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A Kinetic Study of CO_2 Adsorption in Cellulose Acetate Membranes

Sarah Hafeez, X. Fan, and Arshad Hussain

***Abstract*—In this research, the CO_2 adsorption study on glassy pure and modified Cellulose Acetate(ca) polymer is conducted to explore, either "dual mode sorption model" of glassy polymers can be supported by pure and modified ca membranes or not. These membranes were fabricated and characterised by SEM and FTIR analysis techniques. According to results, the CO_2 gas was adsorbed by both membranes and adsorption capacity reached the maximum at different pressures. The experimental results were calculated and validated by pseudo first order, pseudo second order and intra-particle diffusion models. According to correlation factor R_2, the Pseudo second order model was fitted well with experimental data. The experimental and calculated data has confirmed the dual mode sorption model of CO_2 capture in dense pure and modified ca membranes.**

***Index Terms*—Cellulose acetate, gas adsorption, pseudo order models, CO_2, global warming.**

I. MAIN TEXT

In 2005, world CO_2 was estimated as 28051 million metric tons (MMT) and it was estimated that it will reach at 42325 MMT in the year 2030. Other than this, Natural gas reservoirs also need to be purify by capturing CO_2 [1]. The various techniques such as membrane gas separation, cryogenic distillation, amine absorption, and membrane gas absorption and adsorption processes are being implemented to capture CO_2 gas. But membrane gas separation and adsorption processes has been considered and explored more, because of low capital and operation cost, low energy requirement, environment friendly, small foot print and flexibility in handling of higher flow rate, pressure and various feed composition [2].

Since last decade, CO_2 adsorption technique, utilizing particles or fillers as adsorbent, is getting importance day by day. Various adsorbents have been fabricated to study adsorption of CO_2 gas on them. The activated carbon has been extensively utilised due to low cost, thermal stability and less sensitivity towards moisture [3]. On the other hand, single wall, multi wall CNTs [4] and grapheme have also been studied thoroughly for CO_2 adsorption. In recent years, Zeolite, alumina [5] and silica [6] have produced remarkable results in CO_2 adsorption [7], [8]. Lately, Metal-organic frameworks (MOFs) have attracted the attention of many researchers in recent years due to high CO_2 capture efficiency. But the main drawback of low CO_2 selectivity persuades the researchers to work with amine functionalized adsorbents.

With development in this technique, membranes are also considered to be investigated for CO_2 capture by adsorption of gas in membranes. In this regard, different studies have been made such as Zeolite Y membranes were studied by M. T. Sinder *et al*., for CO_2 adsorption [9]. Zeolite Imidazolate membranes were researched thoroughly for CO_2/CH_4 adsorption process and I. Inzoli *et al*. has worked on silicalite-1 membrane to know the thermal effects during n-butane adsorption [10]. In 2011 the nano composite (B)-MFI alumina membranes were investigated for CO_2/N_2 gas adsorption by Nicholas *et al.*, [11]. Interestingly, all the membranes mentioned above, contained pores (meso or nano) which help in adsorption of CO_2. Surprisingly, no work regarding CO_2 adsorption in dense polymeric membranes has been presented.

The dense polymeric membranes have been used in membrane gas separation applications. The gas transports through these membranes depend upon principle of solution-diffusion mechanism [12], in which the gas molecules absorbed, diffuse and penetrate downstream under pressure gradient. In glassy polymers, dual mode sorption model is used to describe sorption and penetration of gas molecules in glassy polymers This model consist of a Henry's law 'dissolved' mechanism of gas sorption through polymer and Langmuir 'hole-filling' mechanism, gas adsorption in voids and cavities in glassy polymers [13], [14].

The above mentioned laws are important in a respect that in glassy polymeric membranes, gases sorbed, dissolved and adsorbed. This adsorption can affect the permeability and selectivity of gases through membranes. It can also modify the gas rejection properties of membrane.

In this work, Diffusion Induced Phase Separation (DIPS) technique was utilised to synthesize pure and modified ca membranes by APTMS. The morphological studies were done by SEM, whereas qualitative studies of membranes were done by FTIR analysis. The data was modelled using pseudo first order and pseudo second order models. To complete the kinetics study, intra- particle diffusion model was also studied to explore the steps involve in the gas sorption process.

II. EXPERIMENTAL

A. Chemicals

The Cellulose acetate (ca), Acetone, Isopropyl Alcohol,

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Sarah Hafeez is with School of Chemical and Materials Engineering (SCME), National University of Sciences & Technology, Islamabad, Pakistan and Institute for Materials and Processes, School of Engineering, University of Edinburgh, Scotland, UK (e-mail: sarah@scme.nust.edu.pk).

