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Effective Separationof Carbon Dioxide using Graphene Oxide Based Membrane

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Abstract. Graphene oxide (GO) was made *via* improved Hummer's method, which excludes the use of sodium nitrate ($NaNO_3$) has done in conventional Hummer's method. The exclusion of $NaNO_3$ from the process eliminates nitrogen dioxide/dinitrogen tetraoxide (NO_2/N_2O_4) toxic gases. The presence of sodium (Na^+) and nitrate (NO_3^-) ions in the final product, therefore making this process more environmentally friendly and impurities free relatively to Hummer's method. XRD and FTIR characterized prepared membranes. Graphene oxide exhibits a sharp peak at 11.40° in the XRD test. From FTIR results, the broad absorption peak at 2950.98 cm^{-1} can be recognized as the stretching and bending trembling of hydroxyl groups and surface absorbed water. Furthermore, GO indicates weak absorption peaks related to the presence of GO at about 1538.85 - 1650.39 cm^{-1}, conforming to C=C, C-OH and C-O-C stretching vibrations in FTIR. The peaks at 1377 cm^{-1}, 1062 cm^{-1} and 1375 cm^{-1} 1064 cm^{-1} show the deformation of the -OH functional group, epoxy C-O-C stretching and carboxyl C-O stretching pulsations. The separation of carbon dioxide (CO_2) and nitrogen (N_2) gas was observed by calculating the permeability of CO_2 gas and flux through a GO membrane with the help of flow rate, concentration and gas pressure at the inlet and outlet of a gas module.The separation of carbon dioxide gas increases as the permeability and flux increase. It was observed that CO_2 gas separated through the GO membrane from N_2 gas in the membrane.

Keywords: chemical vapour deposition, graphene oxide, carbon dioxide, Hummer's method, polyvinylidene fluoride membrane

Introduction

The world is facing various sets of circumstances. However, it also significantly impacts our daily lives by affecting our environment. From the beginning of the industrial revolution, humans have started to rely on fossil fuels heavily. These fossilfuels are organic compounds composed of hydrogen and carbon. The most common fossil fuel is coal which has the most application in industries. When these fossil fuels are burnt, they react with oxygen in the atmosphere. This reaction produces more heat and energy but our concern is by-products like carbon dioxide (CO_2) and water. CO_2 has been the primary cause of concern for the environment and various harmful toxic impacts on humans. The worst effect of CO_2 is global warming, where by carbon dioxide traps the heat, reflecting it towards the earth and warming it up. Since, the industrial era, the climate has changed drastically worldwide and has been the primary cause for hundreds of people to die. As in today's chemical industries, such as refineries, power plants and others, flue gas emission is the primary cause of concern. Its emission to minimize, one way could be to separate the toxic gases from the flue gas. Various proposals and ideas have been tested in this regard. Graphene is a layer of pure carbon. A single layer of a carbon atom bonded tightly packed together to form a hexagonal honeycomb lattice. Two hundred times stronger than an equivalent weight of steel. Mobility of up to two hundred and fifty times silicon (Yang *et al*., 2020; Yousefi *et al*., 2019).

In various separation fields, membrane-based separation technology has attained great attention, including gas separation. It offers the benefits of energy efficient, easy scale-up, eco-friendly and operation accessibility. Numerous innovations are being utilized to expel CO_2 (acid gas). Absorption is an actual interaction, where gas is specifically broken up in a fluid and therefore, re-cuperated through the activity of heat, pressure and additionally another substance. Adsorption measure a strong substrate having a high surface region has used to eliminate the desired part from the stream. This interaction is additionally utilized, where high purity is

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required. Cryogenic interaction utilizes an exceptionally low temperature to isolate a gas combination and division is accomplished by refining. The fundamental rule is the boiling temperature difference of each gas. Membrane process a particular obstruction between two stages, separation accomplished by driving force moreover exist as strain, concentration or voltage contrast across the membrane.

