

CARBON DIOXIDE ADSORPTION CAPACITY OF INDONESIAN NATURAL ZEOLITE

by

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ABSTRACT

Natural gas is an important commodity for the economy and development of Indonesia. In addition to its riches in petroleum resources, Indonesia is also endowed with other mineral resources, among which is natural zeolite.

This paper describes a study made to combine these two resources, the use of zeolite in natural gas processing, specifically for CO₂ removal by zeolite as solid adsorbent.

The experimental results presented in this paper indicate that this Indonesian natural zeolite has good CO₂ adsorption capacity, although the value is only about one half of that obtained from synthetic zeolite. Both zeolites were shown to follow the Langmuir adsorption isotherms and their parameters were established. These and other relevant data are presented in this paper.

I. INTRODUCTION

One of the characteristics of Indonesian natural gas is its low sulphur and high carbon dioxide content. The natural gas from Badak field, for example, contains 4.42% vol. CO₂ by volume, and virtually no H₂S³. The Arun gas, another one that is liquefies into LNG in Indonesia, contains 15% vol. CO₂ and 0.007% vol. H₂S (Inman and Soetopo, 1979). An extremely high carbon dioxide content is observed in gas from Natuna field, a large gas field in Indonesia's archipelagic territorial waters in South China Sea, which has a 71.5% vol. carbon dioxide content and 0.5% vol. hydrogen sulfide. This large gas field is yet to be developed pending satisfactory solution to its carbon dioxide problem.

The relatively high carbon dioxide in Indonesian natural gas attracts interests in CO₂ removal process. Generally, CO₂ removal is carried out by conventional amine or hot potassium absorption processes, but the potentialities of adsorption by solid adsorbent should also be of explored.

Natural zeolites are found in several places in Indonesia, and this paper reports a study made on the CO₂ adsorption capacity of a natural zeolite found in Indonesia. The use of zeolite for drying natural gas

and removal of carbon dioxide, hydrogen sulphide and sulphur bearing compounds have been reported in literature.⁵⁾

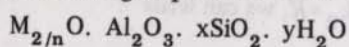
II. NATURAL ZEOLITE OF INDONESIA

The natural zeolite investigated in this study originates from a natural deposit in West Java, Indonesia. Zeolites are crystalline, hydrated aluminosilicates of alkali and alkaline earth cations with a special structure consisting of frameworks enclosing pores which are occupied by cations and water molecules. These molecules have considerable freedom of movement, and thus permitting zeolite to be used for reversible adsorption.

Natural zeolites are found in sedimentary deposits and are formed after burial of the enclosing sediments by the reaction of aluminosilicate materials with water. It is believed that the aluminosilicate material that most commonly served as the precursor for the zeolite is silicate volcanic glass, although materials such as feldspars, feldspathoids, and gels also have reacted to form zeolites.⁵⁾

Zeolites have a three dimensional crystalline framework constructed of tetrahedra of oxygen ions, each of which has a silicon ion at its centre. Some of

the tetravalent silicon ions are substituted by trivalent aluminium or other trivalent ions such as ferric ions, leaving the framework a net negative charge. This charge is balanced by additional alkali or alkaline earth cations in the interstices. Zeolite mineral has thus the following empirical formula :



where M is alkali or alkaline earth cation, n is the valence of the cation, x is a number from 2 to 10 and y a number from 2 to 8⁴⁾.

Loosely bound molecular water is present in the structure of zeolite and may constitute 10 to 20 percent of its weight. If the water is removed, usually by heating for several hours at 350 to 400°C, it leaves a considerable void space within the simple polyhedra building blocks and the large framework structures formed by the interconnection of several polyhedra. Although water and other inorganic molecules may move freely through a dehydrated zeolite framework, the entry channels leading into the simple polyhedra units are small. Molecules which have effective diameter smaller than the entry channel may enter the structure and be adsorbed on the surface, while those larger are excluded. This gives the molecular sieving capability to crystalline zeolites.

The structure and analysis of zeolites vary from one locality to another. The mineral and chemical analyses of the Indonesian zeolite used in this experiment are presented in Tables 1 and 2 where they are compared with natural zeolites found in deposits in two foreign countries. It contains 69.1% of zeolite of mordenite and clinoptilolite type, with a mixture of minerals consisting of feldspar, quartz, mica, iron oxides, etc.

