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Novel Zeolite-Polyurethane Membrane for Environmental Applications and gas separations

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Abstract. This research work investigates the effect of polyurethane polymer on the separation of CO₂, CH₄ and C₃H₈ through a zeolite/polyurethane mixed matrix membrane. A methodology based on the modification of porous ceramic inorganic support with the aim to achieve high selectivity for the hydrocarbons has been developed. Polyurethane-zeolite nanoparticles were prepared by combined blending and casting method. The physical properties of the zeolite/polyurethane mixed matrix membrane were investigated by Scanning Electron Microscope (SEM), Fourier Transform Infra-Red spectroscopy (FTIR) and Nitrogen physisorption (BET). These confirmed the homogenous and nanoscale distribution of zeolite particles in the polyurethane-zeolite membrane. The Nitrogen physisorption measurements showed the hysteresis isotherm of the membrane corresponding to type IV and V that is indicative of a mesoporous membrane. The surface area and the pore size determined using the Barrett, Joyner, Halenda (BJH) desorption method showed a pore diameter of 3.320 nm, a pore volume of 0.31 ccg⁻¹ and surface area of 43.583 m² g⁻¹. Single gas permeation tests were carried out at a pressure range of 0.01 to 0.1 MPa. The membrane showed the permeance of CH₄ to be in the range of 5.189 x 10⁻⁷ to 1.78 x 10⁻⁵ mol s⁻¹ m⁻² Pa⁻¹ and a CH₄/C₃H₈ selectivity of 3.5 at 293 K. On the basis of the results obtained it can be concluded that for the recovery of volatile organic compounds the addition of polyurethane polymer to the zeolite membrane did not increase the performance of the membrane.

Keywords: Polyurethane, polymer, gas separation, membrane and zeolite

Nomenclature:

Different gasses	A, B
Dosed volume	n _{dosed}
Effective membrane area	A
Flow rate	Q
Flux	J
Kelvin radius	r _k
Pore radius	r _p
Pressure	P
Selectivity	α
Thickness	t
Void volume	n _{void}

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1 Introduction

There has been great concern regarding the emissions of Volatile Organic Compounds (VOCs) from oil and gas industries in recent years. Different countries around the world have regulations in place that tightly control these emissions, although, in some countries emissions of VOCs and Non-Methane Volatile Organic Compounds (NMVOCs) are not subject to control and these emissions can cause harmful consequences to both plants, animals and humans as well as monetary loss. There are various processes that cause the release of these compounds to the atmosphere. These includes; storage, production and transportation of crude oil and gasoline products as well as loading and offloading operations of shuttle tankers. In the last few years, the potentialities of membrane operations have been widely recognised. In some preliminary investigations, polymeric membranes such as silicone rubber have been used. The membranes that are more permeable to lighter hydrocarbons are the polyacetylene polymers, the microporous absorbent carbon and the silicon rubber [1]. However, enhancing the durability of polymeric membranes under

rigorous conditions is one of the main challenges that needs to be addressed to overcome the drawbacks of plasticization of these membranes which limits the use of such membranes at high temperatures and pressures which in turn leads to a decline of the separation performance and loss of efficiency of the membrane [2, 3, 4]. Although polymeric membranes possess excellent performance potential, further enhancement of their thermal and chemical stability remain challenging. Ceramic membranes, on the other hand, have adequate thermal and chemical durability [5]. The use of ceramic membranes has grown considerably both academically as well as industrially and can be used for several applications. They are more fragile and expensive to fabricate than polymeric membranes, but they can withstand more rigorous separation conditions that include high temperatures or corrosive solvents. Ceramic membranes do not only have higher thermal and chemical stability but have higher permeability as well [6]. There are several types of materials that can be used to modify the ceramic support layer to enhance selectivity.

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These include zeolites, silica, alumina and stainless steel [7]. The progress of catalytic membrane reactor (CMR) technology greatly depends on the development of new membrane materials and the performance of dense mixed conducting ceramic membranes is strongly dependent on the properties of the membrane materials. The major applications of these membranes include hydrogen separation and purification to get ultra-pure hydrogen, recovery of CO₂ from natural gas and power station flue gases and oxygen or nitrogen enrichment of air [8]. Ceramic membranes can also be incorporated into chemical reactors where they can serve as catalysts to effect equilibrium-shift for enhanced product yield [8]. The process of gas separations from shuttle tankers using membrane technology is depicted in Fig. 1.

