Iraqi Journal of Chemical and Petroleum Engineering
Vol.18 No.2 (June 2017) 57 - 67
ISSN: 1997-4884

University of Baghdad
College of Engineering

Study the Performance of Nanozeolite NaA on CO_2 Gas Uptake

Najwa Saber Majeed and Jwan Taher Majeed
Chemical Engineering Department, College of Engineering, University of Baghdad
Email: dr.najwa_saber@yahoo.com and eng.jwan1@yahoo.com

Abstract

The adsorption isotherms and kinetic uptakes of CO_2 were measured. Adsorption isotherms were measured at two temperatures 309 K and 333 K and over a pressure range of 1 to 7 bar. Experimental data of CO_2 adsorption isotherms were modeled using Langmuir, Freundlich and Temkin. Based on coefficient of correlation it was found that Langmuir isotherm model was well suited with the experimental data of CO_2 adsorption isotherms. In addition**,** Adsorption kinetic of CO_2 mixture with N_2 containing 10 % by volume CO_2 and 90 % by volume N_2 were determined in a temperature 36 °C and under the atmospheric pressure .When the flow rate was increased from 0.5 l/min to 2 l/min the time required for complete column saturation decreased. Also the effect of bed length on breakthrough curves was studied. The adsorption capacity increases by bed length increasing for adsorption of carbon dioxide.

Key words: Carbon dioxide, Nanozeolite, Adsorption.

Introduction

Global warming outcome from the emission of greenhouse gases has received common attention [1]. Although there is little agreement on the causes of global warming and environmental problems, many scientists believe that the emission of greenhouse gases contributes to the majority of environmental problems. CO_2 is the most significant among all the anthropogenic greenhouse gases (GHGs). Approximately 60% of global warming effects are attributed to carbon dioxide emission [2].

The term “Greenhouse Effect” was first coined by French physicist Joseph Fourier. The greenhouse effect is the absorption of infrared radiation by the atmospheric gases resulting in the trapping of heat, which results in heating of Earth’s surface. Greenhouse gases contribute significantly to climate change. According to the Intergovernmental Panel on Climate Change (IPCC), the increase in the global temperature is a result of increased concentrations of greenhouse gases caused by human activity such as fossil fuel burning, industrialization and deforestation [3].

In the past, the total amount of CO_2 was relatively maintained remained constant and the atmospheric source was considered large enough to accommodate any additional carbon dioxide until the industrial revolution

[2]. The CO_2 concentration in atmosphere now is closed to 400 ppm which is significantly greater than the pre-industrial level of about 300 ppm [1]. According to the Intergovernmental Panel on Climate Change, the atmosphere may include up to 570 ppm of CO_2 in the year 2100 causing a rise of approximately 1.9 °C in the mean global temperature, and a raise of 3.8 m in the mean sea level [2].

Currently fossil fuels supply more than 98% of the world's energy needs. However, the combustion of fossil fuels is one of the major sources of the green house gas CO_2 account roughly 40% of total CO_2 emission [4], [5].

Growing concerns for global warming and climate change in recent years have motivated research activities toward improved and developing more efficient processes for carbon dioxide capture from large point sources, such as coal-fired power plants, natural gas processing plants, and cement plants. The development of efficient technologies for the capture of carbon dioxide produced by existing point sources will prove vital in controlling the environmental impact of anthropogenic emissions. In order for these technologies to be economically viable, capture carbon dioxide system must include adsorbent regeneration and operate effectively in realistic conditions [6]. There are several technologies available for CO_2 capture such as absorption, adsorption, gas separation, membrane, cryogenic separation, etc [4].

Adsorption appears to be a more promising technology due to its easy operation and low energy requirements [7]. Many conventional adsorbents are used for CO_2 adsorption such as bentonite, activated carbons and modified mesoporous silica [8].

Zeolites represent one of the most innovative adsorbents for a wide range of applications including air separation, air drying, CO removal from reforming gas, andCO_2 removal from natural gas [9]. Zeolites are porous crystalline aluminosilicates with high surface areas and molecular sieving properties. The development of an effective carbon dioxide capture system is critical in reducing global greenhouse gas emissions. Zeolites are considered particularly promising as CO_2 capture materials because their high surface areas and adjustable pore functionality enables the selective adsorption of large quantities of CO_2.

The primary cost in any CO_2 capture process is to obtain the energy required to regenerate the CO_2 loaded adsorbent after it has become saturated with CO_2. In zeolites, the strength of the interaction of CO_2 with the pore surface can be tuned to minimize the energy required for capture of a given amount of CO_2. The decrease in the particle size of zeolite crystals from the micro-level to the nano-level leads to a significant increase in specific surface area, thus providing more active sites for adsorption of CO_2 [8].