In addition to their ability to separate gas molecules on the basis of size, the characteristic charge distribution within a dehydrated central cavity allows many species with permanent dipoles to be adsorbed selectively. Thus polar CO₂ is preferentially adsorbed by certain zeolites over non-polar CH₄, providing a means for CO₂ removal from natural gas by zeolites. The objectives of the present work is to investigate the CO₂ adsorption capability of a natural zeolite found in a locality in Indonesia.

Table 1
Mineral Composition of Natural Zeolites⁶⁾

Mineral	Indonesia A %	Foreign B %	Foreign C %
Mordenite] 69.1	66.3	—
Clinoptilolite		—	90.2
Cristobalite	—	9.5	1.0
Plagioclase	2.4	—	—
Monmorilonite	—	6.8	—
Quartz	3.9	8.4	0.7
Feldspar	3.1	0.8	—
Glass] 19.8	7.0	—
Mica		—	2.6
Iron Oxides	1.3	—	—
Amorphous	—	—	5.5

Tabel 2
Chemical Analysis of Natural Zeolites⁶⁾

Element	Indonesia A %	Foreign B %	Foreign C %
SiO ₂	61.62	64.32	60.85
Al ₂ O ₃	13.79	13.22	13.66
TiO ₂	0.23	0.22	0.33
Fe ₂ O ₃	2.23	2.29	0.82
CaO	1.43	2.28	1.87
MgO	0.42	0.47	1.02
Na ₂ O	0.35	2.23	2.56
K ₂ O	3.93	1.44	3.61
Loss	16.00	13.53	15.28

III. ADSORPTION

Adsorption is a process in which molecules of a fluid are held on the surface of a solid by surface forces. The adsorption of gas molecules to the surface of solids are generally categorized into physical adsorption and chemical adsorption (chemisorption) depending on the nature of the force which forms the bond.

As a surface phenomena, adsorption is influenced by the surface area and the purity of the adsorbent, as well as by the size and polarity of the adsorbate molecules. Large area with no impurities occupying the surface area would open up more adsorbent molecules to be attached by the adsorbate. The adsorbate molecular size determines the ability of the molecules to enter the capillary pores of the solid and be attached to the molecules in their walls. The polarity will affect the attraction or repulsion between the two types of molecules.

Adsorption is an equilibrium process which is influenced by pressure and temperature. As a bond forming process it is generally exothermic, and is favoured by a lower temperature. The effect of pressure is generally expressed in the form of adsorption isotherms. There are several types of expression on adsorption isotherms, but a simple one which can adequately represent the adsorption of gas molecules on solid adsorbent is the one proposed by Langmuir. This is derived from the equilibrium that is set up between the gas phase and the partially formed adsorbed monolayer on the adsorbent surface.¹⁾

When the gas is at a pressure P , the fraction of the surface that is covered is represented by a . The equilibrium state can then be expressed in terms of the dynamic equilibrium that results from an equal rate of evaporation of the adsorbed material and condensation of the gas phase molecules.

The rate of evaporation can be taken as proportional to the surface covered and can be written as $k_1 a$, where k_1 is a proportionality constant. The rate of condensation is proportional to the gas pressure P which determines the number of molecular collisions per unit area per unit time, and to the fraction of the surface not already covered by the adsorbed molecules, $(1 - a)$, and hence can be written $k_2 P(1 - a)$, where k_2 is another proportionality constant. At equilibrium,

$$k_1 a = k_2 P(1 - a) \quad (1)$$

$$\text{or } a = \frac{k_2 P}{k_1 + k_2 P} \quad (2)$$

Expressing $k_1/k_2 = K$, we can write :

$$a = \frac{P}{K + P} \quad (3)$$

The fraction of area covered, a , by the monomolecular layer is equal to the ratio of the volume of gas molecule v covering the area and the total volume v_m of the gas molecules needed to cover the whole area of the adsorbent surface, or

$$a = \frac{v}{v_m} \quad (4)$$

Thus

$$\frac{v}{v_m} = \frac{P}{K + P} \quad (5)$$

or

$$\frac{P}{v} = \frac{K}{v_m} + \frac{P}{v_m} \quad (6)$$

A plot of the value of P/v against the adsorption pressure P would give a straight line. It would be possible to determine the values of K and the maximum adsorbable material v_m .

