



Capture of CO₂ from power plants Using Different Adsorbent materials

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Received date : 8 / 12 / 2015

Accepted date : 14 / 9 / 2015

ABSTRACT

Emission of carbon dioxide from power plant has direct effect to increase the warm of earth due to combustion of fossil fuels by power plants. Pressure swing adsorption is an economic process used to control CO₂ emission to atmosphere. In the present study single column of 1m length and 2.54 cm inside diameter used to study the breakthrough time curve of CO₂/N₂ separation using zeolite (13X), carbon molecular sieve (CMS), and activated carbon (AC). The range of adsorption pressure was (1-3) bar at ambient temperature and product flowrate of about 0.5 ml/min. The results showed significant separation of CO₂ and low level of CO₂ observed in the product line of the adsorber column. Longtime of breakthrough curve observed by zeolite 13X. Regeneration of Zeolite 13X by heating at 350 C° for 12hours increased breakthrough time from 70 minutes to 175 minutes. Maximum purity of the CO₂ at the vacuum pump product line was 87% and Zeolite 13X was better than others in spite of steeper mass transfer zone observed by activated carbon adsorbent.

Keywords: Single Column, adsorption, breakthrough time .

التقاط CO₂ من محطات توليد الطاقة باستخدام مواد مازة مختلفة

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تاريخ قبول البحث: ٢٠١٥ / ٩ / ١٤

تاريخ استلام البحث: ٢٠١٥ / ١٢ / ٨

المخلص

انبعاث غاز ثاني اوكسيد الكربون من محطات توليد الطاقة له تأثير مباشر في ارتفاع درجة حرارة الارض نتيجة استخدام الوقود العضوي من قبل محطات توليد الطاقة. ضغط الامتزاز المتناوب هي عملية اقتصادية استخدمت للسيطرة على انبعاث ثاني اوكسيد الكربون الى الجو. في هذه الدراسة عمود منفرد بطول ١ م و قطر داخلي ٢.٥٤ سم استخدم لدراسة زمن منحنى الاختراقية لفصل CO₂/N₂ باستخدام زيولت 13X ، جزيئات الكربون المنخلي و الكربون المنشط. مدى ضغط الامتزاز كان (١-٣) بار عند درجة حرارة المحيط و معدل جريان الناتج حوالي 0.5ml/min. النتائج بينت فصل كفوء لـ CO₂ و لوحظ انخفاض تركيز CO₂ في خط الناتج لعمود الامتزاز. أطول فترة لمنحنى الاختراقية لوحظ من قبل زيولت 13X. اعادة تنشيط زيولت 13X بواسطة التسخين عند درجة ٣٥٠ C لمدة ١٢ ساعة ادت الى زيادة زمن منحنى الاختراقية من ٧٠ دقيقة الى ١٧٥ دقيقة. اعلى نسبة لـ CO₂ عند خط الناتج للمضخة الفراغية كانت ٨٧% و زيولت 13X كانت الافضل بالمقارنة مع الاخريات بالرغم من ان منحنى الاختراقية للكربون المنشط كان اكثر اقترابا من الحالة المثالية.

الكلمات الدالة : عمود منفرد ، الامتزاز ، زمن الاختراقية .



1. Introduction

Global warming caused by increasing concentrations of greenhouse gases in the atmosphere is one of the emerging threats challenging mankind. Carbon dioxide from flue gas emitted by power plants is the biggest contributor to the current warming, because 36% of the energy supply in the world is by using coal, 321 billion tons of CO₂ has been released to the atmosphere since the middle 18th century, and half of the CO₂ emission has taken place in the recent 30 years. Cutting down the emission of CO₂ has already become one of the major research target in the world [1],[4].

Adsorption process becomes a viable alternative because of the reusable nature of the adsorbents used, availability, flexibility, fully automated operation of the process and production of high purity product. Pressure swing adsorption, and temperature swing adsorption are potential techniques that could be applicable for removing CO₂ from both high- and low-pressure gas streams [5],[6].