Low-cost nanosized zeolite adsorbents that can combine a high adsorption capacity and good selectivity with rapid adsorption kinetics are of importance for carbon dioxide capture from flue gas. While the capacity and selectivity are primarily determined by the chemical and topological features of the pores, the uptake kinetics can also be controlled by reducing the diffusion length, e.g., by decreasing the particle size [10]. The main objectives that study the adsorption of carbon dioxide by using prepared NaA_nanozeolite.

Experimental Work

1. Adsorbate

In the present study two gases carbon dioxide and nitrogen were used as adsorbate with purity a higher than 97.5%.

2. Adsorbents

Prepared NaA nano-zeolite was used as adsorbent. NaA zeolite was synthesized according to sol-gel method by preparing two solutions seeding gel and the feedstock gel (Rahman, 2012). The seeding gel prepared by adding 20 g deionized water, 4.1 g sodium hydroxide, 2.1 g sodium aluminate and 20 g sodium silicate and age at room temperature for 24 hr. The feedstock gel prepared by adding 131 g deionized water, 0.14 g sodium hydroxide, 13 g sodium aluminate and 140.5 g sodium silicate and then stirring vigorously until the gel appears smooth and then the overall gel was prepared by mixing the feed stock gel with 16.5 g of the seed gel for 40 min at room temperature. After that the final gel was stored in a water bath at 87 °C for 24 hr. The product obtained was filtered and repeatedly washed with deionized water until pH reached to 9 and then dried in an electrical oven for 24 hr at 100 °C and calcined 500 °C for 3 hr. Figure 1 shows XRD pattern of prepared NaA nano_zeolite.

Table 1 shows the characterization of nano-zeolite NaA.

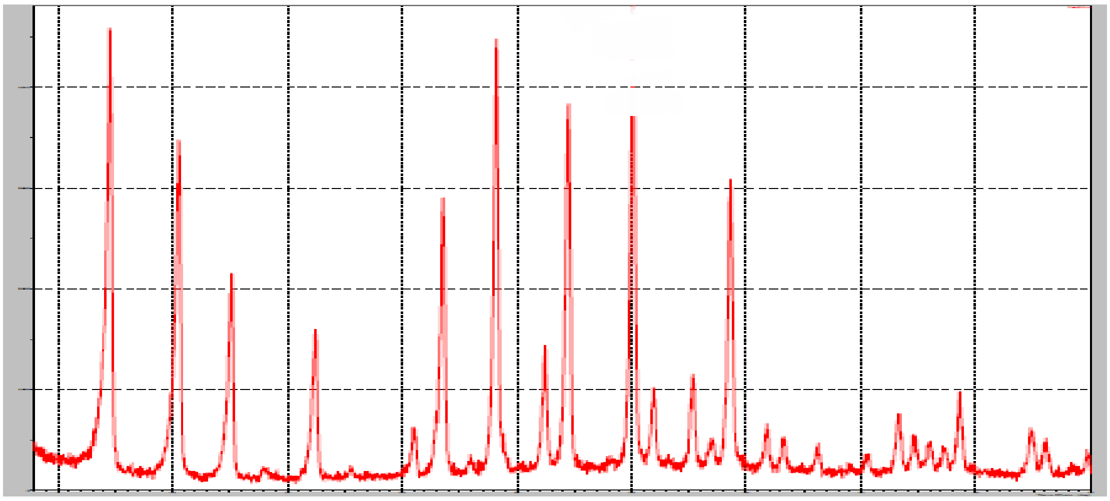

Fig. 1: XRD pattern of prepared NaA nano_zeolite

Table 1: NaA nano_zeolite Characterization

Property	**Value**
surface area, m^2/g	581.211
pore volume, cm^3/g	0.355
average particles diameter, nm	74.77
Molar ratio of Si/Al	1.03
Porosity, %	86.9594

3. Adsorption Equilibrium Isotherm Apparatus and Method

A photographic picture of the apparatus is shown in Figure 2. All tubing was (3/8 in) copper were connected by fittings. The adsorption chamber and reservoirs were approximately 20 cm^3 iron sample cylinders. The pressure of gas was measured by a gauge (Helicoid gauge) that ranged from (0-200 psig) with accuracy 1% and sensibility 0.02% of the full scale at all points. Both reservoir and adsorption chamber were put in a water bath to provide constant temperature. All equipment was evacuated by vacuum pump in each experiment. The feed gas supplied from a cylinder that was connect with regulator pressure.

The extrudate adsorbent was packed into the adsorption vessel and evacuated for 1hr under vacuum pump to regenerate the adsorbent (nanozeolite). This pre-treatment was allowed to make the measurements adsorption without change the adsorbents. After the adsorbent was pre-treated, the vacuum pump was powered off. The water bath with electrical hot plate was started up until constant temperature was reached.