This study will investigate whether and how CO_2 adsorption follows Langmuir isotherm behaviour, and to determine the values of the above parameters.

IV. EXPERIMENTAL

A sample of zeolite from a natural deposit in Indonesia was prepared by firstly washing it with water to remove dirt, sand and other foreign matters. It was dried, crushed and ground and screened to size. Three screen sizes were prepared for this experiment, $-10+35$, $-35+65$, $-65+170$ mesh, similar to the reference commercial synthetic zeolite used for comparison.

The sample was activated by heating for four hours at various temperatures ranging from 100 to 900°C at 100°C interval.

A weighed amount of activated sample was placed in a glass tube, and CO_2 gas was injected from a cylinder under a set of conditions. The variable used were particle size, activation temperature, contact time, and operating pressure. The amount of CO_2 adsorbed was evaluated from the weight of the sample

after each run. The results are presented in grams of CO_2 adsorbed per 100 grams of zeolite adsorbent, or grams of H_2O desorbed per 100 grams of zeolite in the case of activation runs.

A sketch of the experimental set up is show in Figure 1.

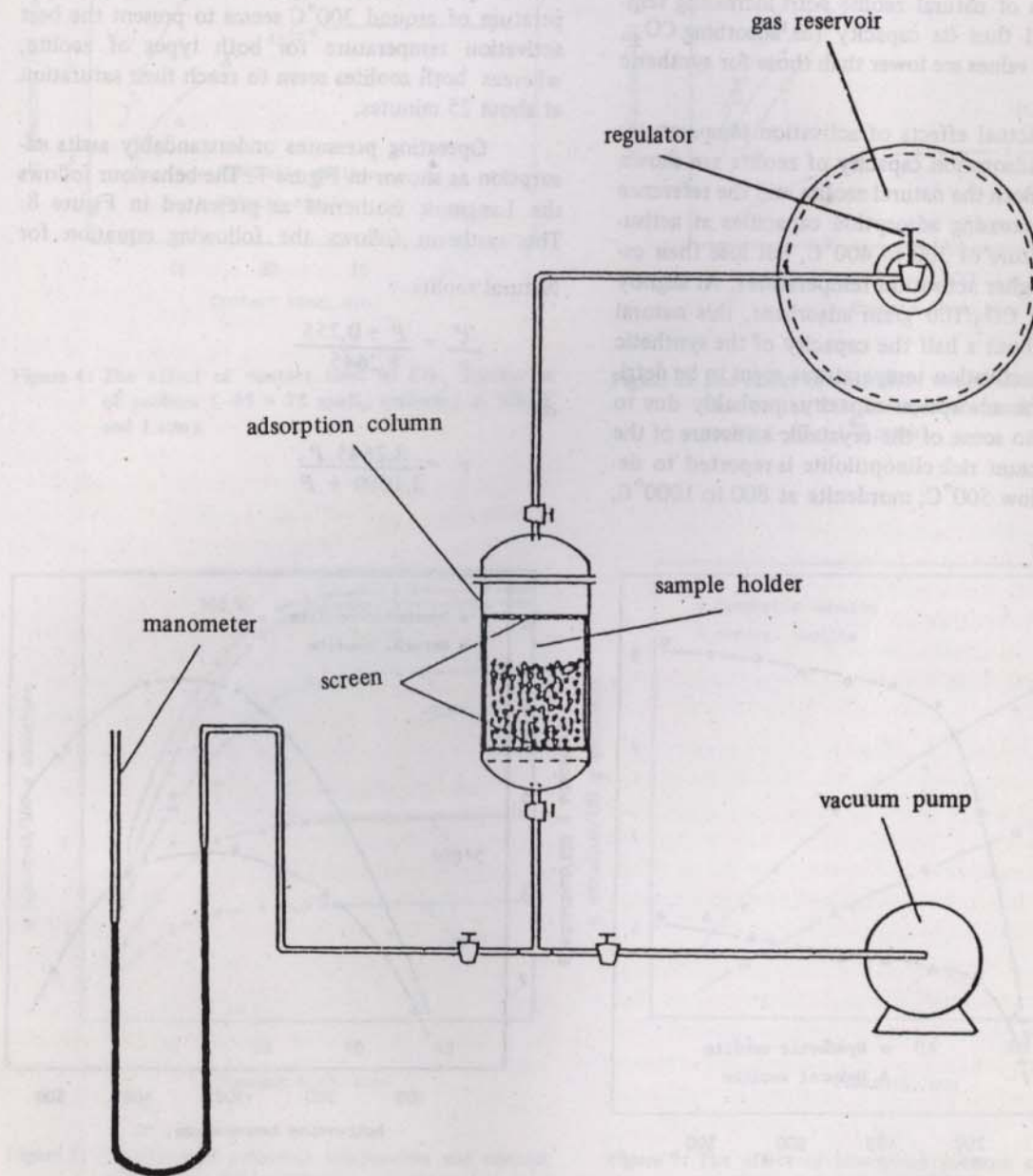


Figure 1 : Experimental set-up for CO_2 adsorption test of zeolites.

V. RESULTS AND DISCUSSION

The moisture desorbed during the activations runs at various activation temperature is presented in Figure 2, where the results for Indonesian natural zeolite are compared with those for reference synthetic zeolite. The results show the normal pattern for moisture loss of natural zeolite with increasing temperature, and thus its capacity for adsorbing CO_2 , although the values are lower than those for synthetic one.

