

Amine Bearing Windows Opening Membrane for CO₂ Adsorption

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Abstract: Membrane technology is one of the most efficient technologies for capturing CO₂ from a gaseous mixture and provides a way for minimizing the pollution problem around the whole world. Dendrimer incorporated polymeric membrane is mostly CO₂ selective and this membrane can be used for separation of CO₂ from a gaseous mixture. We have prepared CO₂ selective Polysulfone composite dendrimer membrane and characterized by IR, XRD, TGA- DTA, SEM analysis. IR data confirms the incorporation of NH₂ group in the membrane which plays an active role in the CO₂ adsorption. From the XRD data it is confirmed that the membrane is completely homogeneous in nature. SEM photograph shows the morphological change of the membrane due to facilitated transport mechanism. From the results, it is established that adsorption of CO₂ onto membrane is a chemical adsorption process. It is seen that the membranes have change in its crystalline structure after adsorption. The adsorption process was affected by the feed gas pressure, feed flow rate etc. The adsorption isotherm was investigated for the process and found that the adsorption behaviour for CO₂ adsorption was best fit with the Langmuir isotherm model. Adsorptive interaction is strongly related to the interaction energy between adsorbate and adsorbent. It was observed that the CO₂ adsorption onto the membrane follows the pseudo second order kinetics.

Key words: Dendrimer, membrane, gas separation, adsorption, facilitated transport, interaction energy.

1. Introduction

The concentration of CO₂ increases in the atmosphere and results numerous problems for environment which causes climate change for the whole world. Now a day, a number of technologies are developed for reducing the environmental polluting problems like global warming, greenhouse effect etc. by capturing CO₂ from various gaseous mixtures. Several technologies such as nanotechnology, absorption into a solution etc. are developed for CO₂ storage, but membrane technology for adsorption as well as separation of CO₂ achieves higher efficiency due to simple operation, environmental friendly, low investment cost and for the most selective separation [1-4].

A few numbers of research works have been carried out on membrane separation processes by the researchers throughout the world. However, work on adsorption of CO₂ onto the membrane is very limited. Sirkar et al. [5] reported that the Poly (amidoamine) (PAMAM) dendrimer and ionic liquid composite membranes provide a challenging way for CO₂ selectivity over other gases at one atmospheric pressure. The (Polyvinylalcohol) PVA composite polymeric membrane is also suitable for incorporation of CO₂ because of its higher gas permeability [6]. Youssef et al. [7] reported that amine bearing pore expanded MCM-41 (Mobil Composition of Matter, No 41) Silica can be used for gas purification applications by the adsorption of CO₂ from a gas mixtures. Jin Huang et al. [8] reported the capture of CO₂ using a CO₂ selective facilitated transport membrane. Toshihino et al. [9] reported about the efficiency of Zeolite composite membrane for the separation of CO₂/ CH₄ gaseous mixture. The novelty of our research study lies in the performance of membrane containing Amine compound (Dendrimer) for adsorption of CO₂ from CO₂/ N₂ gaseous mixture, as detail adsorption study for adsorption of CO₂ has not been reported elsewhere.

Adsorption of CO₂ occurs via Physisorption and Chemisorption processes. A large numbers of research workers carried out their studies on CO₂ adsorption process. Wang et al; 2011 [10] in their previous research study reported Zeolites as the physical adsorbents for the capture of CO₂. Mesoporous Silica can also be used as a suitable candidate for physical adsorption process as it has high surface area, tunable pore size and good mechanical stability. Liu et al; 2005 [11] Sun et al; [12] also reported about some Amorphous materials (SBA-n), Anionic surfactant – templated mesoporous silica (AMS) etc for physical adsorption process. Some disadvantages of physical adsorption are 1. Long range and weak van der Waals attraction between adsorbate and substrate (ΔH physisorption ~ 20 kJ mol⁻¹) – 2. No activation barrier, fast, 3. Reversible, 4. Surface symmetry insensitive, 5. Multilayer formation possible.

To overcome the disadvantages of physical adsorption processes, solid adsorption processes can be used as an alternative process for gas separation. From the previous research on CO₂ adsorption processes (Sayari et al., 2011, Choi et al.,) [13,14] it is possible to develop a suitable CO₂ adsorbent which satisfies the factors like (1) low heat capacity, (2) high

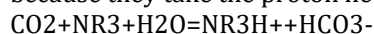
adsorption capacity (3) fast kinetics (4) high CO₂ selectivity etc. In order to improve the CO₂ adsorption and selectivity the researchers developed various Amine based adsorbents which possessed suitable adsorbent properties. Amine based solid adsorbents have been studied by the researchers due to its advantages of low heat of regeneration. Depending upon the type of the interactions between amines and the support the amine bearing adsorbents can be divided into Amine – grafted adsorbents and Amine impregnated adsorbent via strong and weak chemical bonding, respectively as reported by (Sayari et al, 2011) .[13] Wang et al; 2011 [10] introduced an effective method for amine introduction however impregnation of higher amine results larger resistance of the adsorbent for diffusion as reported by Sayari and Guerrero et al; 2010 [13].

From the previous research studies it seems to use supports with larger pore size and pore volume to impregnate amine for gas separation purpose. Amine Impregnated adsorbent can be used as a suitable adsorbent for gas separation via adsorption process. Xu et al 2002 [15] in their study reported the Polyetherimide (PEI)- impregnated mesoporous Silica and Carbonaceous materials as CO₂ adsorbent for gas separation applications. The PEI – impregnated MCM-41 exhibited a highest CO₂ adsorption capacity of about 3.02 mmol/g.

Chaung et al [16]; in their research study reported the beta- Zeolite impregnated with Tetraethylenepentamine (TEPA) exhibited higher CO₂ adsorption efficiency than the amorphous Al₂O₃ and SiO₂ impregnated with TEPA; as reported by Fischer et al; 2009. [17] Chaung et al [16]; again investigated the effect of Polyethylene Glycol (PEG) which was used as an additive for TEPA/SiO₂ for CO₂ adsorption capacity. Plaza et al; (2007,2008)[18] studied the application of activated carbon and Alumina impregnated with various types of amines such as Primary and Secondary alkylamines such as Pentaethylenhexamine (PEHA), sterically hindered 2-amino-2-methyl-1,3-propanediol (AMPD) for gas adsorption applications. In our research study the adsorption of CO₂ onto dendrimer membrane occurs via chemisorption mechanism. So, in this paper we reviewed the various chemisorption processes using amine containing adsorbents.