Metal natural systems (MOFs) has exceptional structural design and crystalline porous materials, which are not found in conventional porous materials. But these materials' existing assured downsides, such as low surface areas, disorderly structures and non-uniform sizes, will significantly bound their applications. Hydrate based CO_2 capture (HBCC) requires mild operating pressure and temperature. Moreover, its continuous operation permits large scale treatment. However, there are some boundaries such as immature technology, large footprint and large energy penalty. Hydrate based gas separation (HBGS) measure has been considered a promising new/novel methodology for CO_2 separation from fuel and flue gas blends. The separation is the specific partition of the CO_2 part of a fuel or vent gas blend between the strong hydrate crystal stage and the vaporous stage upon hydrate crystal arrangement (Khan *et al*., 2017). In every one of these techniques, the membrane process is noticeable because the operation is essential, the cost is low, energy utilization is low, no erosion issue and significant application is utilized in remote, just as offshore areas.

Graphene and its derivatives own remarkable physical and chemical properties as the membrane for gas mixture separation.Graphene oxide is a monolayer form of graphite that is highly oxidized by nature.It is a two-dimensional wrinkled carbon sheet with a few functional groups containing oxygen on its edges and basal planes, around 1 nm thickness and lateral dimensions amid a few nanometers to some micrometers. These sheets can be well-dispersed in water because of the electrostatic repulsion amongst their ionized functional groups (carboxyl and hydroxyl groups) (Ren *et al*., 2019; Wang *et al*., 2019). There are numerous methods by which it is found, such as GO can be obtained from graphite oxide by the exfoliation method but it produces low yield. It is instinctively evident that synthesis of GO membrane by GO suspension is easy and coating method. It can be selected from available methods such as drop casting, vacuum filtration, spray coating, layer-by-layer deposition and spin coating to produce thin layers on the porous form. Another method called the chemical vapour deposition process effectively synthesizes graphene due to its high yield. But it is not economical and involves composite equipment (Ali *et al*., 2019, Zeynali *et al*., 2019).

Similarly, there is another method, called the Hummer′s method, which is most extensively used for graphene oxide synthesis. But, it emits toxic gases and Na^+ and NO^{3-} ions in the final product, which are harmful. So, the improvement has been taken, as improved Hummer′s method, which omits the use of $NaNO_3$, used in conventional Hummer′s method, for making the process environmentally friendly (Ahmed *et al*., 2020; Jin *et al*., 2020; Norahim *et al*., 2019).

Many efforts have been made to CO_2 gas separation, which shows the potential advantage of using GO membranes. Various experimental results illustrate the mechanical and chemical stability of GO membranes at diverse operational conditions because GO owns large oxygen-containing groups that are liable to any punitive condition, such as high temperature.This research of graphene nano-composite develops a platform regarding the innovation of graphene-related products. To deliberate graphene oxide in gas separation, which has not progressed yet and help develop new methods and ideas to make a product for gas separation. Graphene oxide was made *via* improved Hummer's method, excluding sodium nitrate ($NaNO_3$). The exclusion of $NaNO_3$ from the process eliminates nitrogen dioxide/ dinitrogen tetraoxide (NO_2/N_2O_4) toxic gases. Improved Hummer's method was used to synthesize the GO membrane, an efficient, controllable and low-cost synthesis method for the preparation of GO, which is attractive for gas separation and purification of practical applications.

Materials and Methods

Raw materials. Graphite, $KMnO_4$, H_2SO_4 (98% conc.), HCl (37% conc.), distilled water, hydrogen peroxide (H_2O_2), polyvinylidene fluoride (PVDF) membrane. GO membrane is synthesized by dispersion of GO in water *via* sonication. It is deposited on a polyvinylidene fluoride (PVDF) membrane *via* drop-casting. The experiment is accomplished in two phases i-e the first phase, the synthesis of graphene oxide from enhanced Hummer's method by the oxidation of graphite and the second phase is the fabrication of the graphene oxide membrane.