X. Fan is with Institute for Materials and Processes, School of Engineering, University of Edinburgh, Scotland, UK (e-mail: X.Fan@ed.ac.uk).

Arshad Hussain is with School of Chemical and Materials Engineering (SCME), National University of Sciences & Technology, Islamabad, Pakistan (e-mail: arshad.hussain@scme.nust.edu.pk).

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APTMS were bought from Sigma Aldrich UK.

B. Methods

1) Modification of CA

The modification of ca was done according to the reported procedure [6]. ca was dissolved in Acetone and then ultrasonicated for 30 minutes after adding APTMS (3-aminopropyltrimethoxysilane). The mixture was magnetically stirred at room temperature for 6 hrs.

2) Fabrication of membranes

The membranes were fabricated following the procedure published already [15]. The pure blended membrane was synthesized by dissolving in 1.5 g of ca in 10 ml of acetone kept on stirring. The pure and modified membranes were casted on glass slab after the removal of bubbles in mixture. After casting gelling of membranes was done by dipping membrane is cold water for 20 min. In next step membrane was dipped in hot water 80˚C for 30 minutes. Isopropyl alcohol was utilised to dry the membranes. The ca and ca-APTMS modified blended membranes (cap) were considered in this study, which labelled as M (a) and M (b) respectively.

3) Setup to study sorption kinetics

The sorption studies of pure and modified membranes were conducted at 25˚C under various pressures and time. It was comprised of two gas cylinders such as CO_2 and N_2, which were connected to the cell through stainless steel pipes. The gases were controlled by Lab Master Pressure regulators. The whole setup was placed in temperature controlled environment with proper exhaust ventilation (Nederman). The flow meters and pressure gauges (Scotia Instrumentation) were connected to record the required flows and pressures during the experiments. The CO_2 (Cozir) sensor was connected at the other end of the setup which ultimately connected with computer to read data. The membrane cell was 2 cm in diameter and designed in a way that it can hold the gas at particular pressure.

At the first stage of the experiment the N_2 gas was passed through membrane cell. The flow was maintained at 100cc/min with 1 bar pressure. In the second stage, membranes were cut in circular shape with diameter of 2 cm. These membranes were regenerated at 120˚C. After weighing them, these membranes were mounted in adsorption cell and purged with N_2 for two hours before starting the adsorption studies. The following equation was used for calculating CO_2 adsorption.

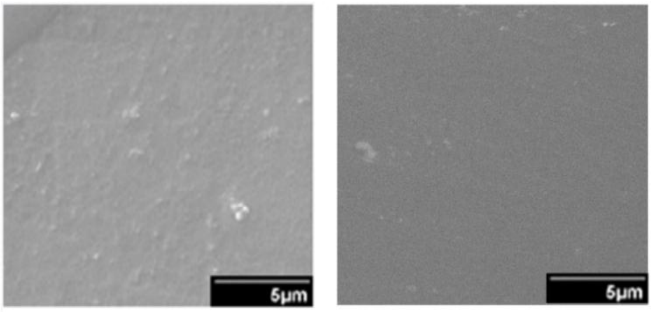
$$q=\left(\frac{m_t-m_o}{m_o}\right) \tag{1}$$

where q is amount of CO_2 adsorbed (mg/g), m_o is the original mass of adsorbent and m_t is the mass of adsorbent, at time t.

III. RESULTS AND DISCUSSIONS

A. SEM Analysis

The surfaces of membranes were studied by SEM, S-4700 Hitachi, Japan).SEM images were captured and represented in Fig. 1. The surfaces of membranes were studied at 5000* magnification, magnifications. The surfaces of pure and APTMS modified ca membranes are dense and completely smooth.



M (a)   M (b)

Fig. 1. SEM micrographs.

B. FTIR Analysis

The qualitative structural analysis of membranes was performed by Fourier Transform Infrared spectroscopy to observe the functional groups in synthesized membranes and represented in Fig. 2. According to the Figure, it can be observed in both spectra, the peaks at 3417cm^{-1}, 1790 cm^{-1}, 1370 cm^{-1} and 1235 cm^{-1} are representing the stretching vibration Carboxylic group (-COOH), C=O group , C-CH_3 bond and C-O-C group.

In FTIR spectrum of CA-APTMS M(b), the wide peaks at 3,434 cm^{-1}, 1,569 cm^{-1} are depicting the presence of NH group confirm the amine functionalization.