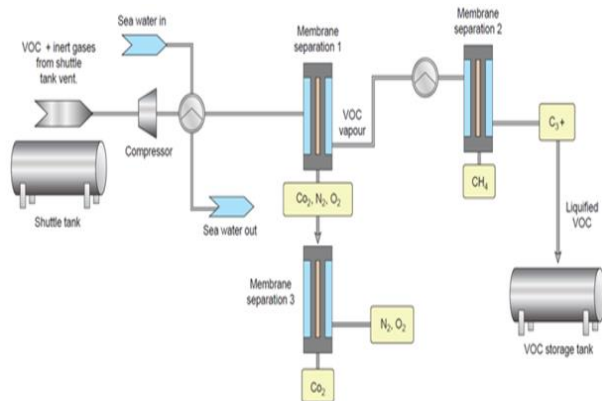


Fig 1: Process of hydrocarbon recovery from shuttle tanks using membrane technology.

In the process of discharging crude oil at terminals, cargo tanks are filled with blanket inert gases that have a typical composition of 84% N₂, 12% CO₂, and 4% O₂. This is done to keep the oxygen level below the explosion limit and also to maintain an overpressure in the tanks. The inert gas affects the equilibrium mechanism which depending on the oil vapour pressure stimulates the release of hydrocarbons from the oil. Subsequently, the cargo tank atmosphere will consist of inert gas mixed with 15 to 25 % of hydrocarbon gas, and hence they will be emitted to the atmosphere during the next loading operation [9].

Different types of membranes have been studied for the separation of hydrocarbons from inert gases. Polymeric membranes were characterised, and their permeation properties for the separation of propylene and toluene was investigated [10, 11, 12, 13]. An important feature of the polymer membrane used for gas separations is the ability to spin them into hollow fibre membranes because of their large area is suitable for large scale industrial applications [14]. The major drawback for the

use of these polymeric membranes is that they are unable to withstand high temperatures and harsh chemical conditions.

In this work, the alumina support is macroporous with an intermediary layer consisting of titanium oxide and a pore size of 15 nm. Upon modification, the pore size is expected to decrease. The membrane pore size together with the mean free path of gas molecules is some of the factors that determine the flow mechanism and separation of gas components through the membrane. The support layer can be modified with various components like metals, silica, zeolites or it can be a mixed matrix membrane containing a polymer incorporated in the zeolitic pores to make new composite membrane materials that are suited for various applications. The choice of membrane material is dependent on the application of the membrane. The aim of this work is to evaluate the performance and effects of zeolite and polymer mixture on the separation of hydrocarbon gases. This is the first report on hydrocarbon vapour permeance and selectivity properties on a polyurethane/zeolite alumina-based membrane.

2.0 Materials and Methods

2.1 Materials

The method of Tirouni et al. [14] was adapted and modified for the membrane preparation. The porous ceramic support used in this study (inner diameter 7 mm, outer diameter 10 mm and length 366 mm) consisted of a α -alumina support which was supplied by CTI, France. Analytical grade silicon oxide, aluminium oxide, sodium oxide and zeolite crystals. Poly(tetramethylene glycol) (MW 2000 g/mol). Butanediol (MW 90.12 gmol⁻¹), Hexamethylene diisocyanate, Dimethyl formamide and N, N-Dimethylacetamide were all purchased from Sigma-Aldrich, U.K.

2.2 Polymer Synthesis

The molar ratio of polyol and hexamethyl diisocyanate was 1:3 as per the method by Tirouni et al. [14]. The solution was kept at 30 – 40 °C for 2 h under N₂ atmosphere to obtain macro-diisocyanate. Chain extender butanediol (mL) was added and the mixture kept at 20 °C. The molar ratio of the components in the synthesised polymer was 1:3:2.

2.3 Membrane preparation

Zeolite/polyurethane membrane was prepared by dissolving 1 g of zeolite powder in 2.4 mL of dimethyl formamide (10 wt%) and stirring at 20°C for 15 min. The resulting solution was then added to the prepared polymer solution, the volumetric ratio of the resulting polymer/zeolite solution was 1:129. The α -alumina support was then immersed into the zeolite/polymer solution using the dip-coating method. It was left in the solution for 17 h at 60 °C. It was then retrieved and air dried for 30 min, and finally oven dried at 65°C for 2 h.

