

STUDY ON THE ADSORPTION OF CARBON DIOXIDE USING CARBON- ZEOLITE COMPOSITE

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Abstract

Nowadays, carbon dioxide is produced extensively by using many industrial processes and domestic processes. The greatest physiological effect of carbon dioxide is to stimulate the respiratory center, able to cause dilation and constriction of blood vessels and formed the environmental impact. In this paper, composite carbon-zeolite sorbent was prepared and utilized to study the adsorption of carbon dioxide. The adsorption of carbon dioxide on carbon-zeolite composite was measured by using volumetric method. The adsorption capacity was studied by using Langmuir equation, Freundlich equation and Temkin equation. The comparison of these results with that of zeolite molecular sieve was also presented. It was observed that very high carbon dioxide uptake was observed with composite during gas adsorption studies.

Keywords: carbon-zeolite composite, zeolite molecular sieve, adsorption of CO₂

Introduction

Zeolites are microporous crystalline solids with well-defined structures. Generally, they contain silicon, aluminium and oxygen in their framework and cations, water and other molecules within their pores. Many occur naturally as minerals, and are extensively mined in many parts of the world. Others are synthetic, and are made commercially for specific uses, or produced by research scientists.

Zeolites have an open structure that can accommodate a wide variety of cations, such as Na⁺, K⁺, Ca²⁺, Mg²⁺ and others. Zeolites have an unusual crystalline structure and a unique ability to exchange ions. Zeolites are an aluminosilicate whose major ion exchangers are potassium and calcium plus other trace minerals. One gram of zeolite provides up to several hundred square meters of surface area for chemical reactions to take place. This characteristic of zeolites gives them great absorbing power (Bekum, 2001).

Zeolites can remove atmospheric pollutants, such as engine exhaust gases and ozone-depleting CFCs. Natural zeolites are uniquely effective in adsorbing ammonia and also adsorb hydrogen sulphide. These properties make natural zeolites ideal for use in pet litter to prevent emanation of irritating odors. For similar reasons, natural zeolites can be used for effective control of irritating gases in horse stalls, barns, kennels, etc. (Breck, 1975).

When two or more materials are mixed together, the resulting composite material very often has physical properties that are very different than the properties of the used composites.

Two types of adsorption process can be distinguished depending on which of these two force types plays the higher role in the process. Adsorption processes can be classified as either physical adsorption (Vander Waals adsorption) or chemisorption (activated adsorption) depending on the type of forces between the adsorbate and the adsorbent (Hadjar, 2004).

Materials and Methods

In this experiments, all chemicals used in this work were produced from British Drug House Chemical Ltd. (BDH). All standard solutions and all other diluted solutions through the experimental runs were prepared by using distilled water.

Commercial zeolite was used for this experiment. Commercial zeolite sample, Zibo Julong chemical Co. Ltd., were used.

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Preparation of Carbon–Zeolite Composites

Zeolite molecular sieve, triethanolamine TEA (5%, 10% and 15%) solution and distilled water were mixed into a conical flask. The mixture was stirred on magnetic stirrer for 2h at ambient temperature and filtered with Buchner funnel. The filtrate was dried at 105 °C for 8h in an oven. The sample was calcined at 400 °C, 500 °C and 600 °C for 2h. Then, it was cooled to room temperature and stored in a desiccator for the removal of CO₂.

Characterization of the Carbon-Zeolite Composites

The physicochemical properties (bulk density, pH, moisture, and porosity) of carbon-zeolite composites were determined by conventional methods. Specific surface area was determined using the methylene blue absorption test (MBT) method.

X-ray diffraction (XRD) analysis was carried out using Rigaku X-ray Diffractometer, RINI 2000/PC software, Cat. No 9240 J 101, Japan.

The scanning electron microscopy (SEM) images were obtained using JSM-5610 Model SEM, JEOL-Ltd., Japan.

FT IR spectrum was recorded in the range of 4000-400 cm⁻¹ by using 8400 SHIMADZU, Japan FT IR spectrophotometer.