Carbon dioxide gas was entered into the reservoir chamber through valve V1 until the required concentration was reached. V1 was then closed and the concentration recorded when it reached a steady value. After that the valve2 was opened and this system allows reaching equilibrium.

The amount of gas adsorbed at equilibrium was determined from a mass balance. The amount of a component in the reservoir vessel before adsorption is equal to the amount remaining in this vessel after adsorption plus the amount in the gas phase in the adsorber vessel plus the amount adsorbed in the adsorber vessel.

This balance can be written as follows:

$$C_{ri}V_r = C_{rf}V_r + C_{rf}\varepsilon_\circ V_a + Wq$$

Rearranging $q = \frac{(Cri - Crf)Vr - Crf\varepsilon oVa}{W}$

In which q is the adsorbent loading at equilibrium (mmol/g), C is a concentration (mmol/l), V is a volume (l), εo is over all bed void fraction, and W is the weight of the adsorbent in adsorber vessel (g). The subscripts r, a, i and f refer to reservoir vessel, adsorber vessel, initial and final condition, respectively.

Fig. 2: Photographic picture of apparatus used for adsorption equilibrium measurement

4. Adsorption Kinetics (Breakthrough Curves) Apparatus and Method

A photographic picture of the apparatus is shown in Figure 3. All tubing was copper (3/8 in), connected with fitting. The column of the adsorption was an iron pipe 65 cm long and 3.5 cm I.D. The gauze plate of mesh is sited at both ends of the column to hold packing in position from column ends.

A pressure gauge was connected at the top of the column to provide the pressure of the process.

The flow rate of inlet gas was controlled by a valve and measured by a rotameter and the outlet gas measured by gas analyzer.

The extrudate adsorbent was packed into the vessel adsorption and evacuated for 1hr under vacuum pump to regenerate the adsorbent (nanozeolite). After the pre-treated of adsorbent, the vacuum pump was powered off. Then carbon dioxide and nitrogen (10/90 v/v) were introduced and the inlet gases flow rate was measured by rotameter and then the gases entered the mixer column and to the adsorber vessel to begin the adsorption process. The outlet gas from the adsorption column was analyzed by gas analyzer periodically (each 5 sec) until reaching equilibrium.

Fig. 3: Photographic picture of apparatus used for adsorption kinetics

Results and Discussion

1. Adsorption isotherm

Adsorption isotherm is basically important to describe how adsorbates interact with adsorbents, and is critical in optimizing the use of adsorbents [11]. Adsorption isotherm study was carried out in three isotherm models, namely the Langmuir, Freundlich and Temkin isotherms their equations were as follows:

Langmuir model $q_e = \frac{q_m k_L C_e}{1+k_L C_e}$

Freundlich model $q_e = k_f C_e^{1/n}$

Temkin model $q_e = \beta \ln A + \beta \ln C_e$

Where q_m (mmol/g) is the maximum loading corresponding to complete coverage of the surface by the gas and k_L (l/mmol) is the adsorption equilibrium constant. C_e (mmol/l) is the equilibrium concentration of the adsorbate q_e is the amount adsorbed at equilibrium, k_f are the Freundlich constants n = the degree of non-linearity. A (l/mmol) is the Temkin isotherm constant related to equilibrium energy, β (J/mol) is the heat of adsorption.

Table 2 shows the three isotherm models used with all the constants and R^2 values obtained from each plot for NaA nano-zeolite at 309 °K and 333 °K. This table shows that for carbon dioxide adsorption on nano zeolite NaA the highest correlation coefficient (R^2) value is for the Langmuir isotherm as compared to that of both Freundlich and Temkin isotherms at 309 K and 333K. Figures 4 and 5 show the adsorption equilibrium isotherm of pure CO_2 on NaA at 309˚K and 333˚K respectively correlated with Langmuir equation.