Synthesis of graphene oxide *via* enhanced Hummer's method. The oxidation of graphite synthesizes graphene oxide. In the experiment, 5g of graphite powder and 115mL of H_2SO_4 (98%conc.) were placed in a 500 mL beaker and stirred for 30min. The mixture is placed in a cold bath to maintain its temperature of less than 20°C. Under vigorous stirring, 15g of $KMnO_4$ was added gradually to maintain the temperature. The mixture was then placed in the water bath at 35°C and stirred for 30min. Then, 230mL distilled water was added slowly to the mix under constant stirring. After this, the mixture was placed in the water bath at 95°C under constant stirring for 15min. and then cooled down. Additional 400mL of distilled water was added, followed by a gradual inclusion of 50mL H_2O_2. This action turns the dark brown colour into yellowish colour. Graphene oxide suspension was obtained.The GO concentration range between 1-10 mg is more suitable for the blend because, in this range, the desired flux and permeability of CO_2 were achieved.

Washing and drying of graphene oxide. The mixture of graphene oxide was centrifuged with 1:3 HCl and distilled water solution three times, followed by washing with distilled water several times until the pH of the supernatant became neutral. Graphene oxide solution was then dried in the oven at 90°C for 10 h. As a result, graphene oxide flakes were obtained, as shown in Fig. 1.

Sonication and fabrication of GO membrane *via* drop casting. The dried GO flakes were converted into powder. Fabricate the GO membrane, a 50 mL aqueous solution of GO mass ranging from 1mg to 10 mg was prepared and sonicated for 3h so, that the particles of GO were wholly dispersed in distilled water. After sonication, the diluted GO suspension was cast over a PVDF membrane. Upon the completion of drop-casting, the membrane was dried at room temperature overnight. As a result, a graphene oxide membrane was obtained, as shown in Fig. 2 (a, b, c).

Gas separation by graphene oxide membrane. After the characterization testing, it is validated that

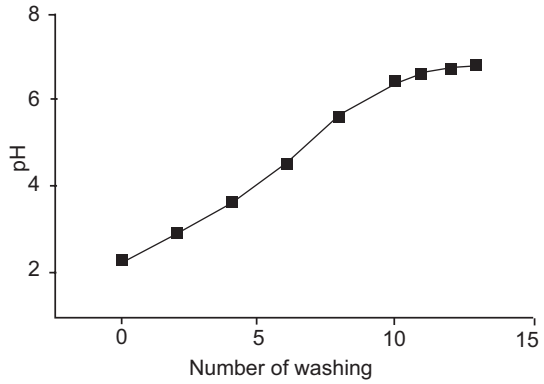

Fig. 1. pH after washing.