Carbon molecular sieve (CMS) is a carbonaceous material which has the pores of molecular dimensions that provide a uniform pore size distribution and a pore size of about 4 to 9 Å and the relatively high adsorption capacity and kinetic selectivity for various molecules, therefore carbon molecular sieves (CMS) have become an increasingly important class of adsorbents for application in the separation of gas molecules, purification process, and liquid separation [7],[12]. The CO₂/N₂ uptake ration was found to be greater than 7, indicating the separation of N₂ from CO₂ is possible using samples of CMS prepared under different condition of carbonization temperature and activation temperature. There is a prolonged time of retention for CO₂ at pressure between 1.5 and 3 bar and ambient temperature approximately 16C° using CMS[11],[12].

Activated carbon has been used as an adsorbent material because of high adsorption capacity for gas adsorption process in air pollution. High capacity to adsorb is related to high surface area is approximately 1000 m²/g, and high porosity. [13] Separation of CO₂/N₂ at different temperature on commercial activated carbon and on a nitrogen-enriched activated carbon, packed in a fixed bed. The results showed that the commercial activated carbon is better for CO₂/N₂ separation processes than a nitrogen-enriched activated carbon [14].

Zeolitic adsorbents have played a major role in the development of adsorption technology by removal of trace or dilute impurities from a gas. It's composed of silica and alumina tetrahedral. The extra framework cations are ion exchangeable and give rise to the rich ion-



exchange chemistry of these materials [7],[9]. The capture of carbon dioxide using zeolite 13X and a feed stream of (12-15) % CO₂ at 15 C^o leads to obtain breakthrough curve at the 10 min. Breakthrough time is shortened when feed flow rates are increased for vacuum levels of 4 kPa and lower, CO₂ purities of >90% are achievable [15],[17].

A novel solid sorbent of (600µm) prepared using a liquid-impregnation technique , novel magnesium-based sorbent, and the novel sodium-based sorbent. All adsorbents were able to capture CO₂ from 15-17 % to parts per million (ppm) at high temperature and can be regenerated at high temperatures[5].

The design of sorption systems is based on a few underlying principles. knowledge of *sorption equilibrium* is required, Mass Transfer Zone moves through the bed, and the time required to increase the concentration of adsorbate in the outlet gas which is called “breakthrough time”. When a feed flows through a fixed bed there is a tendency for axial mixing to occur. Any such mixing is undesirable. The axial dispersion should be reduced because it can reduce the efficiency of separation. The minimization of axial dispersion is as a major design objective. If the mass transfer zone is narrow, the breakthrough curve will be steeper, and most of the capacity of the adsorbent will be used. When the mass transfer zone is wide, the breakthrough curve is greatly extended, and less than half of the bed capacity is used[18],[21].

The purpose of this work is to study the breakthrough time and mass transfer zone (MTZ) of CO₂/N₂ through fixed bed using different adsorbents such as carbon molecular sieve , commercial activated carbon, and zeolite13X , comparison among them, and effect of adsorption adsorption pressure .

2. Experimental work

Single galvanized column of 1 m length and 2.54 cm diameter packed with fresh adsorbent designed for this work to study the break through curve of CO₂/N₂ separation. The feed prepared in the laboratory using two cylinders of pure N₂ and CO₂ (purity of 99.9%). Two pressure regulators used to adjust the pressure of each gas and the volume fraction of CO₂ at the feed adjusted by using two gas rotameter (1-6 lit/min, manufacture in England). Product flow rate adjusted by gas rotameter (0.1-1 lit/min, OMEGA, manufactured in Tokyo- Japan) and the purity of CO₂ measured by inferred CO₂ analyzer (G110, Geotechnical Company, United Kingdom). The feed pressure adjusted by another pressure regulator (1 to 10 bar,



Norgren England). All connections were copper pipes of (1/4 in) at the feed and product lines. A programmed timer used to controller the operating time of the solenoid valves (CASTEL, Italy's manufacture, 220v, 50Hz). The adsorbent materials regenerated by a Vacuum pump ((E.M.G., ELECTTROMECC, NICA, manufactured in Italy). Three types of commercial adsorbent used in the present work carbon molecular sieve, activated carbon, and zeolite 13X. The characteristics of the adsorbents and the column showed in the **Table (1)** . The setup of the single column adsorber showed in the **Fig. (1)** . The parameters studied was the effect of adsorption pressure at the range of (1- 3) bar, depressurizing time 5 second, and evacuation time 30 minutes. The purity measured during each run by CO₂ analyzer.