2.4 Characterisation

The functional groups of the synthesised zeolite/polyurethane solution were investigated by an ATR Nicolet i S 10 FT-IR spectrometer (Thermo Scientific, United Kingdom), in the range of 400-4000 cm^{-1} . A Zeiss Evo LS10 Scanning Electron Microscope (SEM) with an Oxford Instruments INCA System Energy Dispersive X-Ray analyser (EDAX) (Zeiss, United Kingdom) was used to determine the morphology and elemental composition of the prepared membrane respectively. BET nitrogen

physisorption measurements carried out by a Quantachrome autosorb® gas analyser to determine the pore size.

2.5 Single gas permeation measurements

To evaluate the performance of the fabricated membrane, a membrane reactor fitted with digital pressure gauges and Cole- Palmer digital flow meter was used to determine the flow of the gases through the membrane. Gas permeation tests were carried out with single-component gases, namely, carbon dioxide (99.5%), oxygen (99.5%), methane (99.5%), nitrogen (99.5%) and propane (99.5%) supplied by BOC, United Kingdom. The schematic diagram of the gas transport system is shown in Fig. 2. The gas permeation experiment was performed at 30 °C by pressurising the outside of the membrane in the reactor and measuring the flow of the gases with a digital flow meter.

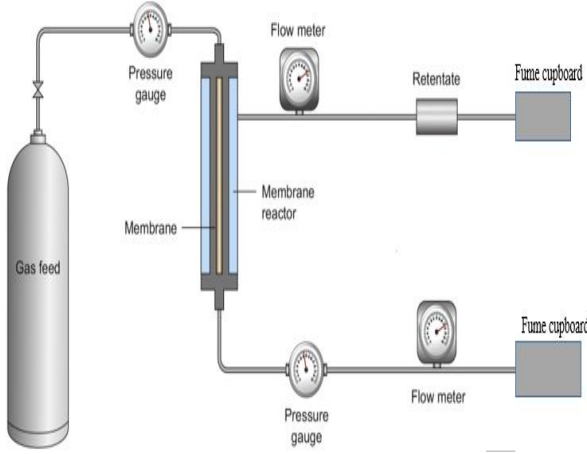


Fig. 2: Gas permeation setup

The flux of the permeating gas through the membrane was determined at various pressures ranging from 0.1 to 1×10^5 Pa using the gas permeation set up in Fig. 2. It was assumed that the gas permeate end of the reactor remained at atmospheric pressure throughout the gas permeation process. The flux of the gas was calculated using the equation (1).

$$J = \frac{Q}{A} \quad (1)$$

Where J is the flux in $\text{mol s}^{-1} \text{m}^{-2}$, Q is the flowrate in mol s^{-1} and A is the effective membrane area in m^2 .

The permselectivity (ideal selectivity) of gas A over B ($\alpha_{A/B}$) was calculated from the single gas permeation tests using equation (2)

$$\alpha_{A/B} = \frac{J_A}{J_B} \quad (2)$$

Where J_A and J_B ($\text{mol s}^{-1} \text{m}^2$) are the molar fluxes of gas A and B respectively.

3 Results and Discussion

3.1 Characterisation

3.1.1 Nitrogen physisorption measurements

One of the most important techniques for the characterisation of nano- sized porous materials in terms of surface area, pore volume and pore size distribution is the physical adsorption of gas on the surface of the material. Different types of physisorption isotherms (Fig. 3) are observed for different materials. Type I: microporous, type II: non-porous or macro-porous, type III: non-porous or macro-porous with weak interaction, type IV: mesoporous, type V: mesoporous with weak interaction and type VI: layer-by-layer adsorption.

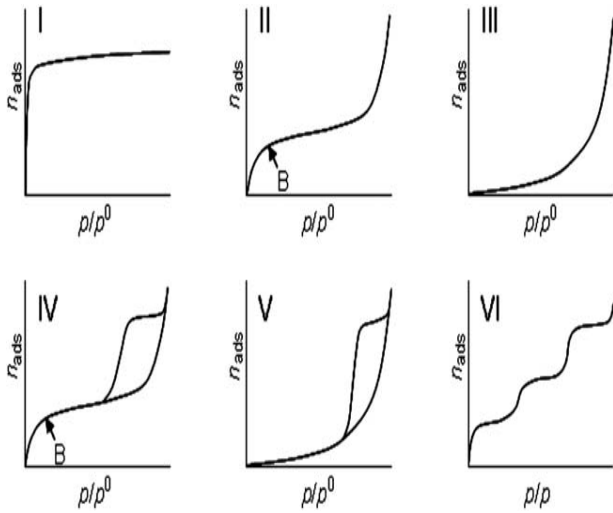


Fig. 3: Different types of physisorption isotherms observed for different materials adapted from [15].