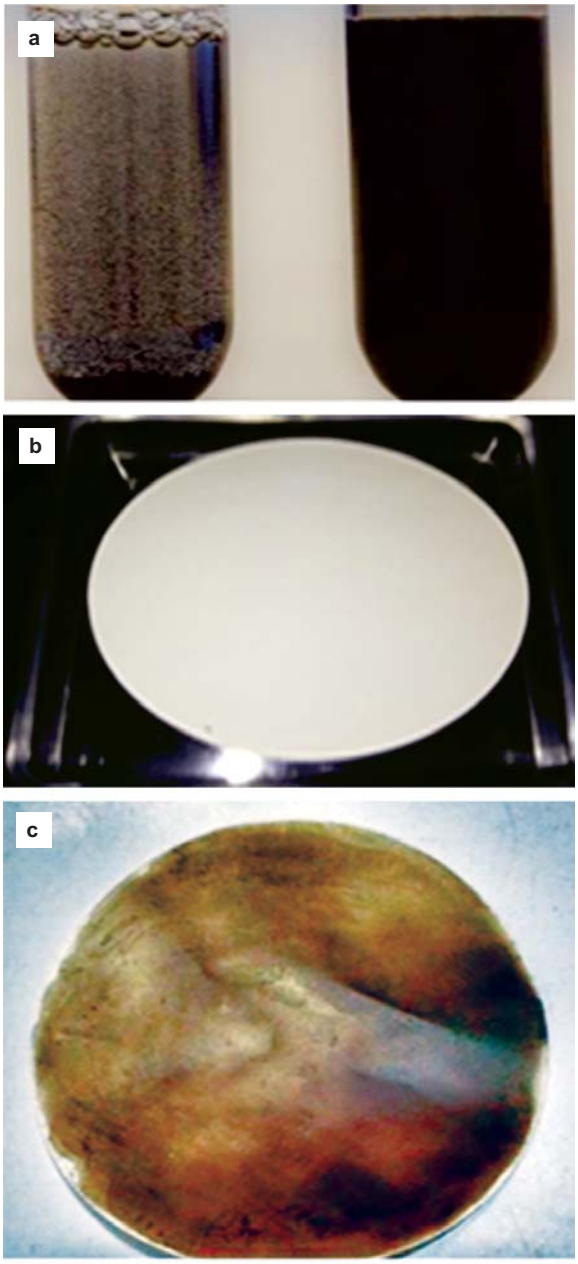

Fig. 2. (**a**) Before and after sonication (**b**) PVDF membrane (**c**) graphene oxide membrane *via* drop coating.

membranes were synthesized with the desired quality required for gas separation. For the membrane testing, gas module equipment was required. The inlet of the gas module was connected by the cylinder, which had a mixture of CO_2 and N_2. GO membrane was placed between the galvanized metal plates having pressure gauges at the inlet and outlet of the pipe assembly. The outlet of the gas module was connected with gas analyzers through which a concentration of permeate gas, that is CO_2 was detected. The condition of the gas module equipment was below standard, leakages were minimized by using Teflon tape but still some leakages could not be prevented entirely. Pressure gauges of the equipment were also malfunctioning which had to be replaced to provide accurate results. The experiment was conducted for two different membranes. The flow rate parameters at inlet and outlet, the concentration and pressure at the inlet and outlet were observed.The resulting graphene oxide samples were tested with X-ray diffraction (XRD) Fourier transforms infrared spectroscopy (FTIR) to confirm the production of graphene oxide material.

Result and Discussion

XRD Test of graphene oxide. To analyze the crystal structure and components XRD test is performed. Graphene oxide exhibits a sharp peak at 11.40° which is compatible with the original graphene oxide peak at 10.6°, hence confirming the formation of GO material as shown in Fig. 3 (Nie *et al*., 2020; Mohan *et al*., 2018; Alonso *et al*., 2017).

FTIR Test of GO and GO membrane. To analyze the functional groups and structure FTIR test is performed.

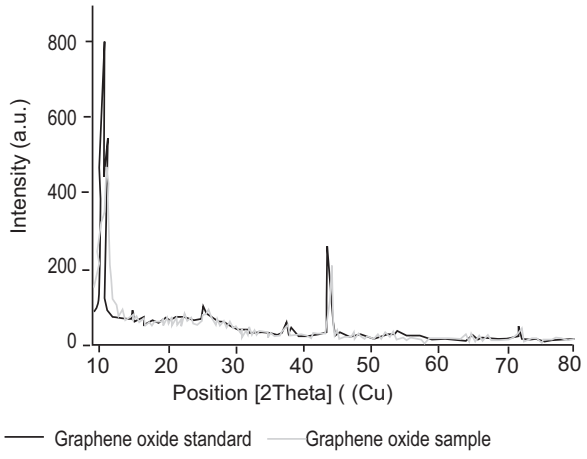

Fig. 3. XRD analysis of graphene oxide.

The broad absorption peak at 2950.98 cm^{-1} can be recognized as the stretching and bending trembling of hydroxyl groups and surface absorbed water. GO indicates weak absorption peaks related to the presence of GO at about 1538.85-1650.39 cm^{-1}, conforming to C=C, C-OH and C-O-C stretching vibrations is shown in Fig. 4 (Mushtaq *et al*., 2021; Bhadra *et al*., 2019; Zhou *et al*., 2017; Mushtaq *et al*., 2014).