The experimental procedure included the following steps:

- 1- Set the pressure of the feed before mixing point greater than adsorption pressure.
- 2- Adjust the two gas rotameters to prepare the feed includes 15% CO₂/N₂.
- 3- Adjust the adsorption pressure by second feed pressure regulator.
- 4- Open solenoid valve (V1)
- 5- Set the product flowrate to 0.5 lit/min.
- 6- Record the purity at the product line with time.
- 7- Close (V1) and then open valve (V2) to depressurize the column.
- 8- Evacuation the adsorbent for 30 minutes by close (V2) and open (V3) .
- 9- Record the purity at the vacuum out line.
- 10- Repeat the same steps for new run.

Table (1) : Physical properties of the column and the adsorbents

Column Length (cm)		100
Column diameter (cm)		2.54
Commercial adsorbents	Physical properties	
13X	Shape	Sphere
	Particle diameter(mm)	1.7-2.6
	Particle density (kg/m³)	1070
	Bulk density (kg/m³)	670
	Bed porosity	0.4
CMS	Shape	Granular
	Particle diameter d_p (mm)	1.7 - 1.8
	Bulk density ρ_B (g/L)	680-700
	Bed porosity	0.37
AC	Shape	Granular/ Columnar
	Surface area(m²/g)	900 min
	Bulk density ρ_B (g/L)	350-510
	Ash(%)	15 max