Dendrimers are a special type of macromolecules having branches, spherical giant molecules with dimensions in nanometre scale. Dendrimers are composed of three parts: a centre, the branches, and an exterior surface layer with functional groups. Thus, those type of structural features of Dendrimer make it applicable as membrane material, besides its other applications like drug delivery, genetic therapy, catalysis, photo activity, size and molecular weight determination, modification of rheology etc [5, 19- 20].

In our current research programme, we have been emphasized on separation of CO₂ by developing high performance CO₂ separation membranes. The gas separation is mainly based on the adsorption property of the membrane. Adsorption is much more efficient technology for CO₂ recovery in comparison to other separation technologies. The pressure swing adsorption technology is widely used method for gas separation purpose [21]. PAMAM (Polyamidoamine) dendrimer immobilized polymeric membranes comprise of some polyvalent linkages exhibits some gas selective property, which makes it applicable in gas separation processes [22-23] . In this research work, we have investigated the adsorption of CO₂ onto the polymeric membranes. The reaction between CO₂ and amine carrier can be explained by Zwitterions mechanism study. Dendrimers are non-volatile and can be used with or without polar solvents such as glycerol, water etc. Pure PAMAM dendrimer liquid provides a high concentration of primary and tertiary amine functional groups such as NH₂. The primary amine group (-NH₂) is known to react strongly with CO₂ to produce a carbamate ion and a protonated base. Although the tertiary amine group is not supposed to react directly with CO₂ like a primary and secondary amine because they take the proton needed in the deprotonation step [8].



Thus for separation of CO₂ molecules the reactions occurred as follows: Bicarbonate: $\text{CO}_2 + \text{H}_2\text{O} + \text{R-NH}_2 = \text{HCO}_3^-$
(Bicarbonate) + R-NH₃⁺ Carbamate: $\text{CO}_2 + 2(\text{R-NH}_2) = \text{R-NHCOO}^- + \text{R-NH}_3^+$

2. Experimental Section

2.1 Materials and Methods a. Materials

Polysulfone (average molecular weight 22000) and Dendrimer (PAMAM G-0) were obtained from Sigma Aldrich Ltd. N-Methyl-Pyrrolidine (NMP) obtained from Rankem, India. Water used was obtained from Millipore water system. (Type 1).

B. Methods

2.1.1 Preparation and characterization of Membrane

For the preparation of flat sheet membranes Polysulfone (PSF) was dissolved in NMP (solvent) at room temperature (26 0-30 0C) .Then to the clear solution a definite amount of PAMAM dendrimer (Zero generation) was added and stirred until it became a homogeneous solution. The solution was casted on glass plates and the glass films were placed in a water bath for about 24 hours. The flat sheet membranes were dried at room temperature and kept in a decicator. The prepared membranes were analysed by IR (PERKIN Elmer system 2000), X-ray Diffraction (JDX-11P-3A, JEOL, Japan), TGA-DTA (PERKIN Elmer PC series, DSC 7). The membrane morphology was studied by Scanning Electron Microscope (LEO 1427 VP, UK). The membrane thickness was measured by thickness gauge meter made by Mitutoyo Corporation, Japan.

2.1.2 Gas Permeation experiment

The permeated amount of the CO₂ gas on the flat sheet polymeric membranes were measured using a mixture of CO₂ and N₂ at 28 0C. The diameter of the circular membrane disc was 3 cm; the permeation area of the circular disc was 28.26 cm². Figure 1 shows the experimental set up for permeation and adsorption experiment. The membrane was fitted in a module made up of Teflon and then sealed. The feed gas pressure was regulated by a pressure regulator. Then the permeated amount of gases were collected in gas sampling bags and analyzed by Gas Chromatography (TRACE 1110, Thermo Fisher).

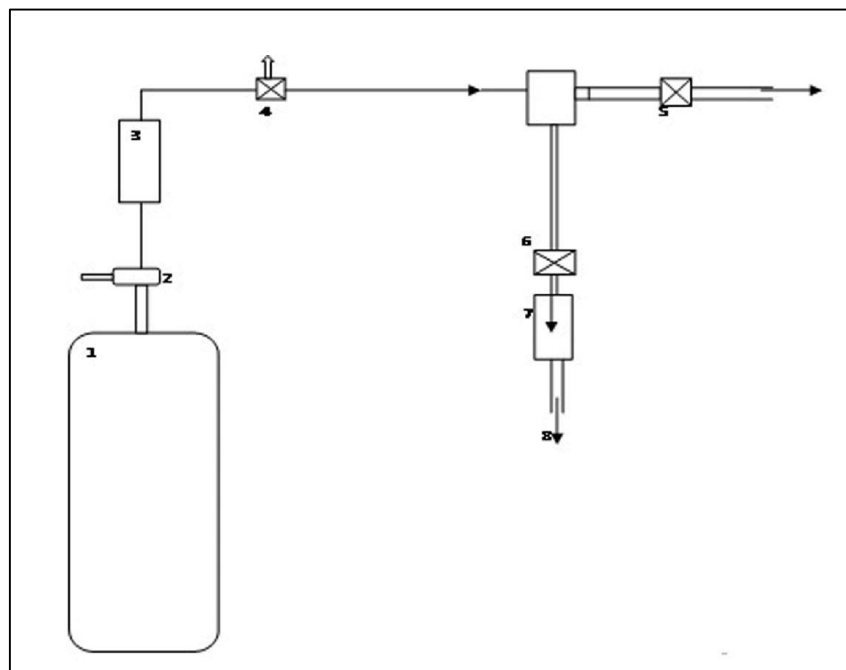


Figure 1. Flow diagram for gas separation experiment

- 1.Gas Cylinder 2. Gas regulator 3.Rotameter 4.Pressure regulator 5. Valve
- 6.Valve 7.Gas rotameter 8.Gas Collector

The Permeance i. e the pressure normalized flux, through the membranes can be obtained by equation (1).

$$(P/l) = Q/ (A.\Delta P) \tag{1}$$

Where Q is the measured volumetric flow rate (at standard pressure and temperature), P is permeability, l is membrane skin layer thickness, A is effective membrane area and ΔP is the Pressure difference across the membrane. The common unit of Permeance is GPU (1 GPU= 10-6 cm³ (STP)/cm² s cm Hg). The ideal gas separation factor or Selectivity is given by

equation (2)

$$\alpha = P_i/P_j \tag{2}$$

Where P_i is permeation of i th component (CO_2) and P_j is permeation of j th (N_2) component.