In membrane 1, the GO membrane exhibits a peak at 3153 cm^{-1}ascribed to the functional group, as shown in Fig. 5. The peak at 2114 cm^{-1} shows symmetric and asymmetric stretching vibrations of C-H bonds in compounds of CH_2 and CH_3. The peak at 1726 cm^{-1} ascribes the adsorption bands for the C=O functional group. The peak at 1618 cm^{-1} ascribes the aromatic C=C skeletal vibration of unoxidized graphite. The peaks at 1377 cm^{-1} and 1062 cm^{-1} show the deformation of the -OH functional group, epoxy C-O-C stretching,

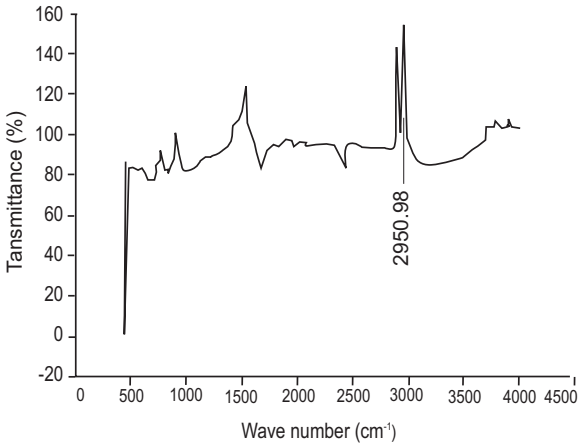

Fig. 4. FTIR analysis of graphene oxide.

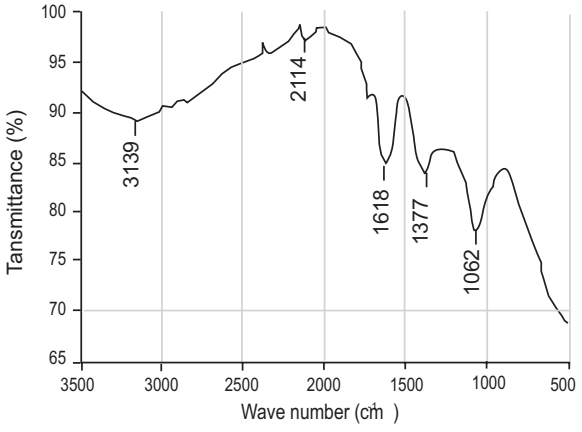

Fig. 5. FTIR of graphene oxide membrane 1

and carboxyl C-O stretching pulsations (Yang *et al*., 2020; Ren *et al*., 2019; Chen *et al*., 2018; Brahmayya *et al*., 2017; Mushtaq *et al*., 2014).

In membrane 2, the GO membrane exhibits a peak at 3139 cm^{-1}, which ascribes to the stretching vibration of the -OH functional group,as shown in Fig. 6. The peak at 2114 cm^{-1} shows symmetric and asymmetric stretching vibrations of C-H bonds in compounds of CH_2 and CH_3. The peak at 1728 cm^{-1} ascribes the adsorption bands for the C=O functional group. The peak at 1619 cm^{-1} ascribes the aromatic C=C skeletal vibration of unoxidized graphite. The peaks at 1375 cm^{-1} and 1064 cm^{-1} show the deformation of the -OH functional group, epoxy C-O-C stretching and alkoxy C-O stretching vibrations (Ren *et al*., 2019; Yang *et al*., 2019; Chen *et al*., 2018; Huynh *et al*., 2018; Maji, 2017; Mushtaq *et al*., 2014).

Membrane permeability of CO_2. CO_2 gas separation from the mixture of CO_2 and N_2 depends on many factors and the concentration of GO is one of them. It clears permeability and the selectivity of CO_2 is increased when there is an increment in the concentration of GO. Like, for 0.065% of GO membranes, the highest selectivity of 73 was acquired for CO_2/N_2 mixture when experiments were conducted with pure gases at room temperature. Similarly, 100 Barrer CO_2 permeability was achieved when a membrane with 0.1 wt% of GO was used. The ideal CO_2/N_2 selectivity of 91 at 25 °C, therefore, in this experiment, GO concentration is varied between 1–10 mg for having desired permeability. Table