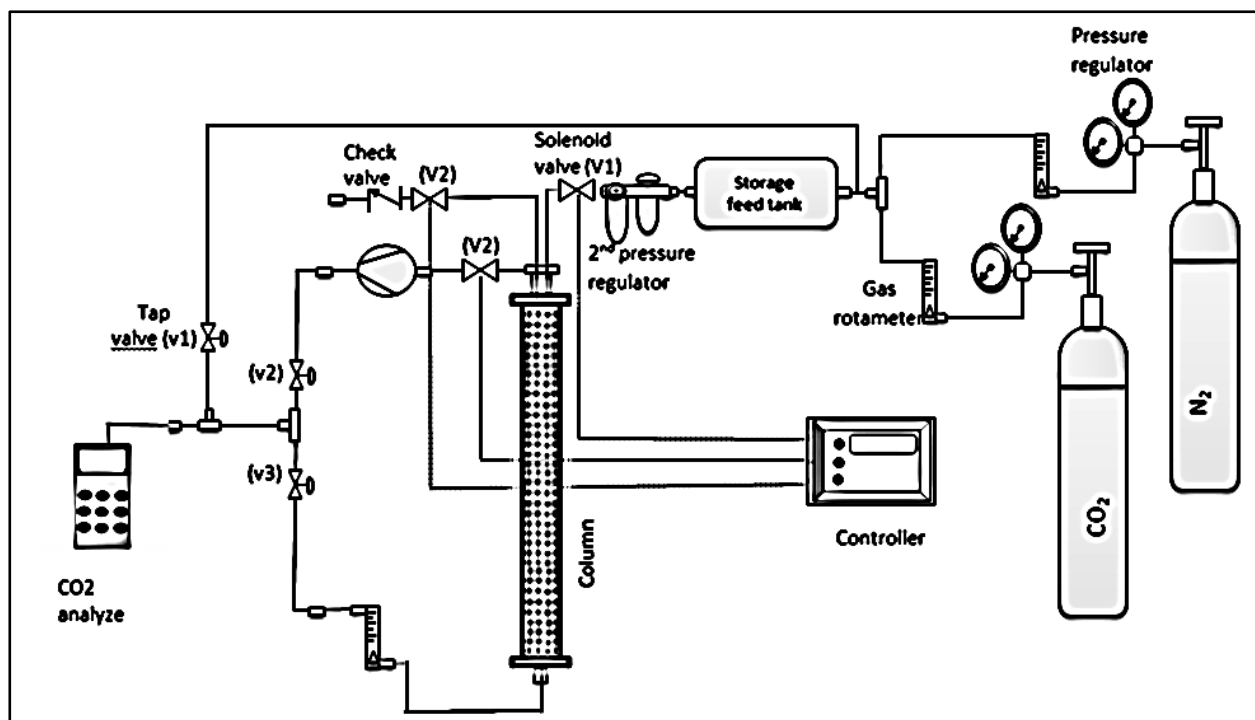


Fig. (1): Experimental setup of single column adsorber of CO₂/N₂ separation.

3. Results and Discussion

Figures (2,3) and (4) show the breakthrough curve of CO₂ separation from a flue gas using different adsorbent materials. Product flowrate of 0.5 lit/min , and the range of pressure is from 1 to 3 bar. All adsorbents showed significant CO₂ gas separation under the effect of different adsorption pressure.

The breakthrough time increased with increases of pressure up to 3 bar using carbon molecular sieve and zeolite 13X this may be attributed to micro porous adsorption obtained at high pressure or increase of adsorption capacity.

For activated carbon there is no of effect of adsorption pressure to the breakthrough time because full capacity of adsorption obtained at the low pressure therefor no increase in the loading with increases of the pressure.

Also the results showed that the breakthrough time of zeolite 13X is better than carbon molecular sieve , and activated carbon due to the difference in the behavior of adsorption isotherm of each adsorbent to adsorb pure CO₂ that's where the results from literature survey showed that the adsorption capacity of 13X is greater than carbon molecular sieve , and activated carbon [12], [17].

The purity of CO₂ in the product line is closer to zero up to breakthrough time and the results are in agreement with the results obtained by Tirzha et al. , Zhang et al., Ranjiani et al., Carlos et al. , and Soares et al [5], [11], [14], [16], [17].

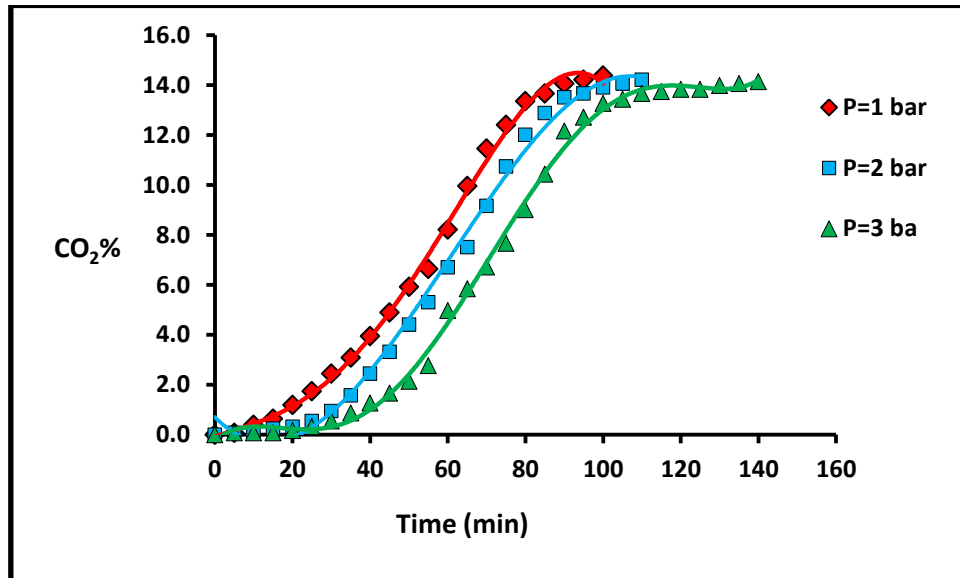


Fig. (2): Breakthrough curve of CO₂/N₂ separation using carbon molecular sieve at different pressure.