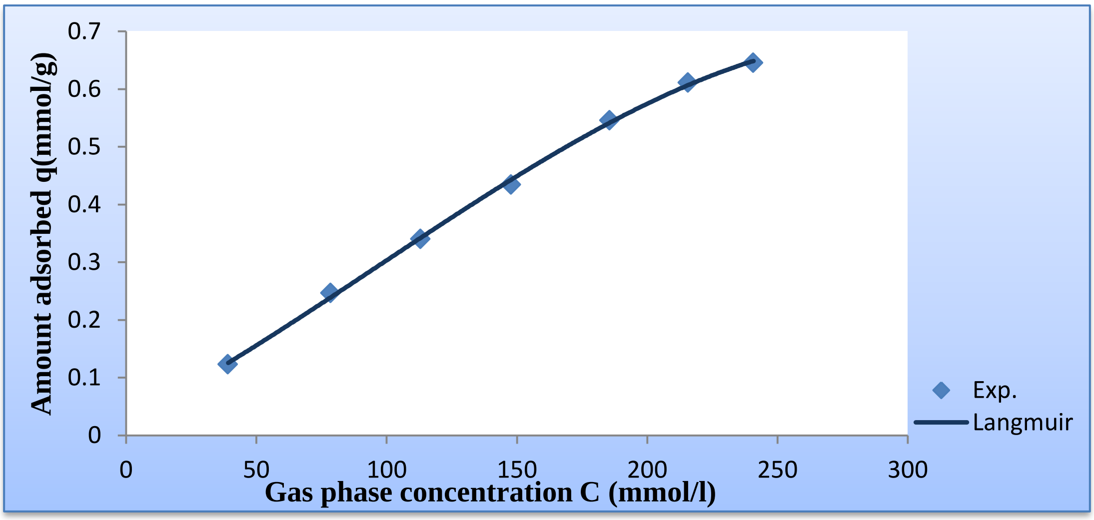

Fig. 4: Adsorption equilibrium isotherm of pure CO_2 on NaA at 309˚K correlated with Langmuir equation

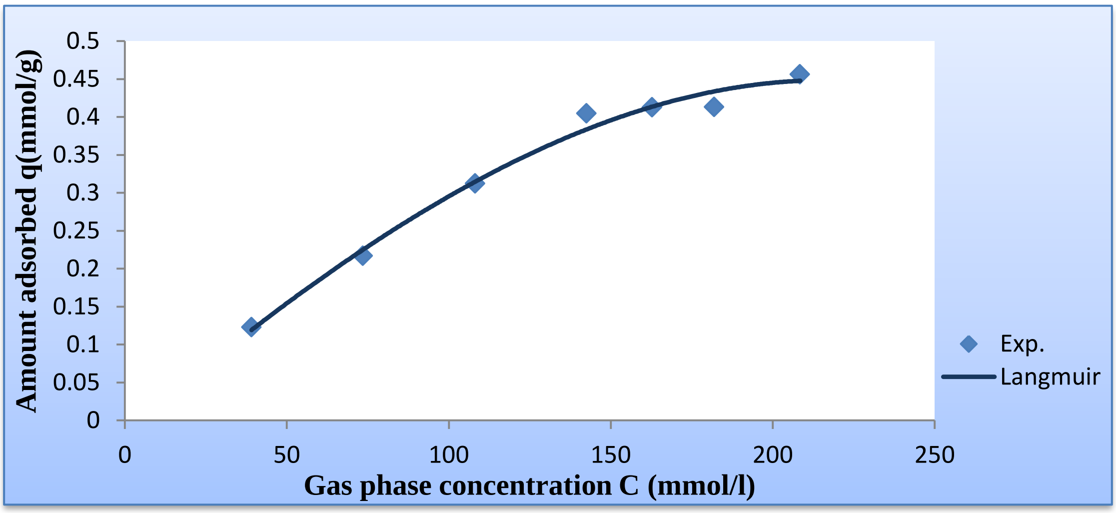

Fig. 5: Adsorption equilibrium isotherm of pure CO_2 on NaA at 333˚K correlated with Langmuir equation

Table 2: Isotherm parameter for carbon dioxide adsorption on nano zeolite NaA

Isotherms	Parameters	Temperature (K)	
		309	333
Langmuir	q_m k_L R^2	5.0761 0.00063 0.999	1.5432 0.000222 0.995
Freundlich	k_f n R^2	0.0043 1.0834 0.997	0.00695 1.2531 0.978
Temkin	K_t β R^2	0.00038 0.296 0.959	0.0437 0.206 0.980

2. Effect of Temperature

Figure 6 shows the effect of temperature on adsorption isotherm for carbon dioxide on NaA nano zeolite. From this figure, it is seen that increasing the equilibrium adsorption temperature decreases the total amount adsorbed on both adsorbents and hence, the capacities of these adsorbents. Therefore, the adsorption of CO_2 onto nano zeolite mostly followed the exothermic nature of the adsorption process. With the increase in temperature, the adsorbed CO_2 becomes unstable on the nano zeolite surface because of increased molecular diffusion, which leads to more desorption of CO_2 molecules. This behavior has also been mentioned by [7].