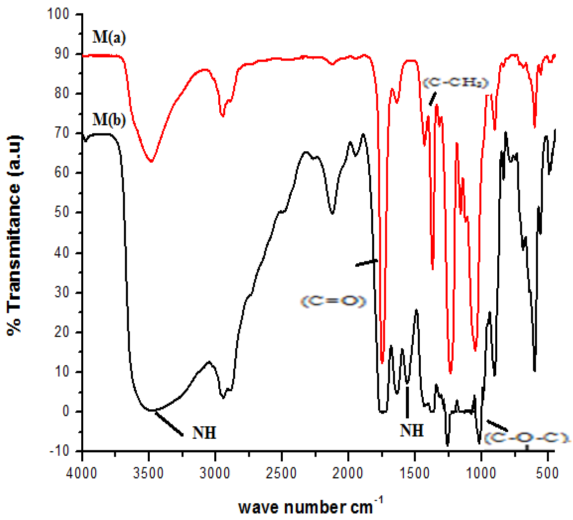


Fig. 2. FTIR spectra.

C. Adsorption Capacity

Theoretically, adsorption of CO_2 in membranes can be explained by three main steps.

1) The gas molecules transport from bulk phase near the surface of membrane.
2) The gas gets diffuse into the external surface of membrane.
3) Further, gas molecules solubilize in membrane and get adsorb in polymeric chains.

The slower process of the adsorption, determines the overall uptake rate [16]. For this reason, CO_2 gas adsorption and its kinetics were explored. The adsorption isotherms of blended membranes are given in Fig. 3. According to these

Isotherms, both dense membranes have adsorbed CO_2 gas. Interestingly, the CO_2 adsorption in cap (M(b)) blended membrane is high as compared to pure membrane. This modified membrane has the acetate and ester groups of ca and amine functionalization of APTMS, which enhanced the CO_2 affinity. The CO_2 adsorption trend is increasing linearly for both membranes, till it reaches maximum at 1 bar for cap and 1.5 bar for pure ca membrane. However, from 1.5 bar the adsorption of CO_2 become constant.

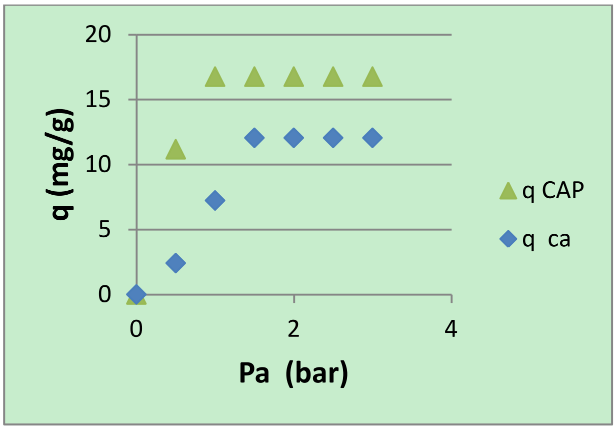


Fig. 3. CO_2 adsorption at pressures.

D. Adsorption Kinetics

The time transient CO_2 adsorption profiles of both CA and CA-APTMS are represented in Fig 4. According to this Figure, it can be observed that CO_2 gas has been adsorbed by dense pure CA membrane, which is very attention-grabbing result with respect to dense membranes but modification with APTMS, resulted in NH- functionality in CA membrane. Which resulted in enhanced CO_2 adsorption. This result is very interesting as the NH functionality and free volume has increased uptake of CO_2.

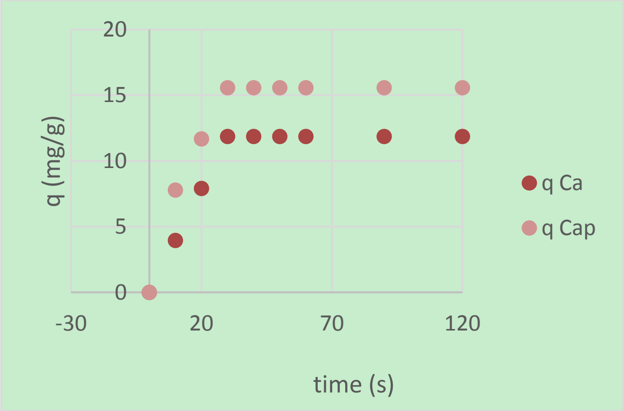


Fig. 4. Time transient CO_2 uptake.