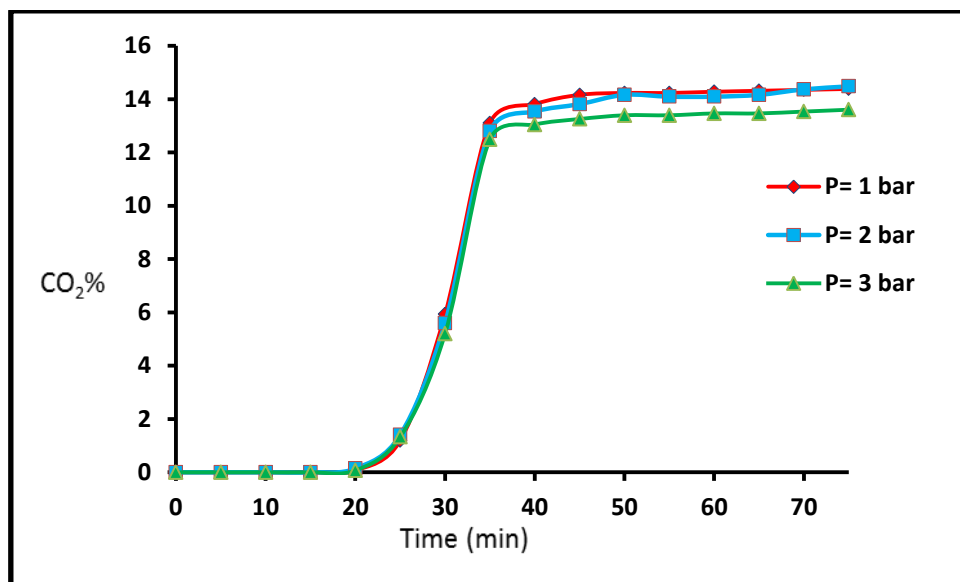


Fig. (3): Breakthrough curve of CO₂/N₂ separation using activated carbon at different pressures.

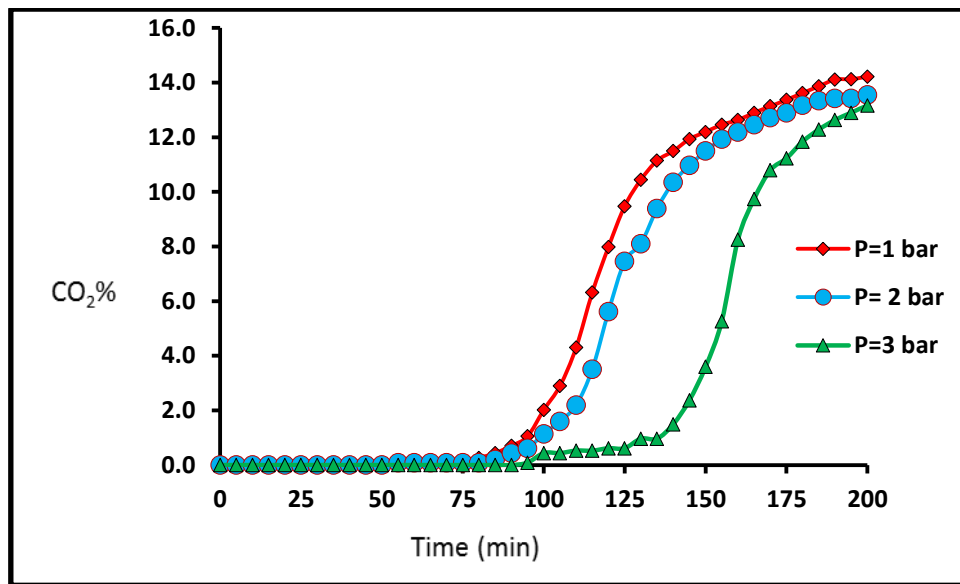


Fig. (4): Breakthrough curve of CO₂/N₂ separation using zeolite 13X at different pressures.