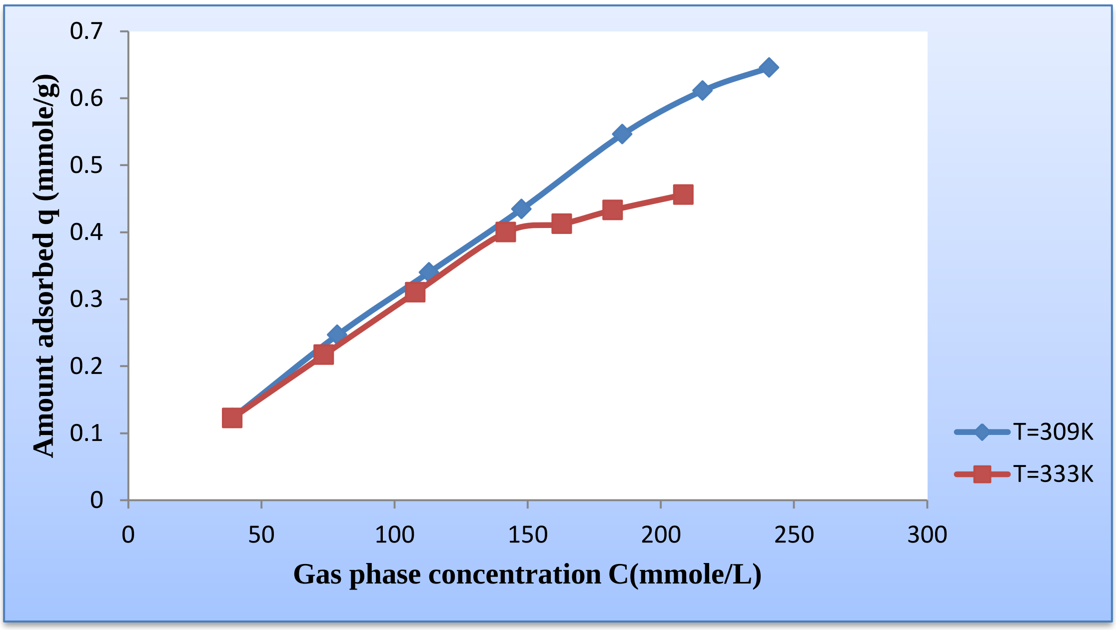

Fig. 6: Adsorption equilibrium isotherm of carbon dioxide on NaA nano zeolite

Adsorption Kinetics (Breakthrough Curves)

Effect of Feed Flow Rate

The effect of CO_2 flow rate on the breakthrough curve on NaA nano zeolite is shown in Figures 7, 8 and 9. It can be seen that increasing the flow rate of the feed decreases breakthrough time and therefore the amount of CO_2 that can be adsorbed.

When the flow rate was increased from 0.5 l/min to 2 l/min the time required for complete column saturation decreased from 160 S to 100 S for 15 g of NaA zeolite and from 375 min to 285 min for 30 g of NaA zeolite and from 470 to 400 for 60 g.

In particular, a less sharp breakthrough curve is obtained at the highest flow rate tested, indicating poor utilization of the column capacity. The use of high flow rates reduces the time that adsorbate are in contact with the adsorbent, thus allowing less time for adsorption to occur, leading to an early breakthrough of adsorbate. In addition longer breakthrough times are desired, because this required less frequent need for regeneration of the adsorbent particles which in terms affect the amount of energy and cost of process operation. This behavior has also been mentioned by Wu et. al. [12].