The specific surface area of the silica and zeolite membrane was determined from the adsorption of nitrogen on the external and internal surface of the membranes at $-195.8\text{ }^{\circ}\text{C}$ using a quantachrome adsorption gas analyser. The operating conditions of the instrument are given in table 1.

Table 1: Optimum operating conditions of the Quantachrome Gas Analyser

Parameter	Value
Area ($\text{A}^2\text{ mol}^{-1}$)	16.2
Non-Ideality (1/mm Hg)	6.58×10^{-5}
Sample cell type (mm)	12
Analysis time (mins)	237
Mol weight (g mol^{-1})	28.0134
Ambient temperature (K)	300
Bath temperature (K)	77

The adsorption and desorption isotherm of the zeolite membrane is presented in Figure 4, and it corresponds to type III isotherm from Fig. 3. This indicates that the zeolite may be macroporous or non-porous adsorbent with weak adsorbent-adsorbate interaction. In theory, zeolites and silica are highly porous and have very large surface area.

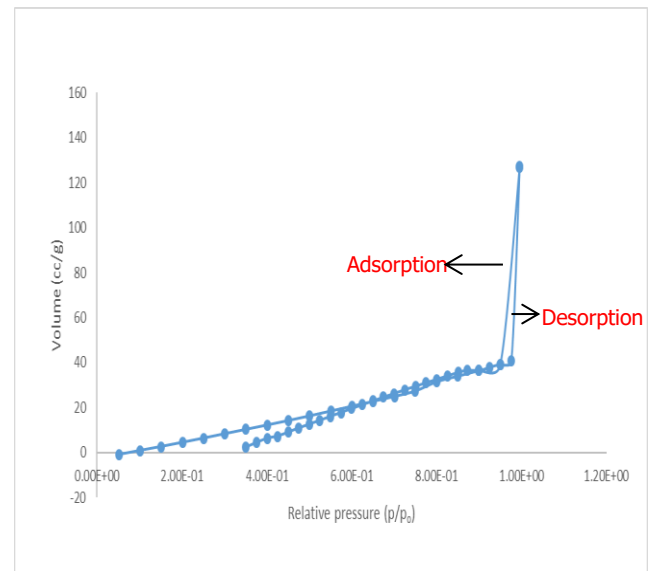


Fig. 4: Physisorption isotherm for zeolite membrane

The physisorption isotherm for the polyurethane/zeolite membrane is presented in Figure 5 and it shows the adsorption and desorption isotherms which correspond to type IV or V which indicates the membrane is a mesoporous adsorbent. The isotherm was

determined by the plot of the volume ($n_{\text{dosed}} - n_{\text{void}}$) against the relative pressure (p/p_0). In the case of the void volume being larger than the volume dosed, there would be a loss of precision and hence a negative volume. The pore sizes and specific surface area of the membrane are given in Table 2.