A schematic representation of CO_2 adsorption onto the membrane is shown in Figure 2 which indicates that the adsorbed amount of CO_2 and selectivity of CO_2/N_2 can be calculated from the amount of retentate and the permeated gas.

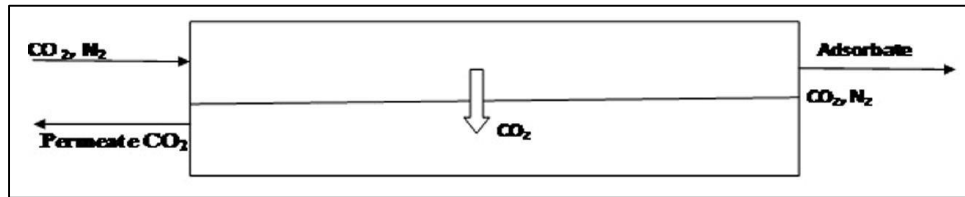


Figure 2. Schematic representation of CO_2 adsorption on membrane

2.1.3 Adsorption Kinetics

The adsorption kinetics of adsorption of CO_2 onto dendrimer membranes were studied at room temperature (280 C) under various pressure and time. For this study CO_2 and N_2 gas cylinders were connected with the experimental set up. The pressures of the gases were regulated by the pressure regulators. In the experimental set up the flow meters and pressure gauges were also connected. By varying the feed gas pressure and time of the experiment the amount of CO_2 adsorbed onto the membrane was calculated and we studied the adsorption kinetics.

The amount of CO_2 adsorbed onto the membrane was calculated by equation (3).

$$q = (m_t - m_0 / m_0) \tag{3}$$

q → amount of CO_2 adsorbed (mg/g)

m_0 → original mass of the adsorbent

m_t → mass of the adsorbent at time t .

2.1.4 Removal of CO_2 by membranes

CO_2 removal capacity of the flat- sheet membrane were measured by a rectangular plate and frame gas permeation cell, which had a membrane area 28.26 cm^2 and thickness was 26 μm . The feed gas was consisted of 77% CO_2 and 23% of N_2 gas. The amount of retentate CO_2 concentration at various feed flow rates were measured by GC analysis.

2.1.5 Analytical methods

The permeated and adsorbed gases were analyzed by Gas Chromatography (GC) (MSA-013201, 230 VEPC). TCD-EPC detector was used and the injector was set as SPK- EPC. The detector temperature was 500 C. The Bridge voltage was set at 6 V. To run the gas sample, the voltage and temperature were stabilized and then 0.5 ml of sample was injected to the injector and run for analysis. The different fractions of gas mixtures were separated in the column, detected in the detector and the sample was identified from the chromatogram by comparing the retention time with the standard gas sample analysis.

2.2 Theoretical Aspects of adsorption of CO_2 on Membranes

Adsorption of CO_2 onto Dendrimer based membranes can be explained by the following steps [15].

1. The CO_2 molecules diffuse from the bulk phase of the membrane surface.

2. The CO₂ molecules transport to the outermost surface of the membranes.
3. The CO₂ molecule undergoes solubilisation into the membrane and adsorption into the dendrimer molecule which was incorporated into the membrane.

We used different types of models viz. Langmuir and Freundlich adsorption isotherms to study the adsorption of CO₂ onto the membranes.

2.3 Langmuir adsorption isotherm

The Langmuir adsorption model is the most common one that was used to represent the amount adsorbed onto adsorbent as a function of partial pressure at a given temperature. The model equation representing the Langmuir adsorption isotherm is

$$\theta = V / V_{\text{mon}} = K p / (1 + K p) \quad (4)$$

The term V represents the volume of adsorbate and V_{mon} the occupied monolayer volume, i.e. the volume required by the adsorbate to complete the monolayer. It is difficult to determine experimentally the monolayer coverage (V_{mon}) accurately. For practical purposes the Langmuir equation is represented in the linear reciprocal form, as shown by the equation as

$$1/V = 1/K V_{\text{mon}} (1/p) + 1/V_{\text{mon}} \quad (5)$$

If the isotherms obeying the Langmuir equation, the volume in the reciprocal form as $(1/V)$ against reciprocal of pressure $(1/p)$ plot is linear. Whereas, if the experimental data plot is nonlinear in nature then Langmuir equation does not hold to describe the given process of adsorption of gases on the solid surface. The monolayer capacity of the isotherm is obtained from the intercept, $i = 1/V_{\text{mon}}$ of the straight line. If we get V_{mon} , the equilibrium constant K can be obtained from the value of slope $s = 1/K V_{\text{mon}}$ of the experimental plot. The value of K is a measure of the strength of the adsorbent-adsorbate interaction, i.e. high values of K represents high strength of interaction between adsorbate-adsorbent, while low values of K shows little strength of interaction [24-25].

2.4 Freundlich Adsorption isotherm

This adsorption equation is used to explain the adsorption properties of gas on heterogeneous solid surface. The empirical equation for gaseous adsorbate can be represented as

$$\theta = x/m = K p^{1/n} \quad (6)$$

Where x is the amount of adsorbate CO₂ molecule adsorbed in moles, m is the mass of the membrane, P is the pressure of CO₂ and K and n are empirical constants for each adsorbent-adsorbate pair at a given temperature. This isotherm can also be represented as

$$\log \theta = \log K + 1/n \log P \quad (7)$$

Here K indicates the capacity of adsorption of CO₂ on the membrane; $1/n$ is a function of strength of adsorption [26-27].

2.5 Thermodynamic parameters for adsorption

The relationship between standard free energy (ΔG^0) and adsorption equilibrium constant (K_{ads}) can be calculated using the following equation

$$\Delta G^0 = -RT \ln K_{\text{ads}} \quad (8)$$

$$\ln K_{\text{ads}} = \Delta S/R - \Delta H/RT \quad (9)$$

Here ΔS , ΔH are the values of change in entropy and change in enthalpy of reaction.