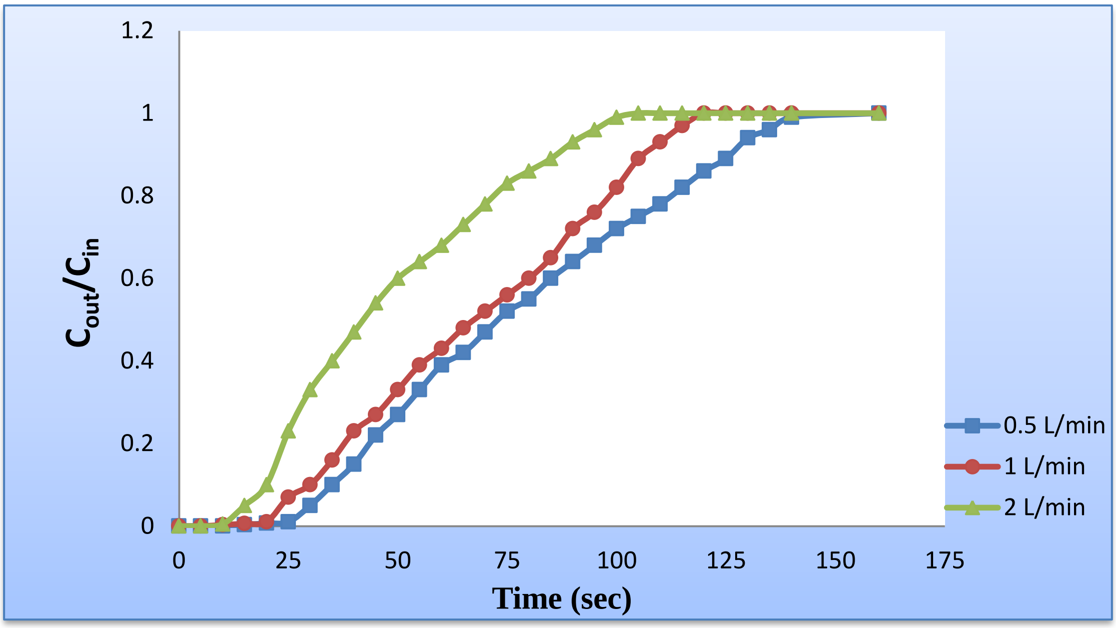

Fig. 7: The effect of feed flow rate on the breakthrough time for (10% CO_2, 90%N_2 at 309K and 15g of NaA nanozeolite)

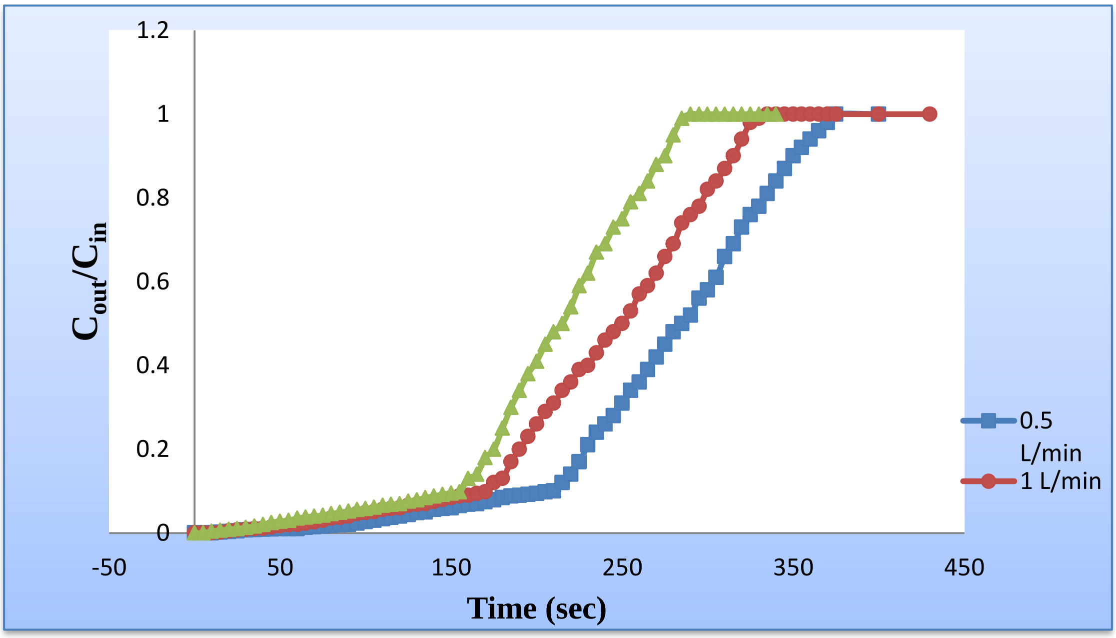

Fig. 8: The effect of feed flow rate on the breakthrough time for (10% CO_2, 90%N_2 at 309K and 30g of NaA nanozeolite)