Figures (5,6) and (7) refer to effect of adsorption pressure on effluent gas purity for different adsorbent materials, the results showed that the breakthrough time of carbon molecular sieve is shorter than activated carbon and zeolite 13X at the pressure of 1 bar , and then gradually approached to the breakthrough time of activated carbon at the pressure of 2 , and 3 bar because increases adsorption capacity.

All figures showed that the longtime of breakthrough is observed by zeolite 13X.

The width of mass transfer zone (MTZ) obtained from single fixed bed gas separation using zeolite 13X, and carbon molecular sieve as a adsorbent is broader than activated carbon because effect of mass transfer resistance and axial dispersion that they contributed to broad the width of mass transfer zone and deviate from ideal case (infinitesimal width and breakthrough curve should be vertical line). Mass transfer zone of activated carbon is more steeper and very closer to ideal case because the structure of activated carbon includes high surface area and diameter of porous is greater than of carbon molecular sieve and zeolite 13X, therefor fast diffusion of CO₂ molecular obtained through the porous.

Turbulent flow or flow abundantly through the bed with high velocity during pressurizing step with feed and significant effect of mass transfer resistance lead to broad the mass transfer zone with using zeolite 13X and Carbon molecular sieve.

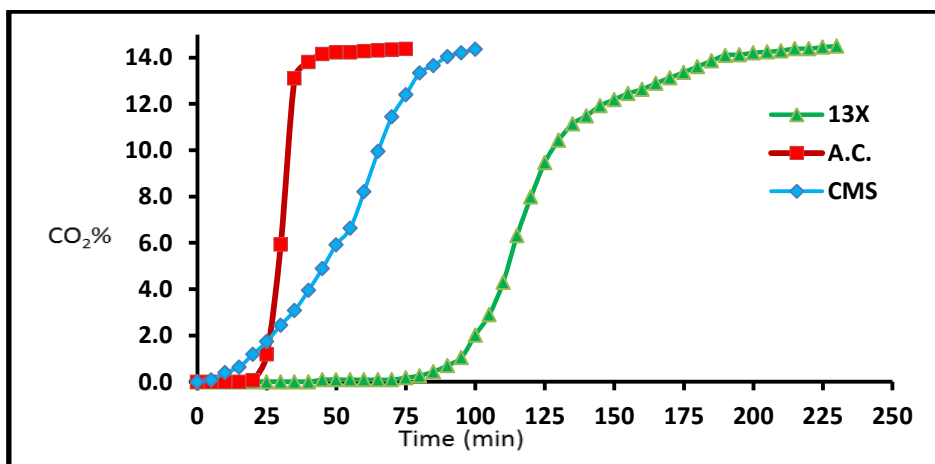


Fig. (5) : Breakthrough time of CO₂/N₂ using different adsorbents at 1 bar.