2.6 Computational Details

The CO₂ gas is adsorbed onto the membrane due to the interaction between CO₂ and dendrimer molecule. The interaction energy between dendrimer and CO₂ was calculated by the following equation:

$$\Delta E_{AB} = E_{AB} - E_A - E_B \quad (12)$$

The consistency of the results were checked using BHandH / 6-31++ G (d, p) and MP2/6-31++G (d, p) levels of theory. The interaction between the membrane component, dendrimer and CO₂ gas mainly involves Hydrogen bonding between the -NH₂ of dendrimer and O sites of CO₂ gas. So we used Density functional theory BHandH, MP2/6-31++G (d, p) levels of theory for the calculation of interaction energy between the components. All these values were calculated using Gaussian 09 software [28-32].

2.7 Results and Discussions:

2.7.1 Characterization of membrane

A. IR analysis: The FTIR spectra obtained for polysulfone, dendrimer composite membranes before and after adsorption process respectively are shown in Figure 3. For polysulfone, broad peak was observed at 3400 cm⁻¹, 2330 cm⁻¹ for O-H group and C-H stretching respectively. A broad peak at 3391 was observed in case of dendrimer for N-H stretching. Other IR peaks for dendrimer were found to be 2919, 1647, 1194 for C-H stretching, C=O and C-N respectively. It was observed that for the membrane there were some IR peaks at 3244, 1278, 2800, 1770 cm⁻¹ due to N-H, C-N, C-H, C=O str. due to the presence of dendrimer in the membrane. After adsorption process an additional peak at 3500 cm⁻¹ was observed due to formation of amide linkage of the dendrimer molecule present in the membrane with CO₂. This occurs due to the facilitated transport mechanism on the membrane. Similar observations were reported by Omidkhah et al. and Jiang et al. for the permeation of CO₂ through the Poly(Vinyl Alcohol) and Carboxymethyl Citosane composite membranes respectively [33,34].

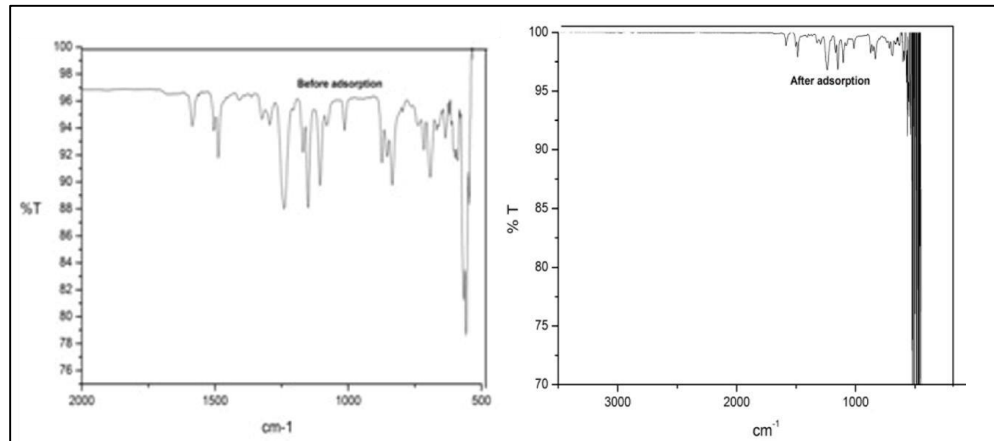


Figure 3. IR analysis of the membrane before/ after adsorption

B. X ray Diffraction analysis: The diffraction patterns of the membranes had been studied by XRD spectra and is shown in Figure 4. The polysulfone - dendrimer containing membrane showed a broad peak in the range of 1.29-3.69 before the adsorption process. The broad peak was observed due to complete homogeneity and compatibility among the components of the membrane. The broad peak of the composite membrane indicated the amorphous state of the membranes. After the adsorption process, the lattice parameters and crystal structure were altered suggesting the deformation of the membrane surface due to interaction of dendrimer with CO₂ resulting in the formation of windows on the membrane surface. The intensity of the peaks in the membrane decreased after the adsorption process. Thus before adsorption greater intensity peaks were obtained in comparison to the after adsorption process. It was due to the formation of windows on the membrane surface during adsorption of CO₂ onto the polymeric membrane. The Full width half maximum value (FWHM) given in Table 1 indicates the value of relative degree of the amorphous phase in the membranes.

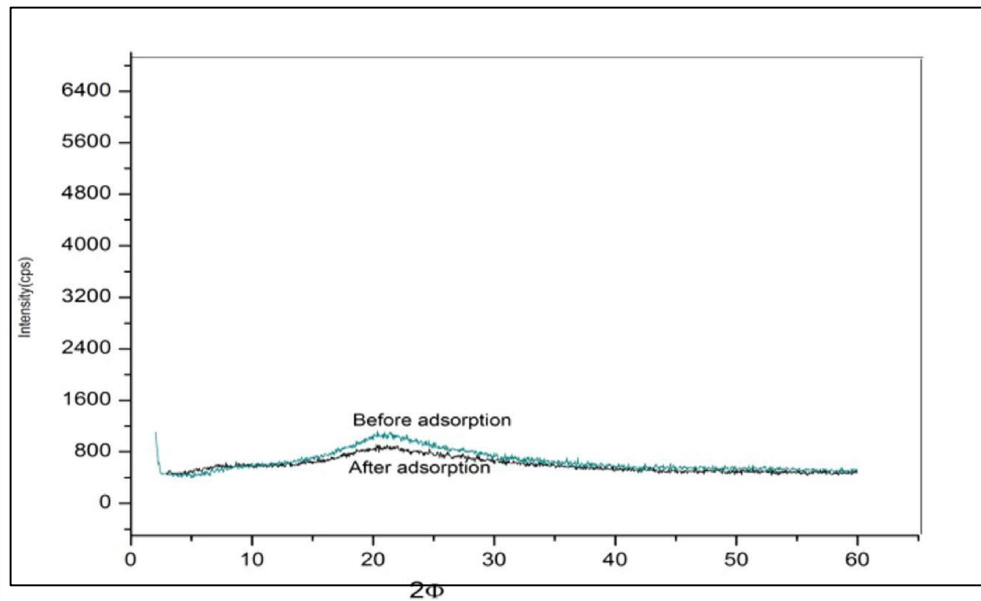


Figure 4. XRD analysis of membranes

Table 1: XRD Analysis of membrane

Membranes	2 ^θ (°)	d (spacing)	Wavelength (Å)	FWHM (cm)
Before adsorption	24	5.15	1.79	9.2
After adsorption	20	4.30	1.79	2.5

C. Thermal properties: The thermal behaviour of the gas separation membranes were studied by thermogravimetric analysis which was carried out under nitrogen atmosphere at a heating rate of 100 C min⁻¹. The decomposition curves were shown in Figure 5a and derivative curves were shown in Figure 5b. From the figure it was seen that the membrane was stable up to 488 OC and a gradual loss of mass of the membrane was observed till 600 OC. The DTA curve for the membrane has one exotherm with peak at around 525 OC-558 OC.