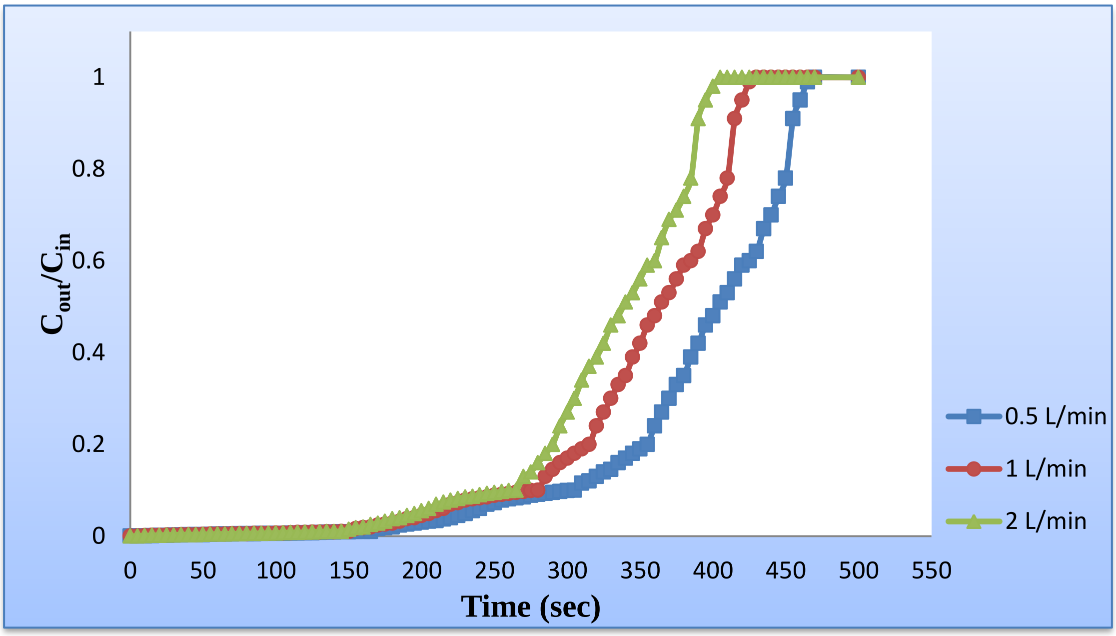

Fig. 9: The effect of feed flow rate on the breakthrough time for (10% CO_2, 90%N_2 at 309K and 60g of NaA nanozeolite)

The Effect of Amount of Adsorbent

Since, the diameter of the adsorption column is constant; therefore the used weight of adsorbent corresponds to different bed lengths.

The use of short bed length leads to shorten the contact time between the adsorbate and adsorbent and reduces the available area to transfer.

Figures 10, 11 and 12 show the effect of bed length on the breakthrough time, from these figures show that the adsorption capacity increases by bed length increasing for adsorption carbon dioxide, because the increase in bed length leads to increasing in the surface area available for adsorption. This behavior has also been mentioned by Grande [13].

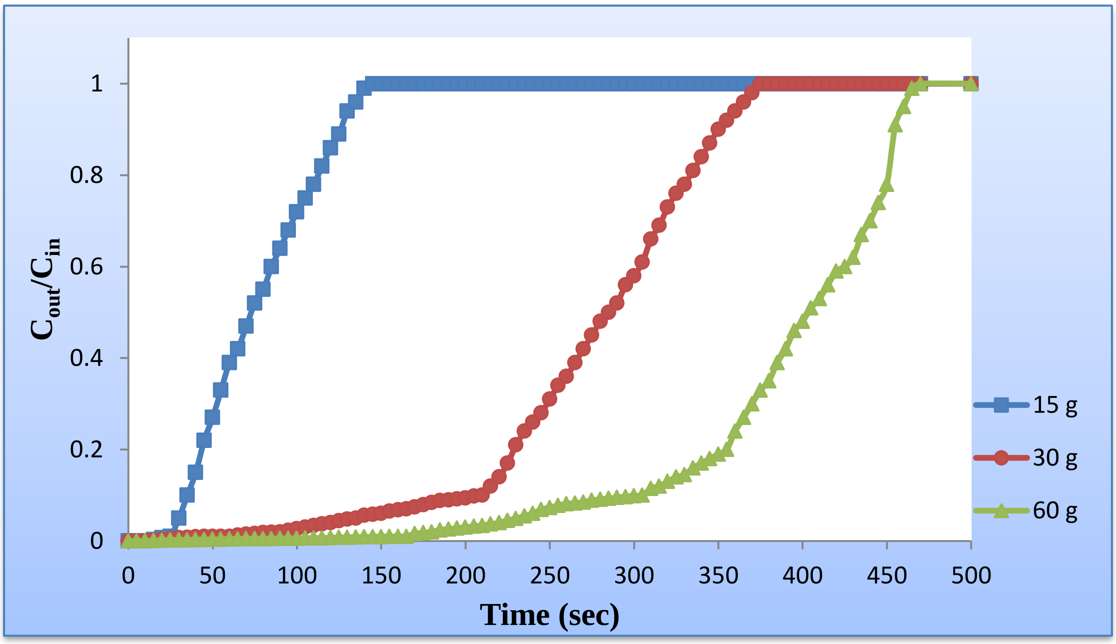

Fig. 10: The effect of bed length on the breakthrough time for (10% CO_2, 90%N_2 at 309K and 0.5 l/min of CO_2)