The kinetics were explored by two models represented in the form of two equations, given below. The pseudo first order and second order equations are given as,

$$\log(q_e - q_t) = \log q_e - k_1 t \qquad (2)$$

$$\frac{t}{q_t} = \frac{1}{k_2 \, q_e^{\,2}} + \frac{t}{q_e} \qquad (3)$$

where q_e and q_t (mg/g) are the quantity of CO_2 adsorbed in membrane at equilibrium and at any time, t is the time (s) of adsorption. Whereas k_1 (g/mg.s) and k_2 (s^{-1}) are the equilibrium rate constant of first and second order pseudo equations. The parameters are calculated by application of pseudo first order and second order on experimental data and tabulated in Table I and II. According to them; the pseudo first order model was not fit very well with the experimental data of both fabricated membranes (see in Fig. 5). The values of R^2 for both membranes are 0.81 and 0.54 respectively.

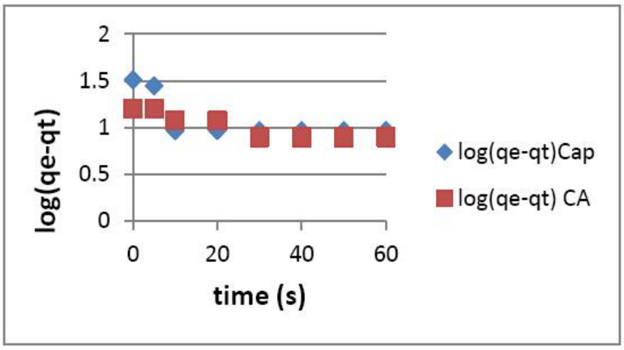


Fig. 5. Pseudo first order model.

TABLE I: PSEUDO-FIRST-ORDER RATE CONSTANTS

Membranes	$K_1(s^{-1})$ E-3	Rate equation	R^2
M(a)	1.0	$Log(q_e\text{-}q_t) = -0.001t+1.089$	0.54
M(b)	5.0	$Log(q_e\text{-}q_t) = -0.005t+1.168$	0.81

To confirm either Pseudo second order equation fits well on experimental data of both membranes, the value of K_2 is calculated using pseudo second order model (see in Fig. 6).

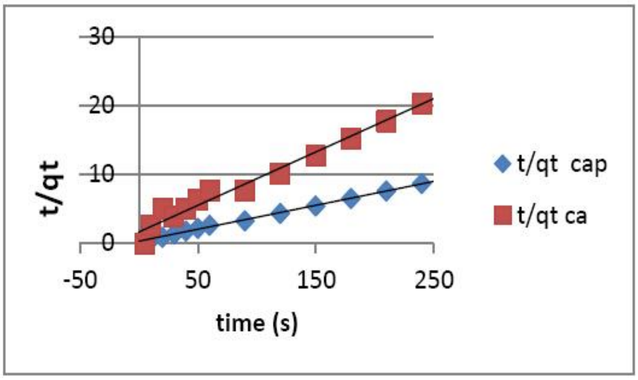


Fig. 6. Pseudo second order model.

The values of correlation coefficient are 0.98 and 0.99. The rate constant K_2 determines the adsorption rate in both membranes. The larger the value of K_2, slower will be the adsorption rate.

Here K_2 is nearly same, so the adsorption rate in both membranes is also nearly similar.

TABLE II: PSEUDO-SECOND-ORDER RATE CONSTANTS

Membranes	K_2 (g/mg.s) E-3	Rate equation	R^2
M(a)	3.5	$t/q_t = 0.077t+1.655$	0.98
M(b)	3.3	$t/q_t = 0.034t+0.341$	0.99

Other than pseudo first order and second order model, intra- particle diffusion model is also very essential to explore complete adsorption process. As written above, the adsorption process is based on diffusion of adsorbate from bulk phase to the surface of adsorbent and is followed by diffusion and solubility inside the active places of adsorbent. According to Ho *et al.*, 2000, the intra particle diffusion was given in the form of equation given below.

$$q_t = kt^{\frac{1}{2}} + C \tag{4}$$

where q_t is the amount of CO_2 amount adsorbed (mg/g) intra in particular time t (s) and k is the intra particle rate constant (mg/s). The Fig. 7 represents the plot of q_t versus square root of time.