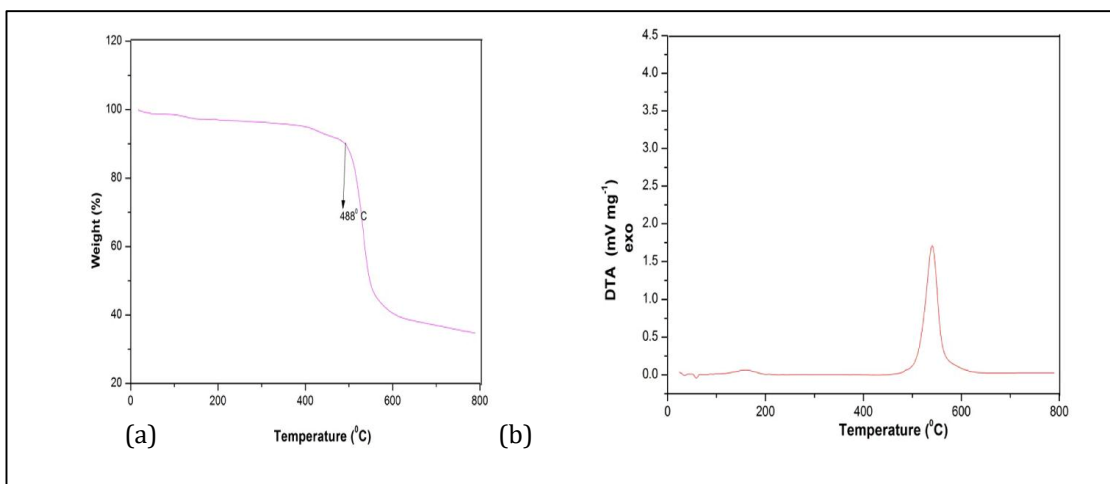
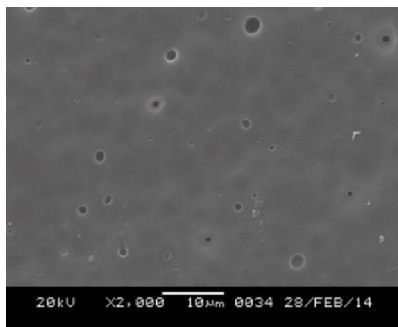
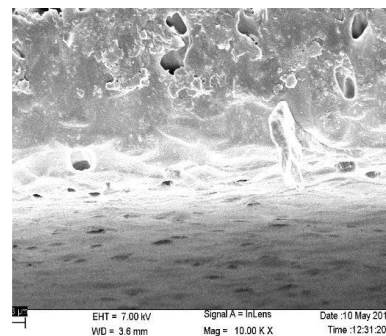


Figure 5. TGA (a) and DTA (b) chromatogram of Dendrimer incorporated membrane

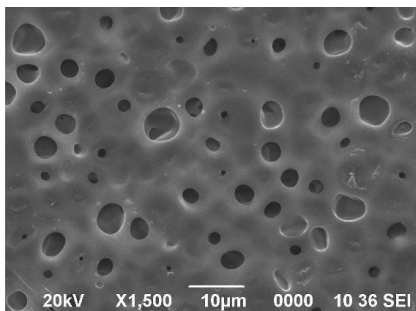
D Membrane Morphological Study: The morphology of the membranes were studied by SEM analysis. The SEM photographs of the membrane are shown in the Figure 6. From the figure it was seen that the morphology of the membranes differ before and after adsorption. It was observed that the adsorption of CO₂ gas onto the polymeric membrane altered the membrane morphology. This can be attributed to the formation of windows due to the reaction between dendrimer and CO₂ molecule during the adsorption process. In windows forming membrane, the windows for gas molecules are occupied solely by CO₂, which acts as a gate to block the passage of the other gases. Consequently, the amount of the other gases leaking to the other side of the membrane was greatly limited and a high concentration of CO₂ gas was adsorbed by the membrane. The higher numbers of pores in the membrane after adsorption process was attributed to its adsorption capacity due to the formation of windows on the membrane.



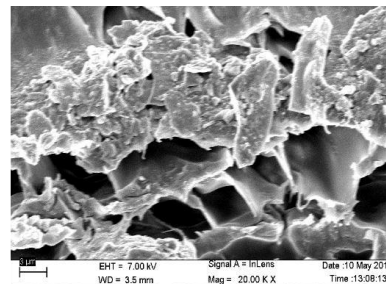
(a) Front view



(b) Side view of membrane before adsorption



(c) Front view



(d) Side view of membrane after adsorption

Figure 6: SEM Photographs of membrane for before adsorption and after adsorption

2.8.1 Effect of feed gas pressure on permeability

The permeability of CO₂ decreased with increase in pressure, the permeance behaviour of N₂ showed similar behaviour with the variation of pressure (Figure 7). The membrane showed a gradual decrease in the CO₂ and N₂ permeability behaviour up to a pressure of 50 cm of Hg. The Permeance capacity of Polysulfone and Cellulose Acetate membranes for CO₂ showed the similar trend of variation with pressure as reported in the previous literature [35]. PDMS/ PSF composite membrane also showed the similar kind of behaviour for Permeance of CO₂ as reported by Mansoori et al [36].

