factor of the (PDMS/GO)/PVL composite membrane at various temperatures for ethylene dichloride solution separation in pervaporation process.

the flux to increase. The presence of nanoparticles also increases the flux. This is due to the hydrophilicity of graphene oxide and the affinity of its hydroxyl groups to chlorine ions of ethylene dichloride.

According to Arrhenius equation [26], the logarithm of the flux is inversely proportional to the temperature. so for two composite membranes; there is a higher flux at higher temperature. But the flux increase for ethylene dichloride is greater than for water. It is due to the higher activation energy of ethylene dichloride than that of water. Thus the separation factor increases with temperature. Since the GO shows higher affinity to ethylene dichloride, so it is expected that to have a higher separation factor.

4. Conclusion

In this research, a novel type of pervaporation membrane was developed by (polydimethylsiloxane (PDMS)/ Graphene oxide (GO))/poly valerolactone (PVL) composite membrane and subjected for ethylene dichloride/water separation. The electrospinning method was used to nanofiber PVL preparation as a support layer for the composite membrane. SEM results showed that the (PDMS/GO)/PVL composite membrane had the similar structure to PDMS/PVL, so that the GO nanoparticles are uniformly distributed in the PDMS polymer matrix and the PDMS/GO skin layer is well attached to the supported PVL membrane. The FTIR spectra of the composite membrane confirmed the presence of functional groups of GO and PDMS in the composite membrane structure. Contact angle measurement showed that the hydrophilicity of PDMS layer improved significantly by the addition of GO nanoparticles (1.5 wt.%) in which the contact angle reaches to 57°. The effect of temperature on the separation properties and total fluxes was investigated for (PDMS)/PVL and (GO/PDMS)/PVL membranes. Results show that the total flux and the separation factor of (PDMS)/PVL simultaneously increase from about 95 to 157 g/(m².h) and from 2.2 to 10.5, respectively. For (GO/PDMS)/PVL membranes, the total flux and the separation factor of (PDMS)/PVL simultaneously increase from about 113 to 191 g/(m².h) and from 3.4 to 11.65, respectively.

Ethical approval:

This manuscript does not report on or involve the use of any animal or human data or tissue. So the ethical approval does not applicable.

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Authors Contributions:

All authors have contributed equally to prepare the paper.

Availability of data and materials:

The data that support the findings of this study are available on request from the corresponding author.

Conflict of Interests:

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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