The actual effects of activation temperatures to the CO_2 adsorption capacity of zeolite are shown in Figure 3. Both the natural zeolite and the reference one show increasing adsorption capacities at activation temperature of 300 to 400°C, but lose their capacities at higher activation temperatures. At slightly less the 5 g CO_2 /100 gram adsorbent, this natural zeolite has about a half the capacity of the synthetic one. Higher activation temperatures seem to be detrimental to the adsorption capacity, probably due to the damage to some of the crystalline structure of the zeolite. Calcium rich clinoptilolite is reported to decompose below 500°C; mordenite at 800 to 1000°C,

and lountentite at 345 to 800°C⁵).

The amount adsorbed at various contact times are presented in Figure 4 for natural and reference zeolites, at -65 +170 mesh size and at 300°C activation temperature, and in Figures 5 and 6 for natural and synthetic zeolites, respectively, at various activation temperatures. Here again it is shown that a temperature of around 300°C seems to present the best activation temperature for both types of zeolite, whereas both zeolites seem to reach their saturation at about 25 minutes.

Operating pressures understandably assists adsorption as shown in Figure 7. The behaviour follows the Langmuir isotherms as presented in Figure 8. The isotherm follows the following equation for

Natural zeolite :

$$\frac{P}{v} = \frac{P + 0,255}{8.2645}$$

or

$$v = \frac{8.2645 P}{2.1089 + P}$$

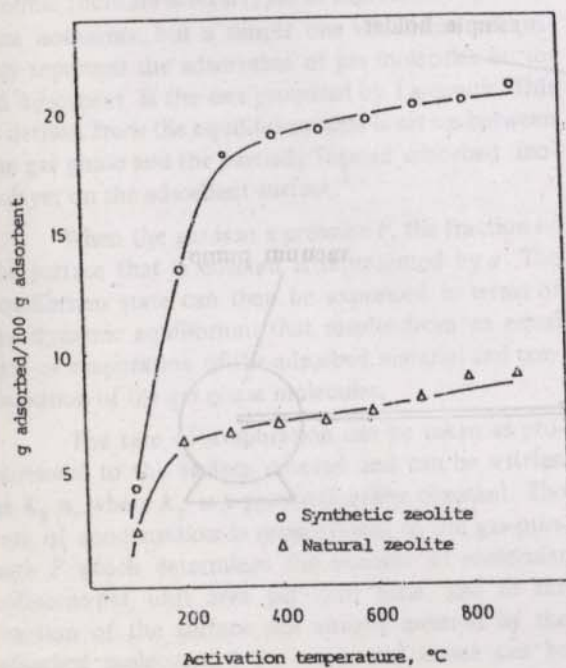


Figure 2: Moisture desorption of zeolites (-65+170 mesh) at various activation temperatures.