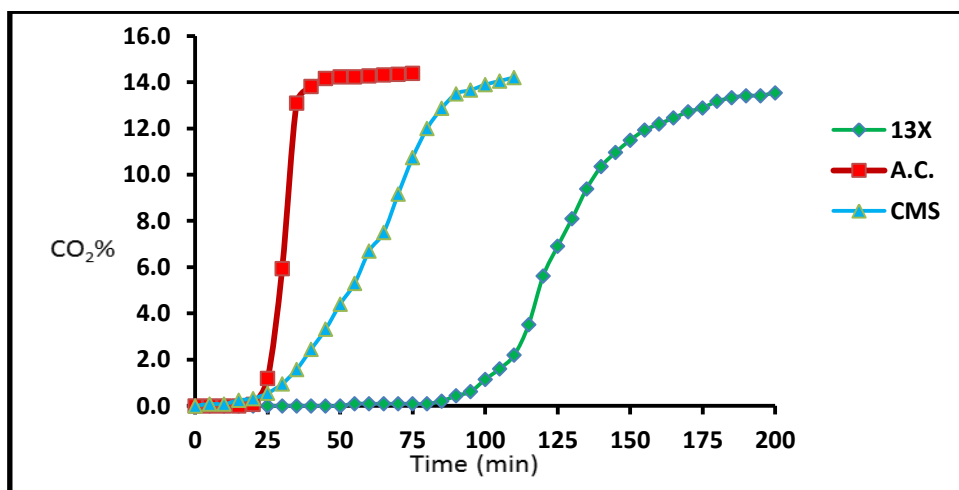


Fig. (6) : Breakthrough time of CO₂/N₂ using different adsorbents at 2 bar.

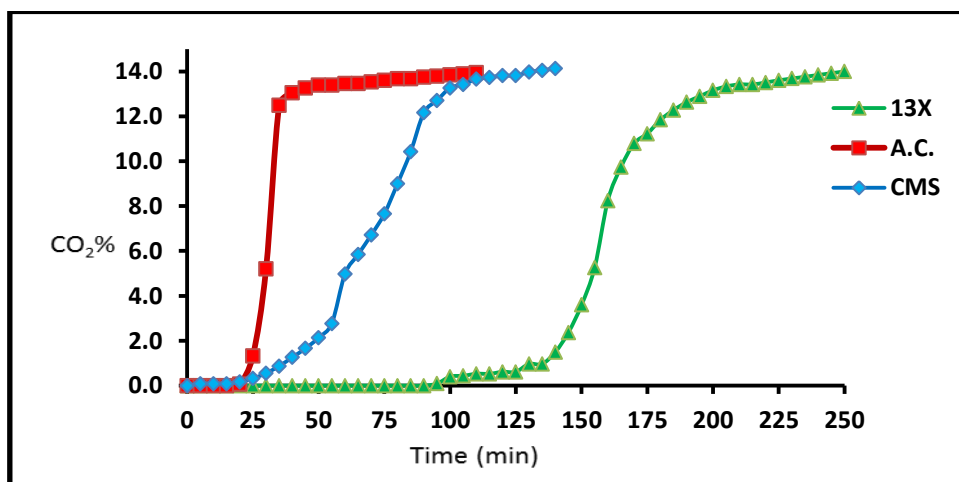


Fig. (7) : Breakthrough time of CO₂/N₂ using different adsorbents at 3 bar.

Fig. (8) shows the different in breakthrough time of zeolite 13X at 1 bar according to the regeneration method, long time observed when the adsorbent regenerated by the heating of about 350 C for 12 hr than regeneration by vacuum pump, because the molecules of CO₂ during pressurizing step can be adsorbed by chemical adsorption and physical adsorption and making two layers on the surface of zeolite 13X first layer formed due to chemical sorption (strong bond formed) and the second layer formed by physic sorption (weak bond formed). The regeneration process can be done by vacuum pump or by the heating .The full regeneration is obtained by heating and long time is observed than vacuum regeneration, because the full regeneration need enough energy to brock the strong bond formed during chemical adsorption. For physic adsorption low pressure by vacuum pump is enough to remove the second layer and regenerate the adsorbent.