Sorption of Carbon Dioxide by Carbon-Zeolite Composites

The different amount of prepared carbon-zeolite composites (0.5, 1.0, 1.5, 2.0 and 2.5 ± 0.0002 g) were packed tightly into the two way glass sample tube carefully. First way was for inlet of CO₂ and the other for the collection of remaining CO₂ by KOH solution. 2 g of calcium carbonate was placed in a flat bottom flask. 2 M hydrochloric acid was slowly added to the flat bottom flask. Vigorous effervescence occurs and carbon dioxide molecules were evolved. The carbon dioxide molecules were passed over the sample tube containing carbon-zeolite composite. The remaining carbon dioxide molecules passed over the carbon-zeolite composite were collected by the potassium hydroxide solution. Then the solution was titrated with 0.1 M hydrochloric acid solution using methyl orange indicator.

Results and Discussion

Characterization of the Prepared Carbon-Zeolite Composites

In this experimental work, effect of TEA concentrations, amount of zeolite and temperature on the preparation of carbon-zeolite composites (S₁-S₁₀) are presented in Table 1. Table 1 shows that the sample S₂ gives the highest yield % of carbon-zeolite composites. Therefore, the optimum ratio of the zeolite and TEA was equal part (10:10 v/v) and pyrolysis temperature was obtained at 500°C.

The physicochemical properties of zeolite and carbon-zeolite composites are presented in Table 2. The bulk density of sample S₂ was lower than the other samples. A low bulk density means the sponge like character of zeolites. The sorptive character of sample S₂ gave better results than the others. The pH values of prepared samples were found to be in the range of 7.86 to 8.63. It can be observed that the prepared samples possessed basic character. Moisture contents of prepared samples were found to be 1.73 to 2.92% out of nine samples S₂ has the highest value indicating more porous nature of zeolites. Table 2 shows that the surface area of S₂ was obtained as 807 m²g⁻¹ while zeolite has 770 m²g⁻¹. The sample S₂ has the highest porosity (48%) whereas zeolite has (26%) respectively.

Table 1 Effect of TEA Concentrations, Amount of Zeolite Molecular Sieve and Pyrolysis Temperature on the Preparation of Carbon-Zeolite Composite (CZC)

Samples	Zeolite (g)	TEA (%v/v)	Pyrolysis temperature (°C)	Yield (%)
ZMS	10	0	500	67.74
S ₁	10	5	500	73.18
S ₂	10	10	500	76.99
S ₃	10	15	500	72.72
S ₄	10	20	500	70.66
S ₅	5	10	500	68.69
S ₆	10	10	500	76.99
S ₇	15	10	500	71.47
S ₈	20	10	500	66.92
S ₉	10	10	300	70.91
S ₁₀	10	10	400	72.22
S ₁₁	10	10	500	76.99
S ₁₂	10	10	600	69.81

ZMS = Zeolite Molecular Sieve

TEA = Triethanolamine

CZC = Carbon-Zeolite Composite

S₁ – S₄ = 10 g of zeolite molecular sieve with different TEA concentrationsS₅ – S₇ = 10 % v/v TEA concentrations with different amount of zeoliteS₈ – S₁₀ = 10 g of zeolite molecular sieve and 10 % v/v TEA concentrations with different pyrolysis temperatures**Table 2 Physicochemical Properties of Zeolite Molecular Sieve and Carbon-Zeolite Composites**

Sample	Bulk density (gcm ⁻³)	pH	Moisture content (%)	Surface area (m ² g ⁻¹)	Porosity (%)
ZMS	1.51	8.82	4.21	770	26
S ₁	0.90	8.39	2.25	800	43
S ₂	0.81	8.24	2.92	807	48
S ₃	0.88	8.36	2.73	803	46
S ₄	0.97	8.41	2.06	801	37
S ₅	1.15	7.91	1.96	790	30
S ₆	0.98	7.89	2.35	795	38
S ₇	1.07	8.63	1.80	797	40
S ₈	1.23	7.86	2.02	782	36
S ₉	1.06	8.03	2.12	793	39
S ₁₀	1.08	8.60	1.73	799	32

XRD Analysis

Figures 1 (a) and (b) show the XRD spectra of zeolite and carbon-zeolite composite S₂. XRD diffractogram of zeolite molecular sieve was found to possess the composition of zeolite A. XRD diffractogram of carbon-zeolite composite shows that the zeolite structure was not destroyed during the heat treatment and embedded in the carbon matrix. The crystallite size of carbon-zeolite composite S₂ was obtained as 36.47nm.