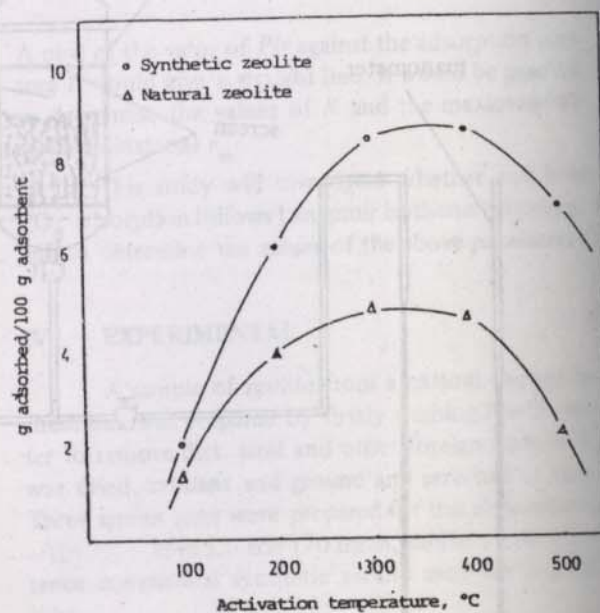


Figure 3: The effect of activation temperature on CO_2 adsorption capacity of zeolites (-65 + 170 mesh)

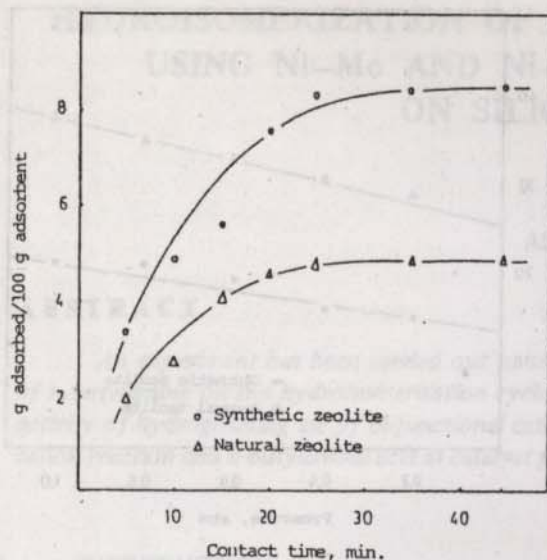


Figure 4: The effect of contact time to CO_2 adsorption of zeolites (-65 + 75 mesh, activated at 300°C and 1 atm).

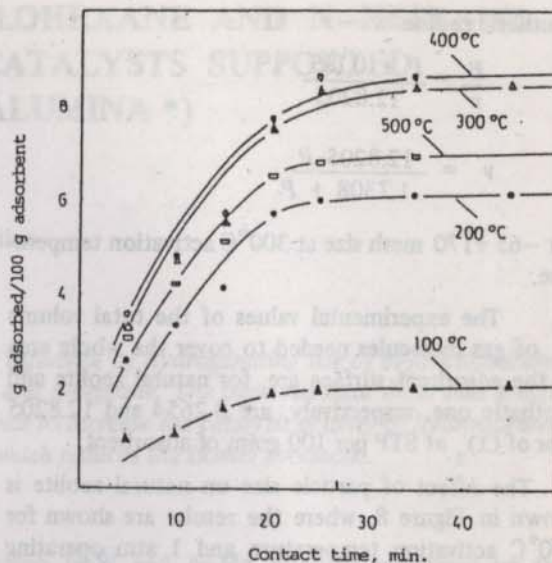


Figure 6: The effect of activation temperature and contact time on the CO_2 adsorption capacity of synthetic zeolite (-65 + 170 mesh).

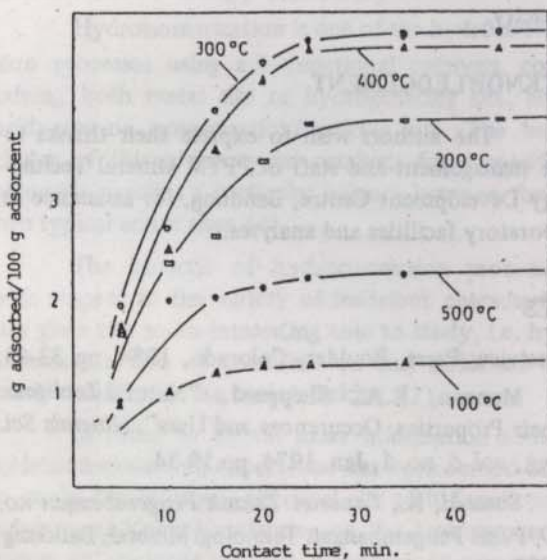


Figure 5: The effect of activation temperature and contact time on the CO_2 adsorption capacity of natural zeolite (-65 + 170 mesh).