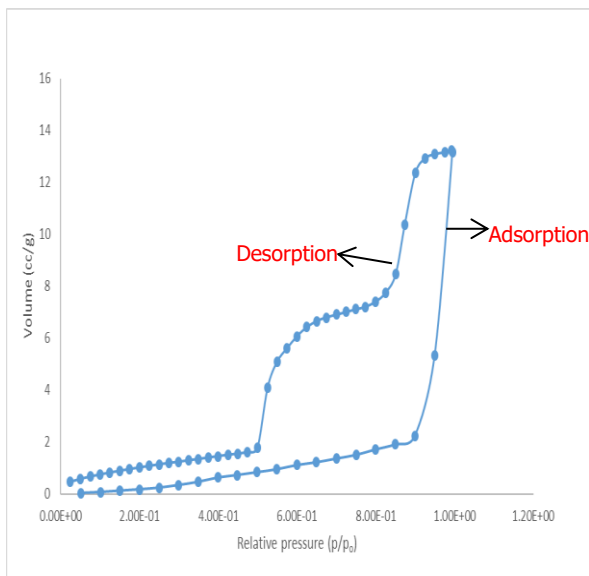


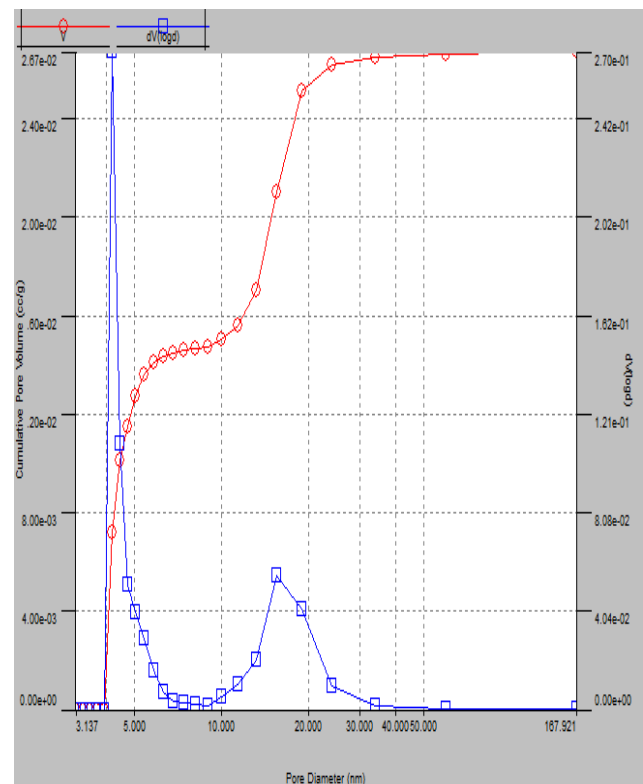
Figure 5: Physisorption isotherm for polyurethane/zeolite membrane

The adsorption behaviour of mesoporous materials is determined by the adsorbent-adsorbate interactions. Hence the Kelvin equation (equation 3) which is based on cylindrical pores is used for the evaluation of the pore size distribution of the membrane layer by

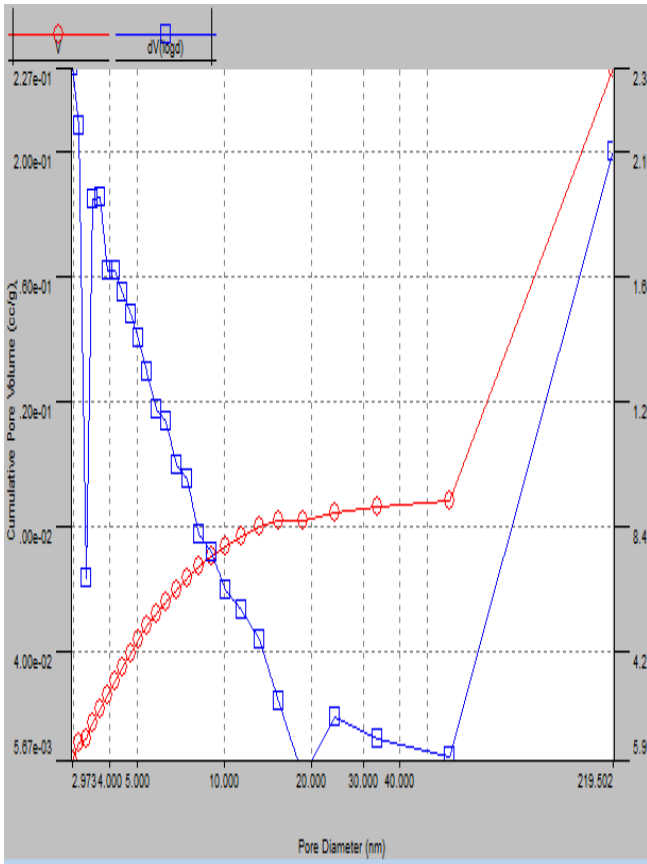
the Barrett-Joyner-Halenda (BJH) method. The BJH graph (Figure 6 (a) and (b)) shows the adsorption and desorption branches which are used to determine the pore sizes of the membrane.

$$r_p = r_k + t \quad (3)$$

Where r_p is the pore radius of the membrane layer, r_k is the Kelvin radius and t is the thickness of the membrane layer.