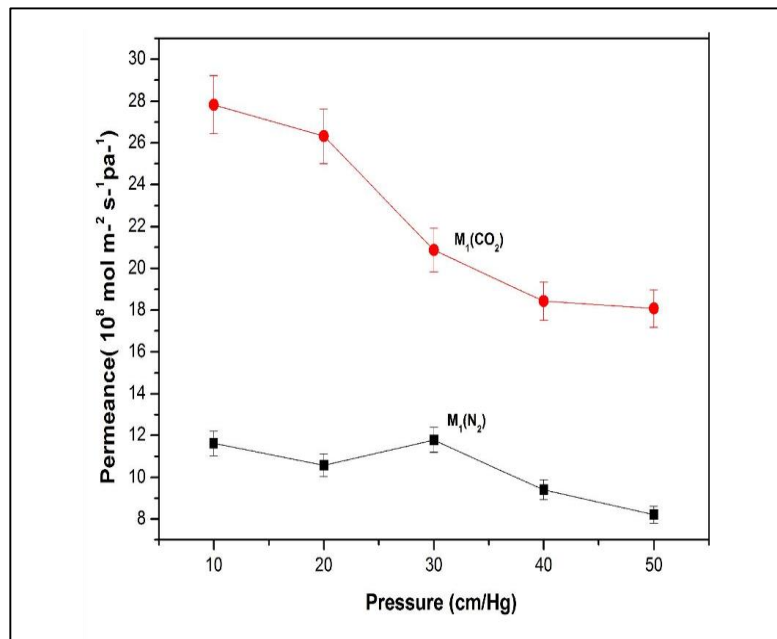


Figure 7: Effect of feed gas pressure on permeability. The error bars corresponds to one standard deviation of mean of five independent experiments.

2.8.2 Effect of feed gas pressure on selectivity of CO2 using CO2/N2 as feed gas

The selectivity of the membrane for CO2 and N2 adsorption decreased with increasing pressure (Figure 8). This was due to the higher rate of CO2-amine reaction. For higher rate of the reaction, adsorbed amount of CO2 decreased for formation of windows on the membranes which facilitated the CO2 permeability. As a result the CO2/N2 selectivity decreased. Thus, the selectivity order of the membranes followed the 'dual-mode' sorption model of permeation of gas through the membrane. The selectivity of CO2/N2 is comparable with that of other membranes reported in literature [37]. The effect of pressure on selectivity of CO2 over CH4 also showed the similar behaviour as reported in literature [38]. The separation performance of the dendrimer composite membrane was compared to the separation performances of the membranes reported in the previous literatures which are given in table 2.

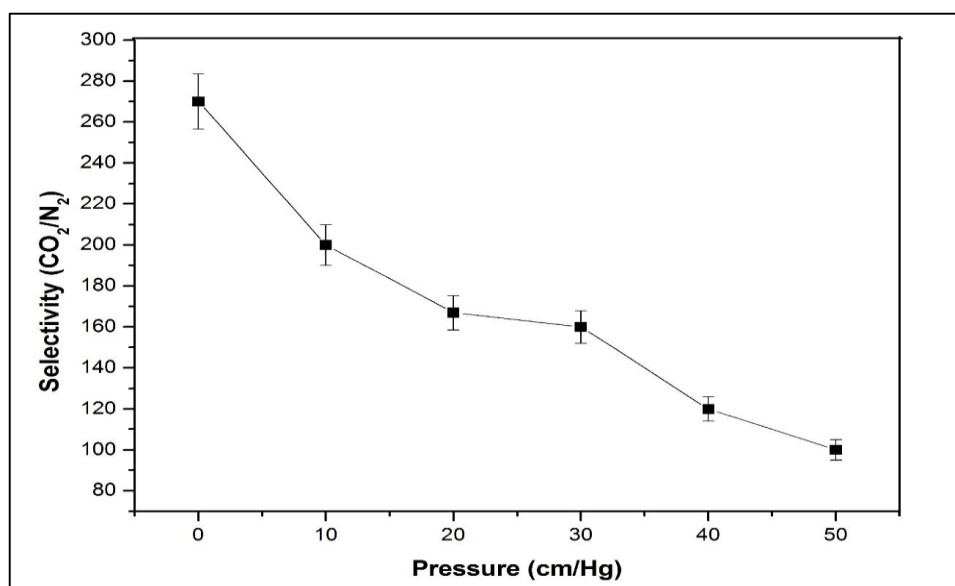


Figure 8: Effect of feed gas pressure on selectivity of CO2. The error bars corresponds to one standard deviation of mean of five independent experiments.

Table 2: Comparison of CO₂ separation performances of some membranes

Sl no	Types of Membranes	CO ₂ Permeance PCO ₂ ($\times 10^8$ mol m ⁻² s ⁻¹ pa ⁻¹)	Separation factor (α)	References
1	DDR -Type membranes	30	200	9
2	Zeolite - T membrane	4.6	400	39
3	SAPO-34-membranes	20	36	40
4	Polysulfone-Dendrimer	27.2	270	Current work

2.8.3 Effect of Feed flow rate on Exit CO₂ concentration

The effect of feed molar flow rate on the exit dry CO₂ concentration was studied considering five different flow rates keeping gas composition constant. From Figure 9, it was seen that exit dry CO₂ concentration increased with increasing flow rate and achieved a high CO₂ concentration 7.62 m mole /g when flow rate was 20L/min. This amount of exist dry CO₂ concentration was attributed to high CO₂ permeability of the membrane.

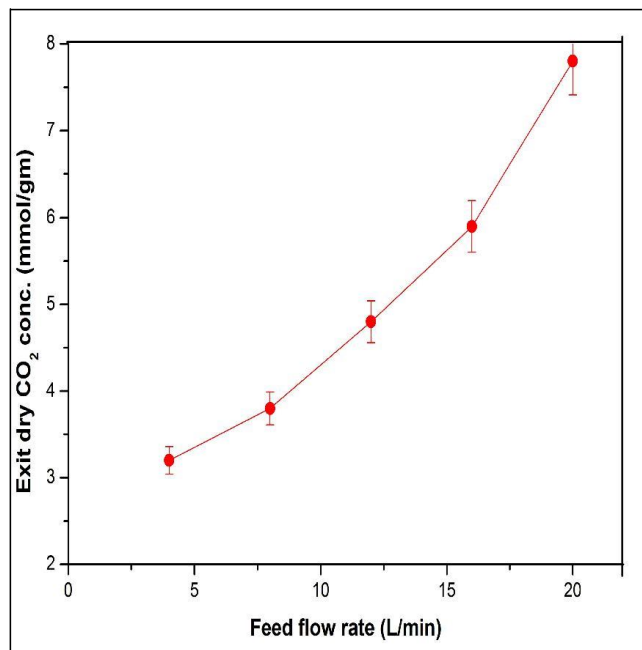


Figure 9: Effect of Feed Flow rate on exit dry CO₂ concentration. The error bars corresponds to one standard deviation of mean of five independent experiments.