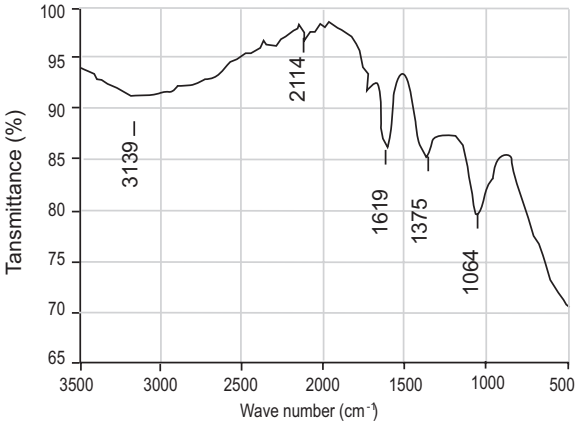

Fig. 6. FTIR of graphene oxide membrane 2.

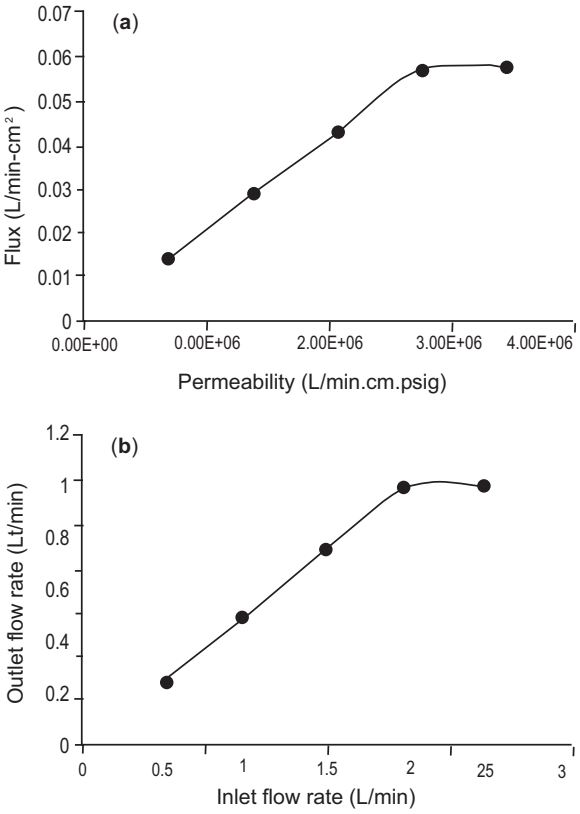

Fig. 7. Membrane 1 (**a**) Effect of flux on permeability (**b**) Comparison ofinlet and outlet flowrate.

Table 1. Experimentation results membrane 1

	Inlet			Outlet			
Flow rate	Concentration %	Partial pressure of CO_2 psig	Flow rate L/min	Concentration %	Partial pressure of CO_2	Permeability of CO_2 L/min.cm.psig x 10^{-6} L/min.cm^2 psig x 10^{-6}	Flux L/min.cm^2
0.5	52.5	262.5	0.25	21.02	0.42	0.693151	0.01441753
1		262.5	0.5		0.42	1.3863	0.02883506
1.5		262.5	0.75		0.42	2.07945	0.0432526
2		262.5	0.99		0.42	2.74488	0.05709343
2.5		210	1		0.378	3.46645	0.05767013

Table 2. Experimentation results membrane 2

	Inlet	Outlet				Permeability	
Flow rate L/min	Concentration %	Partial pressure of CO_2	Flow rate L/min	Concentration %	Partial pressure of CO_2 psig	of CO_2 L/min.cm. psig x 10^{-6}	Flux L/min.cm^2
1	52.5	131.25	0.75	21.02	0.252	4.16024	0.0432526
1.5		131.25	1.25		0.252	6.93373	0.0720877
2		131.25	1.5		0.252	8.32047	0.0865052
2.5		131.25	1.75		0.252	9.70722	0.1009227
3		105	2		0.21	13.8686	0.1153403
4		105	2		0.21	13.8686	0.1153403
5		105	2		0.21	13.8686	0.1153403

1 and Fig. 7 (a, b) shows the permeability, flux of membrane and inlet, outlet flow rate for membrane 1.