(a)



(b)

Fig. 6: BJH desorption branch for pore size determination for (a) polyurethane/zeolite and (b) zeolite membrane

Table 2: Pore size and surface area of polyurethane/zeolite and zeolite membranes

	Polyurethane/zeolite membrane	Zeolite membrane
Pore size (x10 ⁻⁹ m)	3.32	11.394

Specific surface area (m ² /g)	0.31	0.619
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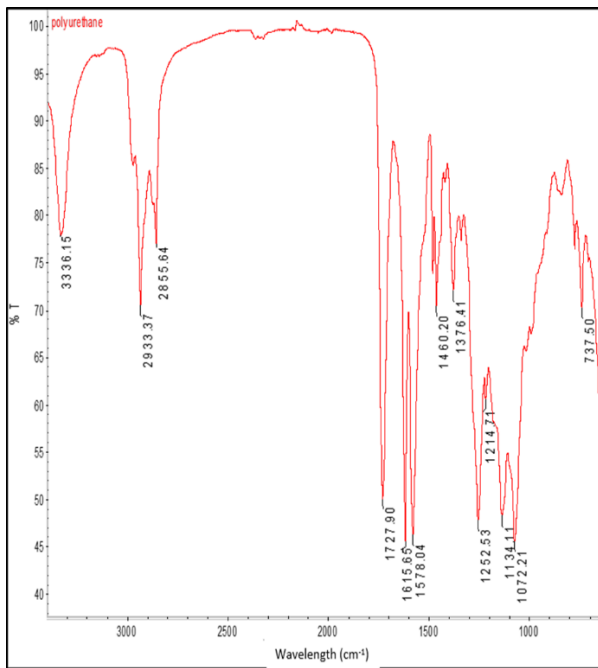
The pore size of the polyurethane/zeolite membrane is smaller than the pore size of only the zeolite membrane by 8.07×10^{-9} m and surface area by $0.309 \text{ m}^2/\text{g}$ (Table 2); this could be because of the polymer filling the zeolitic pores. This pore size difference is supposed to be reflected in the flow and separation of gases through these materials.

3.1.2 FTIR Analysis

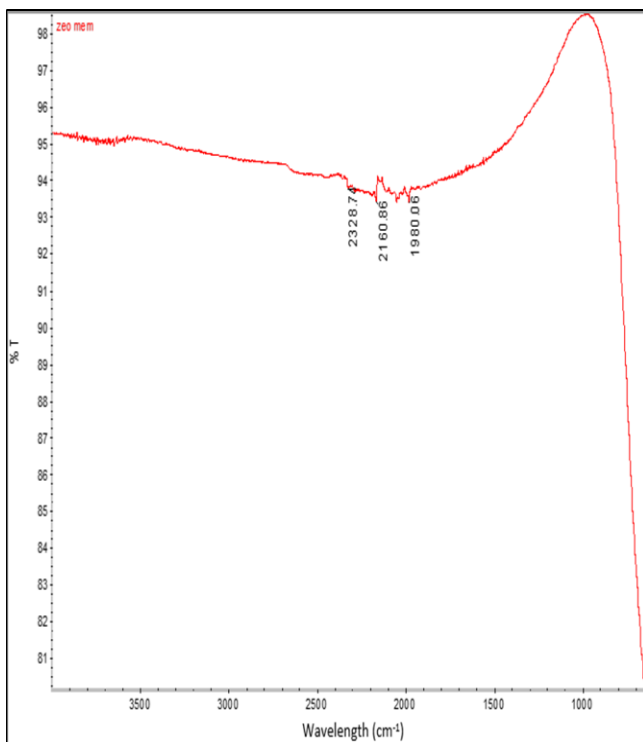
Structural characteristics of the zeolite/polyurethane mixture and the zeolite membrane were determined by FTIR analysis (Fig. 7 a and b).

An asymmetric vibration of Si-O-Si peak at 1072.2 cm^{-1} can be easily observed. Presentation of absorption peaks of the urethane carbonyl group is in the region of 1615.65 cm^{-1} . This is absent in the zeolite membrane, indicating the presence of the polymer mixture in the zeolite membrane. The presence of peaks at 1727 cm^{-1} to 2855.64 cm^{-1} indicates that the zeolite polar group in the y-type zeolite membrane is

connected to the N-H group of the polyurethane polymer.