2.8.4 Adsorption Isotherm Study

The adsorption of CO₂ onto Dendrimer membrane was measured under an isothermal condition (i.e. 280 C). It was observed that the membrane showed a general behaviour of the extent of adsorption with pressure, i. e the amount of CO₂ adsorbed on membrane increased in a rapid manner with the increase in pressure. This isotherm indicated monolayer adsorption behaviour. Besides, the slope of adsorption isotherm determined the extent of interaction between CO₂ and adsorption site of membrane. It was obvious that the membrane showed a greater extent of adsorption at a pressure of 50 Bar. For the optimization of the adsorption isotherm model it was required to establish the suitable adsorption equilibrium curve. We derived the adsorption equilibria from Langmuir and Freundlich values and their corresponding coefficients of correlation (R²) which are given in Table 3. The adsorption isotherms for adsorption of CO₂ on the membranes were best fitted in Langmuir adsorption isotherm as shown in Figure 10. From the Table 3 it is seen that R² values are greater than 0, but less than 1 for each model.

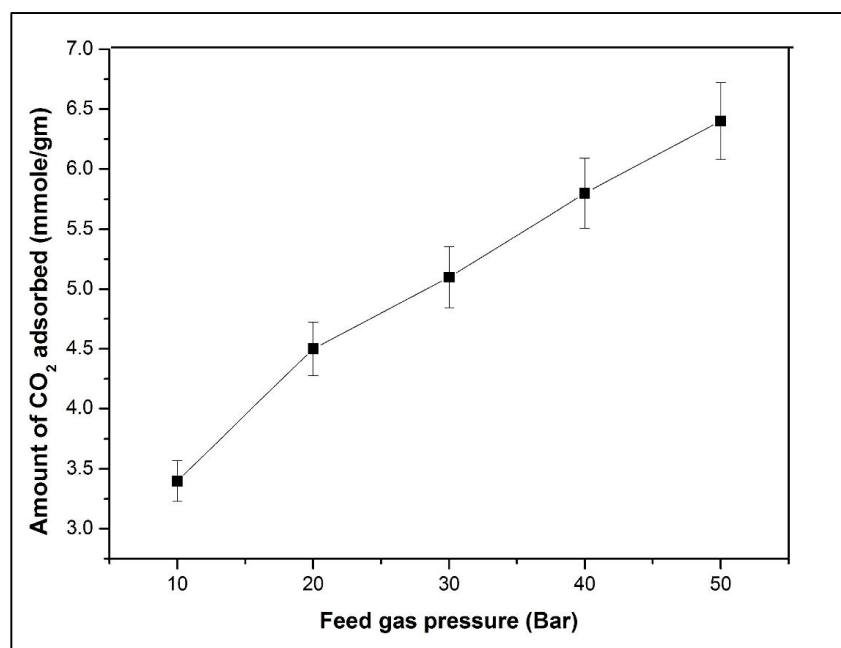


Figure 10: Adsorption isotherm of membranes for adsorption of CO₂ onto membrane.

The error bars corresponds to one standard deviation of mean of five independent experiments.

Table 3: Adsorption Isotherm constants for adsorption of CO₂ on the Polymeric membranes

Isotherm	Langmuir Isotherm			Freundlich Isotherm		
	q _m (mmol-1g-1)	K _L (gmmol-1)	R ²	1/n	K _f (mmol-1g-1)	R ²
Polysulfone Dendrimer	4.24	39.06	0.997	0.46	7.01	0.965

The Freundlich adsorption isotherm model (Equation 6) was examined by plotting lnq_e vs ln C_e and the value of R² is shown in Table 3. The values of 1/n for adsorption of CO₂ were found to be less than unity shows that the adsorption process was favourable. From the comparison of the correlation coefficients (R²) of all the adsorption models, it was found that the Langmuir adsorption isotherm showed the most satisfactory representation for the adsorption process. The CO₂ adsorption performance of the membrane was compared with the other materials which were reported in the previous literature are given in the table 4.

Table 4: Comparison of CO₂ adsorption performances with some other materials

Types of Materials	Types of isotherms fitted	Isotherm parameters			References
		q _m (mmol-1g-1)	k(gmmol-1)	R ²	
Zeolite 13 X	Langmuir adsorption isotherm	4.245	19.03	0.987	41
Zeolite 4A	Langmuir adsorption isotherm	3.263	11.202	0.997	41
AC(Activated Carbon) Polysulfone-dendrimer composite membrane	Langmuir adsorption isotherm	2.828	21.956	0.961	41
	Langmuir adsorption isotherm	4.24	39.06	0.997	Current work

2.8.5 Adsorptive Interaction

The calculated BSSE corrected energy of interaction between membrane component dendrimer and CO₂ molecule at three different levels of theory, B3LYP/6-31++G (d, p), MP2/6-31++G (d, p) and BHandH/6-31++G (d, p) are given in the Table 3. From the values given in the table, it was seen that enthalpies of adsorption depended on adsorptive interaction energy. Enthalpy of a process indicates the strength of solute-sorbent binding interaction and thus it significantly affects the adsorption affinity of an enthalpic process. Negative value of Gibbs free energy indicates the feasibility and spontaneous nature of the adsorption process.

 Table 5: Interaction Energy Δ_{int} (K cal mol⁻¹) and thermodynamic parameters of adsorption

Interacting components	B3LYP/6-	MP2/6-	BHandH/6-	ΔG_0	ΔH_0
	31++G(d, p)	31++G(d, p)	31++G(d, p)	(KJmol-1)	(KJmol-1)
Dendrimer-CO ₂	-36.457	-37.613	-42.263	-21.09	-12.81

In all the above three theory, it is observed that, dendrimer interacts favourably with CO₂ gas, which results in selective adsorption of CO₂ from a gaseous mixture.

2.8.6 Adsorption Kinetics study

For the investigation of the time transient adsorption profile we studied the pseudo first order and pseudo second order kinetic models.