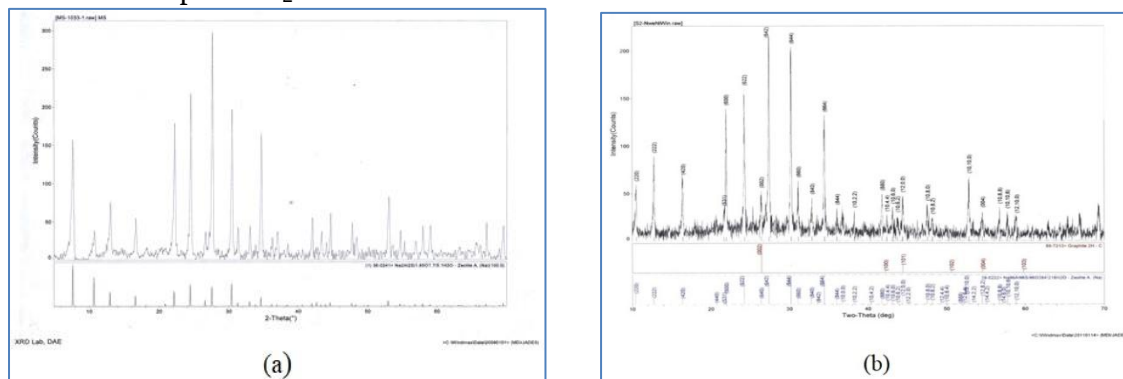


Figure 1 X-ray diffractograms of (a) spectrum of zeolite molecular sieve and (b) spectrum of carbon-zeolite composite S₂

SEM Analysis

SEM images in Figures 2(a) and 2(b) show the surface morphology of the carbon-zeolite composites and zeolite structure. White crystal indicates the zeolite molecular sieve crystals and the black spots indicate the carbon domains. The zeolite crystals are well dispersed in carbon matrix.

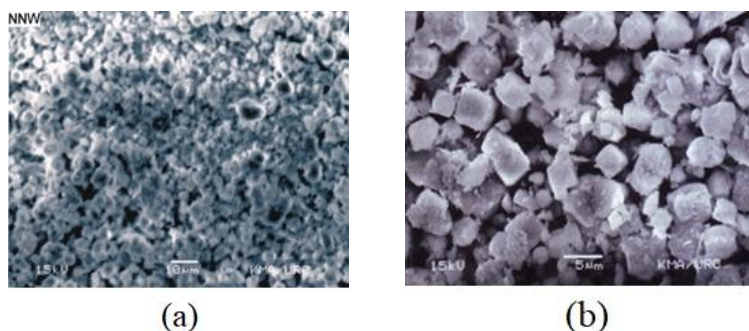


Figure 2 Scanning electron micrographs of (a) zeolite molecular sieve and (b) carbon-zeolite composite S₂

FTIR Analysis

The FT-IR spectrum of carbon-zeolite composite S₂ is shown in Figure 3. In the spectrum: the band at 3410 cm⁻¹ indicate the O-H and N-H stretching, the organic compounds such as C = C stretching bands at 1666 cm⁻¹ and C- H bending of CH₃, CH₂ at 1489 cm⁻¹ and Si – O (or) Al-O tetrahedral stretching bands at 1018 cm⁻¹ were found (Table 3).