(a)

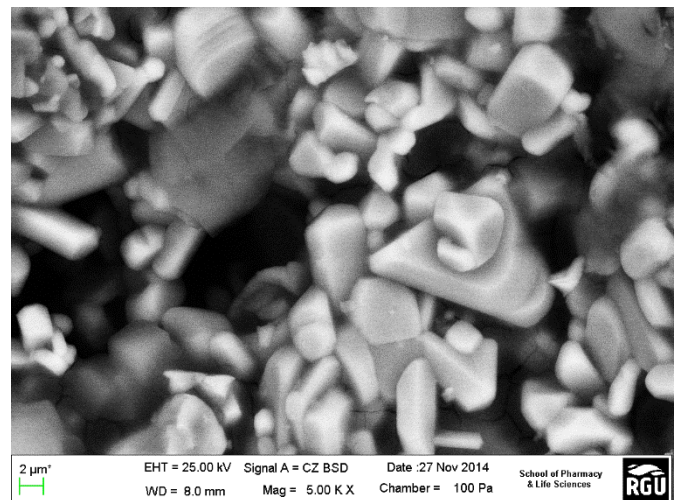


(b)

Fig. 7: FTIR functional groups of (a) polyurethane/zeolite membrane and (b) zeolite membrane.

3.1.3 SEM Analysis

The SEM micrograph (Fig. 8) shows that polyurethane has been embedded in the pores of the zeolite. This has confirmed the deposition of polyurethane and zeolite on the support. From the micrographs, it is observed that both the polyurethane and zeolite are bonded on the surface of the alumina support.



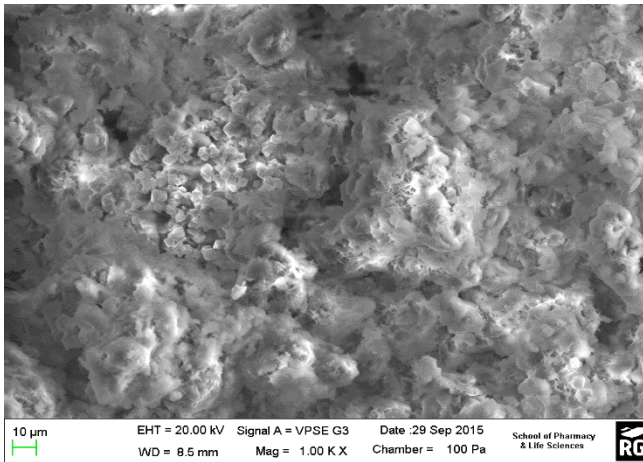


Fig. 8: SEM micrograph of (a) zeolite membrane and (b) polymer/zeolite membrane.

3.2 Single gas permeation test

Fig. 9 shows that the molar fluxes of the gases increase with an increase in gauge pressure. Methane has a higher flux than propane and carbon dioxide at a pressure of 1.0×10^5 Pa. The contribution of viscous flux to the overall mass transfer at higher pressure for zeolite membrane might have caused this.

The molar flux of propane and carbon dioxide are close; this indicates that the membrane will not be suitable for their separation.

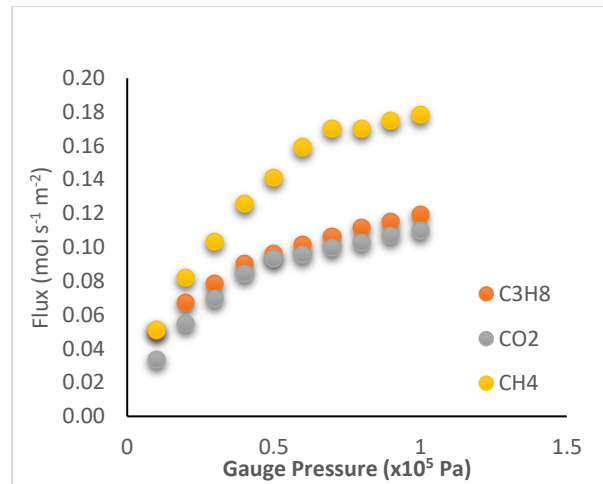


Fig. 9: Flux of C₃H₈, CO₂ and CH₄ through the polyurethane/zeolite membrane.