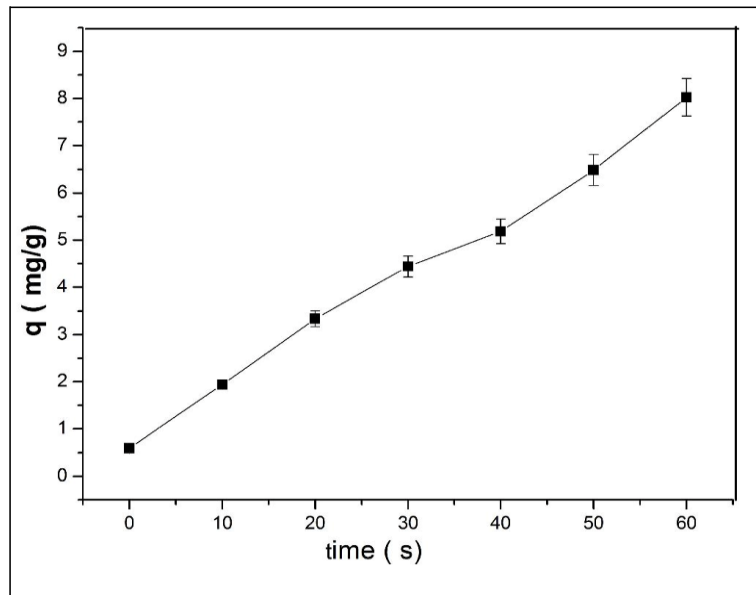


Figure 11: Time transient CO₂ uptake. The error bars corresponds to one standard deviation of mean of seven independent experiments.

The pseudo first order and second order equations are given as [37]

$$\log (q_e - qt) = \log q_e - k_1 t \tag{13}$$

$$\frac{t}{qt} = \frac{1}{k_2 q_e} + \frac{t}{q_e} \tag{14}$$

Where; q_e and qt (mg/g) are the amounts of CO₂ adsorbed on the membrane at equilibrium and at time t (s). Here, k_1 (g/mg.s) and k_2 (s⁻¹) are the rate constants of first order and second order pseudo equations. Applying the pseudo first and second order kinetics on the experimental datas, the parameters for the adsorption process were calculated which are given in Table 6. From the figure 12, it was observed that the pseudo first order model was not fitted for the adsorption process of the membrane for which R² value was obtained as 0.921.

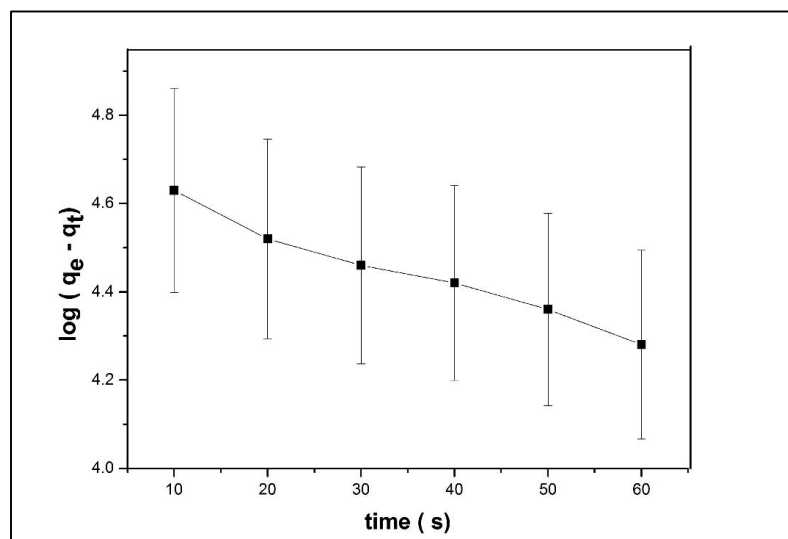


Figure 12: Pseudo first order model. The error bars corresponds to one standard deviation of mean of six different independent experiments.

Table 6: Rate constant for the Adsorption Kinetics

Dendrimer Membrane	Pseudo first order rate constant		
	K1(s-1)E-3	Rate equation	R2
	7.4	$\log(q - e^{-qt}) = -0.00744t + 4.716$	0.921
	Pseudo Second order rate constant		
	K2 (g/mg. s) E-3	Rate equation	R2
4.2	$t/qt = 0.404t + 1.456$	0.99	

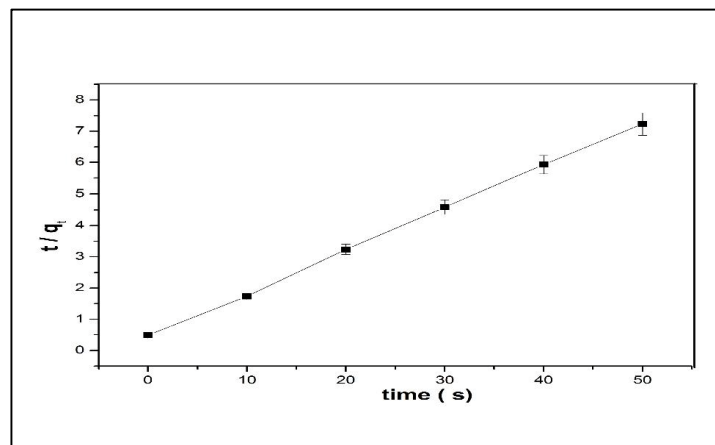


Figure 13: Pseudo second order model. The error bars corresponds to one standard deviation of mean of six different independent experiments.

While fitted the experimental values in Pseudo second order model the value of the correlation coefficient obtained was 0.99, from the values of K₁ and K₂, we get the ideas about the adsorption rate of the membrane. The larger K₂ value indicates slower adsorption process and vice versa [38].

Thus; it was observed that the adsorption process on the membrane followed the pseudo second order kinetics. The results obtained from the kinetics study were comparable with the datas reported in the earlier literature. Sarah et al. [38] in their study of CO₂ adsorption in Cellulose Acetate membrane observed that the adsorption process in the Cellulose Acetate membrane also followed the pseudo second order kinetics with a value of correlation coefficient 0.98-0.99 [38].

3. Conclusions

The adsorption of CO₂ gas onto the polymeric membrane was studied using a gaseous mixture of CO₂ and N₂. It was observed that the adsorption process was affected by the feed gas pressure, feed flow rate etc. The adsorption isotherm was investigated and adsorption behaviour for adsorption of CO₂ was best fitted with the Langmuir isotherm. Adsorptive interaction was strongly related to the interaction energy between adsorbate and adsorbent. It was observed that the adsorption kinetics followed the pseudo second order kinetics for CO₂ adsorption process onto the dendrimer membrane.

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Conflict of Interest

The authors declared no conflict of interest.

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