The experiments of graphene oxide membrane were conducted, which is placed between the metal plates of a gas module.Table 2 and Fig. 8 (a, b) shows the permeability, flux of membrane and inlet, outlet flowrate for membrane 2.

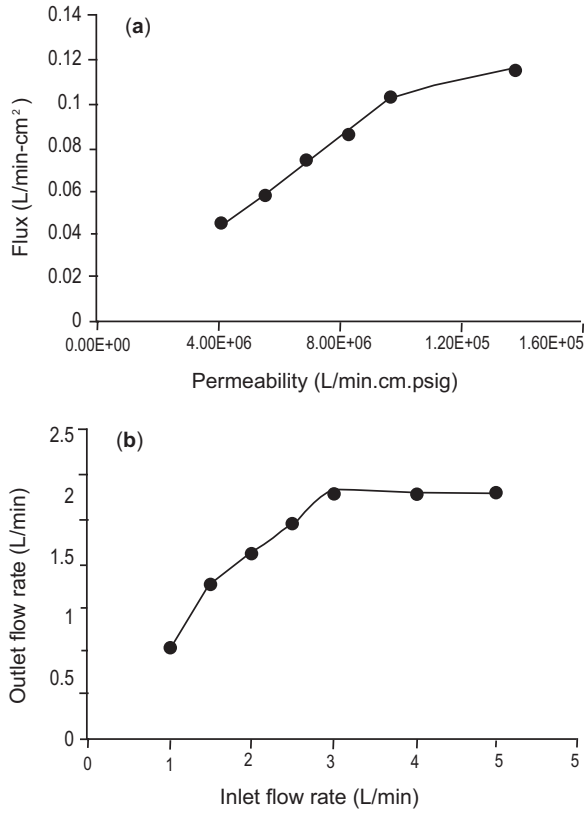

Fig. 8. Membrane 2(**a**) Effect of flux on permeability (**b**)Comparison ofinlet and outlet flowrate.

Experimental results for both membranes show that by adjusting the flow rate, partial pressure and gas concentration, the flowrate, concentration and partial pressure decrease at the outlet. And by increasing the flow rate keeping concentration and partial pressure constant at the inlet, the gas flow rate will decrease only at the outlet, but permeability and flux increase. Figures of permeability with flux developed on these experimental results show that flux and permeability are directly proportional to each other thus, the separation of carbon dioxide gas increases as the permeability and flux increase (Mushtaq *et al*., 2021; Jin *et al*., 2020; Mushtaq *et al*., 2019; Norahim *et al*., 2019; Ren *et al*., 2019; Chen *et al*., 2018).

Conclusion

The membrane fabrication is accomplished by drop-casting of GO over a PVDF membrane. Then the separation of carbon dioxide gas using graphene oxide membrane has been observed. The gas module systemis used to discrete a mixture of CO_2 and N_2 through the GO membrane. The technique used to characterize GO membrane includes XRD and FTIR. All the tests confirm the synthesis of GO and GO membrane, marking the achievement. In membrane 2, the inlet flow rate is 5 L/min, the concentration is 52.5 % and partial pressure of CO_2 is 105 psig, the flow rate for outlet become decreases 2 L/min and concentration also decreases to 21.02 %, the partial pressure of CO_2 0.21 psig, the permeability of CO_2 was found to $13.8686x10^{-6}$ L/min.cm.psig and flux 0.11153 L/min.cm^2. The final product of graphene oxide membrane can separate the mixture of gases like CO_2 and N_2, CO_2 and SO_2, CO_2 and CH_4 and many others. Even though adequate efforts have been conceded on the potential advantage of GO

membranes for the separation of CO_2, it is still required to report numerous significant concerns to attain exceptional CO_2 permeability and selectivity beneath practical operational conditions. In recent practice, vacuum filtration utilized to synthesize membranes is hydrated through water molecules. It is essential to advance the existing membrane designfor CO_2 separation to raise the process and be used commercially.

Conflicts of Interest. The authors declare that they have no conflict of interest.

Acknowledgment

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