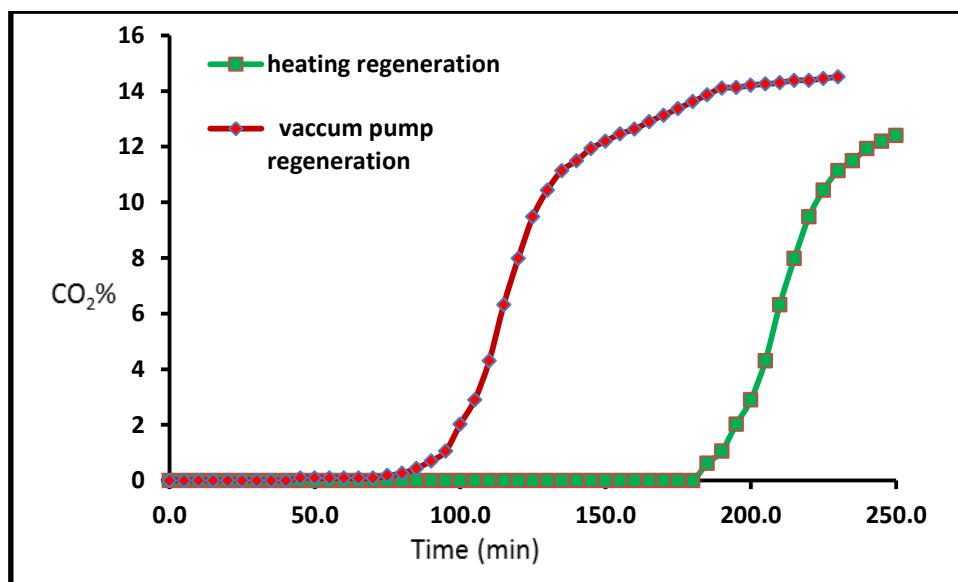


Fig. (8): Difference between breakthrough time of zeolite 13X for CO₂/N₂ separation according to regeneration method.

Fig. (9) represent the effect of adsorption pressure on the purity of CO₂ in the outline of vacuum pump , the results showed that the purity increased with increases of pressure up to 3 bar . Maximum purity observed by using zeolite 13X of about 87%. Also the results showed no significant effect of the pressure to activated carbon to improve the purity of CO₂.

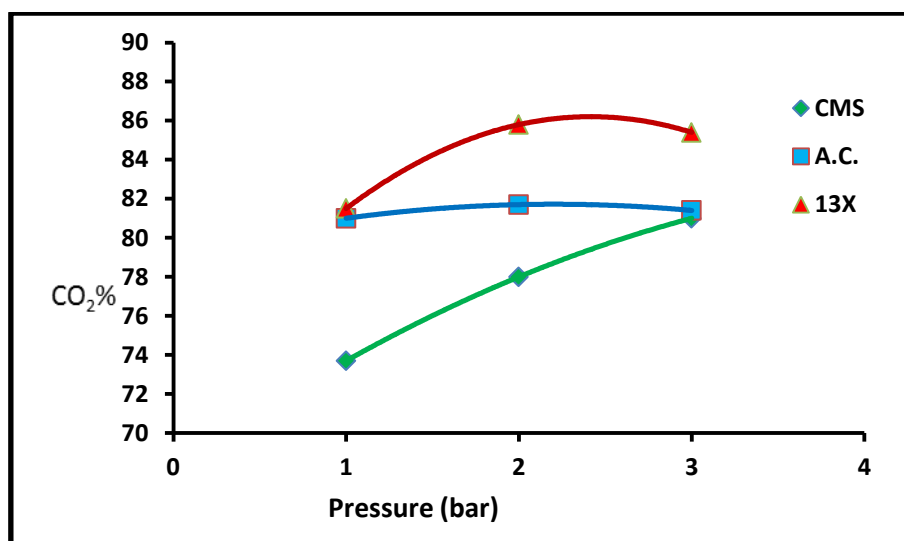


Fig. (9) : Effect of adsorption pressure on the CO₂ purity on the vacuum pump product.

4. Conclusion

All adsorbents showed significant separation of CO₂ at ambient temperature, the concentration of CO₂ in the product line is minimized approach to zero for all runs , and longtime of breakthrough curve observed by zeolite 13X of about 74 minutes at the pressure of (1 – 3) bar, and greater than 150 minutes when the adsorbent regenerated by the heat. No significant effect of adsorption pressure to the breakthrough time of the adsorbents. Zeolite 13X is better than carbon molecular sieve and activated carbon for CO₂ separation, in spite of mass transfer zone of activated carbon is steeper than of zeolite 13X and carbon molecular sieve. The purity of CO₂ in the product line of vacuum pump is greater than 80% and maximum purity observed by zeolite 13X of about 87% at the pressure of 3 bar.

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