In the literature, a straight linear plot is observed for adsorption process which obeys intra particle diffusion mechanism. Which means that particles are obeying only diffusion mechanism during adsorption. On the other hand, according to Fig. 7, the curve is divided into two main steps. This curve is confirming that this adsorption is not exclusively depends upon intra particle diffusion mechanism. The linear increasing region range from 10-40 s is probably due to attraction sorption of gas molecules on the surface of membrane and the region from 40s to onwards be reflecting intra particle diffusion mechanism.

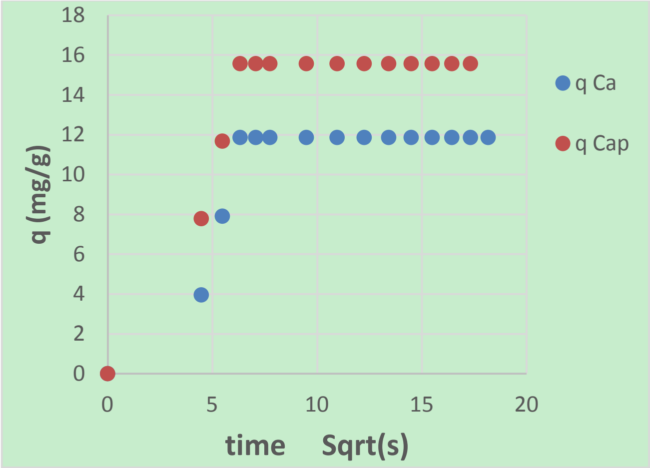


Fig. 7. Intra particle diffusion model.

IV. CONCLUSION

Cellulose acetate polymer belongs to the class of glassy polymer. According to literature, glassy polymeric membranes follow the “dual mode sorption model” of gas transport. This model is comprised of two main parts, the dense structure and molecular scale cavities. This shows that there must be chances of CO_2 adsorption in dense membranes. In this research, the pure CA membrane and APTMS modified CA membranes were fabricated to study the gas sorption process through these membranes. The resulting membranes were analyzed by Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM). SEM of all membranes reveal smooth and dense surface layer. The CO_2 adsorption study was done on both membranes and surprising results were obtained that CO_2 gas was adsorbed in membranes. But CO_2 adsorption capacity is high in case of APTMS modified CA membranes which showed that the free volume, OH and NH-functionality have affected the CO_2 adsorption capacity. As CA and APTMS CA membranes are mostly utilised for gas separation processes, so adsorption studies has showed that adsorption capacity of CO_2 can affect the permeability and selectivity of gases. As permeability of gas depends on diffusivity and solubility of gases.

The pseudo first order and second order models were applied to confirm the experimental results of CO_2 adsorption on membranes. The pseudo second order model validated all experimental results as its R^2 value is near 1. The intra particle diffusion model validated that adsorption mechanism in membranes was not one step procedure, it’s not the surface phenomena; probably diffusivity and solubility were also involved in CO_2 adsorption. This study is very promising as it reveals that dense polymeric membranes also capture CO_2 by adsorption to purify the environment.

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Sarah Hafeez is a PhD researcher at National University of Sciences and Technology Pakistan. She has completed her M.S. degree in energetic materials from (NUST) National University of Sciences and Technology with gold medal. She has visited University of Edinburgh, Edinburgh, UK under the supervision of Dr. X. Fan. She has published seven papers in Thomas Reuters enlisted journals and 2 papers have been accepted in international conferences. Her research interests are gas separation technologies, gas separation membranes, polymers, composites.

X. Fan has done B.Eng., M.Sc., Ph.D. degrees in chemical engineering, materials and metallurgy. He was a senior lecturer in petroleum and chemical engineering in London South Bank University and then joined School of Physics and Astronomy, & Department of Chemical Engineering, University of Birmingham, UK as a research fellow. Now he is a senior lecturer in University of Edinburgh, UK. He has published 148 papers in reputed journals. He is a editorial board member of Journal of Materials Science and Chemical Engineering and Nano Science and Technology. He is working in the projects of CO_2 capture and waste water treatment.

Arshad Hussain has joined the Department of Chemical Engineering at CCE&MS. He has gone through extensive work in process and maintenance operations. He was involved in management of day-to-day operation, monitoring and maintenance of the production units. He got his M.S. and Ph.D. degrees in chemical engineering from Germany. His research work was focused on the characterization of different inorganic membranes used for membrane reactors to be employed for partial oxidation and dehydrogenation reactions. As a postdoctoral fellow at Center for Marine CNG, St. Johns Canada, he worked on a research project to study the natural gas compositional, thermo-physical and fluid phase analysis under varied pressure and temperature conditions during loading and unloading operations using custom designed PVT systems.