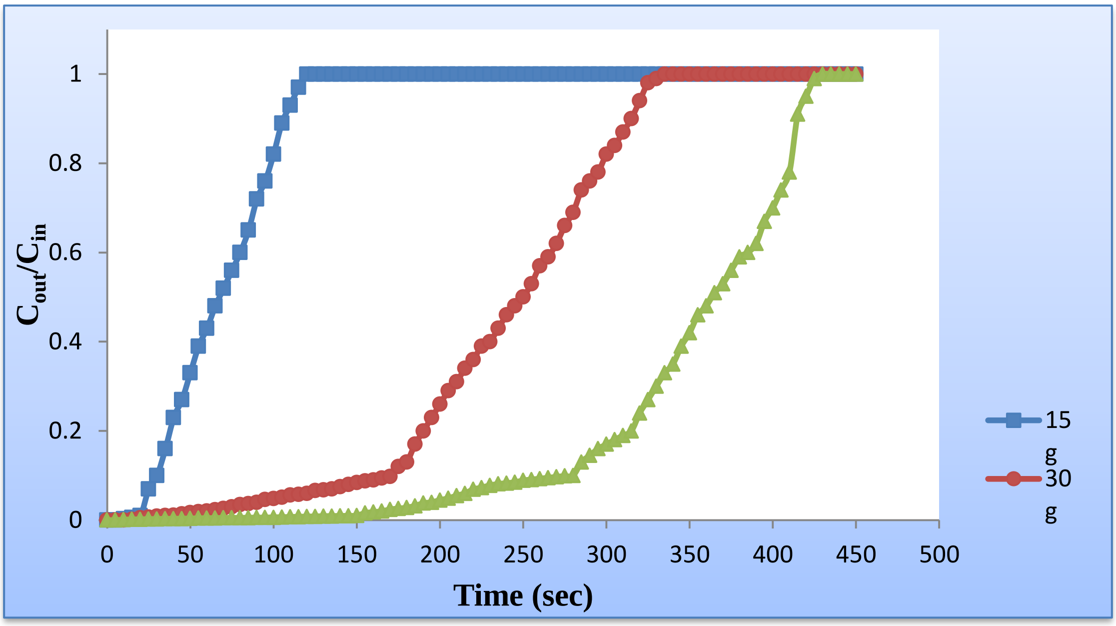

Fig. 11: The effect of bed length on the breakthrough time for (10% CO_2, 90%N_2 at 309K and 1 l/min of CO_2)

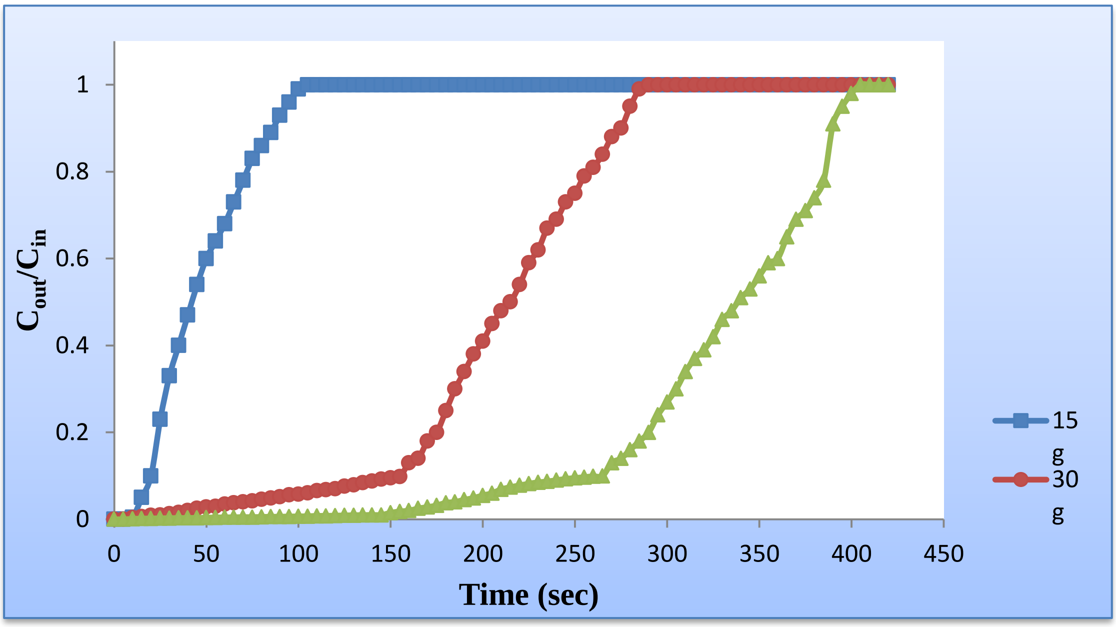

Fig. 12: The effect of bed length on the breakthrough time for (10% CO_2, 90%N_2 at 309K and 2 l/min of CO_2)

Conclusions

Carbon dioxide adsorption are investigated and the following were concluded

1- Equilibrium isotherm for pure CO_2 is fitted with the Langmuir isotherm at 309 °K and at 333 °K.
2- The effect of temperature showed that when temperature increases the adsorbed CO_2 decrease proving that the adsorption process is exothermic.
3- Effect of feed flow rate for mixture CO_2 and N_2 on breakthrough curves showed that when the flow rate was increased from 0.5 l/min to 2 l/min the time required for complete column saturation decreased from 150 sec to 100 sec.

4- The adsorption capacity increases by bed length increasing for adsorption carbon dioxide.

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