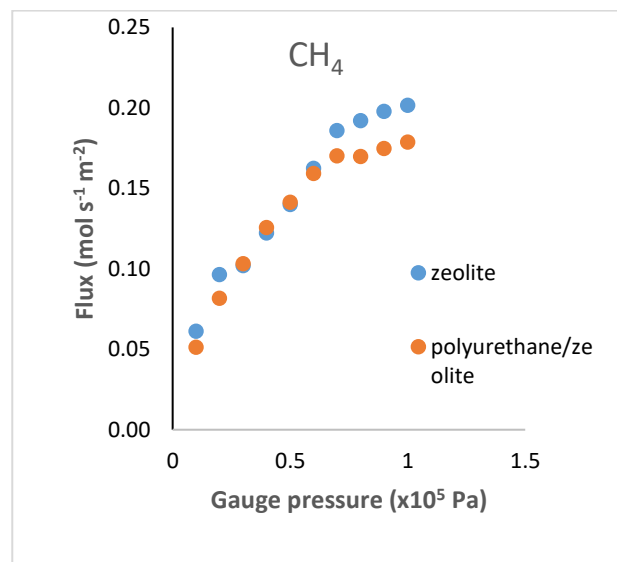


Fig 10: Flux of CH₄ through zeolite and polyurethane/zeolite membrane.

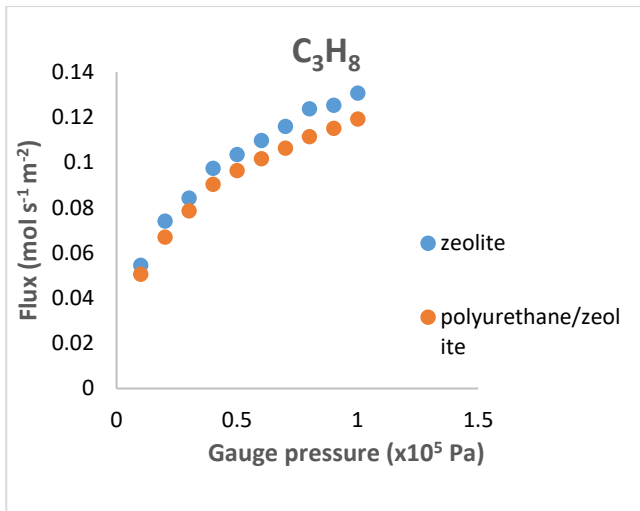


Fig 11: Flux of C₃H₈ through zeolite and polyurethane/zeolite membrane.

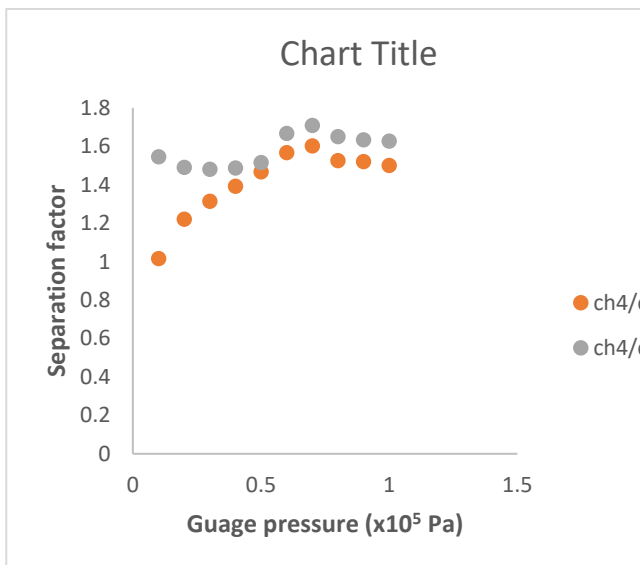


Fig. 12: Selectivity of the membrane to methane against CO₂ and C₃H₈

CH₄ and C₃H₈ move through the zeolite and polyurethane/zeolite membrane at a similar rate (Fig. 10 and 11), this could indicate the same transport mechanism is responsible for the movement of these gases and it is independent

on the pore size of the membrane. Separation factors of CH₄/CO₂ and CH₄/C₃H₈ were determined using equation (2) and it can be observed that the pressure drop is not an influencing parameter for the separation of these gases (Fig. 12).

4 Conclusion

Polyurethane and zeolite were successfully embedded on the surface of an alumina support. The molar flux of propane and carbon dioxide has indicated that this membrane will not be suitable for their separation, this could be because of their identical molar mass (44.1 g mol⁻¹) as the transport mechanism exhibited by these gases through the membrane was based on their molar mass rather than their kinetic diameter (0.38 nm and 0.43) respectively. Methane had a higher molar flow rate of 0.179 mol s⁻¹ m⁻² (molar mass 16.04 g mol⁻¹, kinetic diameter 0.37 nm) as compared to CO₂ having 0.109 mol s⁻¹ m⁻² at 1 x 10⁵ Pa. The addition of polyurethane polymer to the zeolitic pore did not show a significant difference in the flux of the gases despite the reduction in the pore size of the membrane.

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