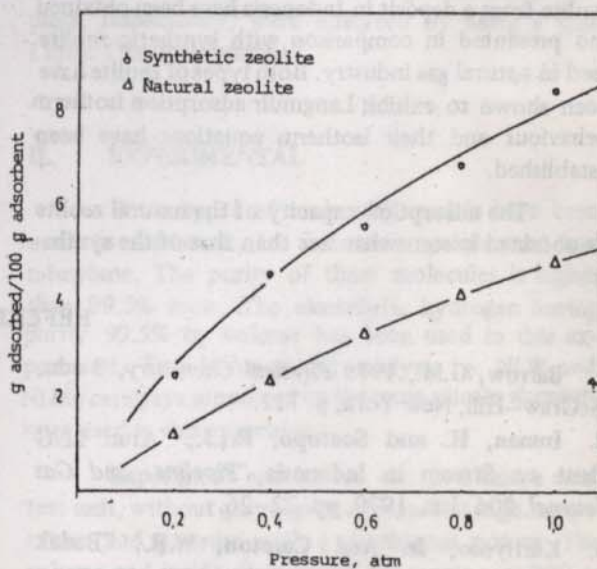


Figure 7: The effect of adsorption pressure on CO_2 adsorption of zeolites (-65 + 170 mesh activated at 300°C).

Synthetic zeolite :

$$\frac{P}{v} = \frac{P + 0.135}{12.8205}$$

or

$$v = \frac{12.8205 P}{1.7308 + P}$$

for -65 +170 mesh size at 300°C activation temperature.

The experimental values of the total volume v_m of gas molecules needed to cover the whole area of the adsorbent surface are, for natural zeolite and synthetic one, respectively, are 8.2654 and 12.8205 liter of CO₂ at STP per 100 gram of adsorbent.

The effect of particle size on natural zeolite is shown in Figure 8, where the results are shown for 200°C activation temperature and 1 atm operating pressure. A finer particle size favors the adsorption, but in operating practice, the counter effect of higher pressure drop must also be taken into account.

VI. CONCLUSIONS

The data on adsorption behaviour of a natural zeolite from a deposit in Indonesia have been obtained and presented in comparison with synthetic zeolite used in natural gas industry. Both types of zeolite have been shown to exhibit Langmuir adsorption isotherm behaviour and their isotherm equations have been established.

The adsorption capacity of the natural zeolite as obtained is somewhat less than that of the synthe-

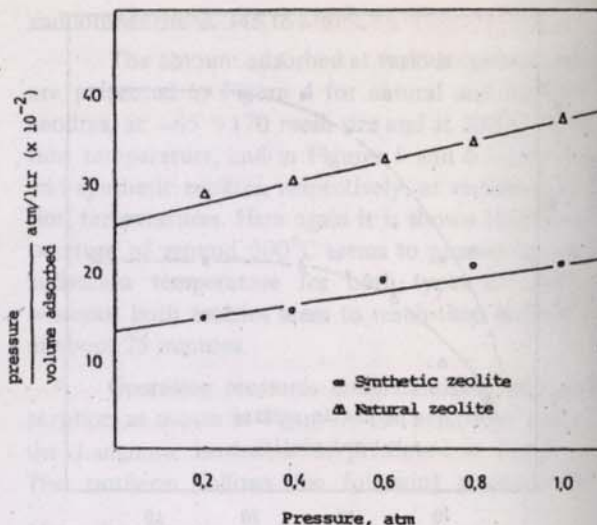


Figure 8 : The langmuir plot for the adsorption of CO₂ on zeolites (-65+170 mesh, activated at 300°C, 1atm).

tic one, but its possibilities for use as CO₂ adsorbent do exists. Its future application will depend on the local economics and possible treatment to improve its capacity.

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