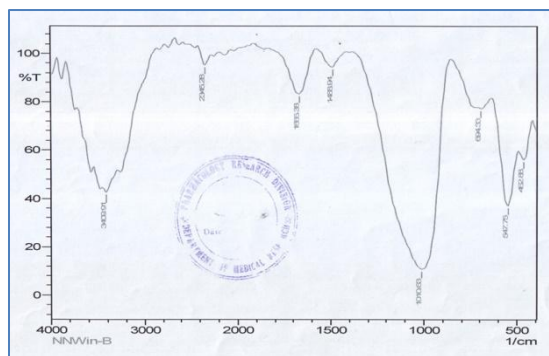


Figure 3 FTIR spectrum of carbon-zeolite composite (S_2)

Table 3 Structural Assignment for FTIR Data of Carbon-Zeolite Composite (S_2)

Observed Frequency (cm^{-1})	Reference Frequency* (cm^{-1})	Assignment
3410	3600-3200	O-H stretching, N-H stretching
1666	1680-1600	C=C stretching
1489	1400-1300	C-H bending of CH_3 , CH_2
710	820-750	Si-O-Al stretching

*Nyquist and Kagel,1991; Silverstein and Terence,1991

Preliminary Sorption Study of Carbon Dioxide on Carbon-Zeolite Composites (S_1 to S_{10})

Table 4 shows the removal of carbon dioxide by carbon-zeolite composites (S_1 to S_{10}). It was found that sample (S_2) was found to have higher percent adsorption than others by using volumetric method.

Table 4 Percent Adsorption of Carbon Dioxide on Carbon-Zeolite Composites by Volumetric Method (Dosage of sample = 1g)

Sample	Amount of carbon dioxide in KOH solution (mmol)	Adsorbed amount of carbon dioxide (mmol)	Percent adsorption of carbon dioxide (%)
Without sample	13.761	-	-
S_1	8.214	5.547	40.31
S_2	7.670	6.091	44.26
S_3	8.152	5.609	40.76
S_4	8.199	5.562	40.42
S_5	8.800	4.961	36.05
S_6	8.694	5.067	36.82
S_7	8.163	5.598	40.68
S_8	8.932	4.829	35.09
S_9	8.225	5.536	40.23
S_{10}	8.650	5.111	37.14

Sorption Isotherms

In this research work, adsorption capacity was studied by using Langmuir, Freundlich and Temkin equation. The nature of the adsorption reaction could be described by relating the adsorption capacity (mass of solute adsorbed per unit mass of adsorbent) to the equilibrium concentration of the solute remaining in the solution such a relation is known as an adsorption isotherm.

Table 5 and Figure 4 show Langmuir model of carbon dioxide adsorption onto CZC. Estimated adsorption parameters by the Langmuir model are shown in Table 8. The Langmuir constant b (5.855) for CZC the square of regression coefficient ($R^2 = 0.9792$) for CZC suggesting that the adsorption of carbon dioxide on CZC can be modeled well by Langmuir equation while adsorption of carbon dioxide. It is well documented that the essential characteristic of the Langmuir isotherm may be expressed in terms of the dimensionless parameter (R_L). R_L has been defined as the isotherm shape that predicts if an adsorption system is favourable or unfavourable (Saswati and Ghosh 2005). R_L indicates the isotherm shape according to the following characteristics.

$R_L > 1$ (is unfavourable), $R_L = 1$ (linear adsorption), $R_L = 0$ (is irreversible) and $0 < R_L < 1$ is favourable. It has been expressed as, $R_L = \frac{1}{1 + bC_i}$

For individual component system the R_L were found to be $0 < R_L < 1$ indicating that adsorption of carbon dioxide on CZC is favourable. The values of R^2 show that Langmuir equation can be used to describe removal of carbon dioxide by CZC very well and averagely for carbon dioxide adsorption. Based on the Langmuir parameters, that is, X_m (mg g^{-1}) for monolayer formation of sorption follows this order of: CZC 0.267 mg g^{-1} . It means to point out the attachment of carbon dioxide on CZC was of stronger binding nature.

It have been reported that Freundlich isotherm is an empirical relationship, which often gives a more satisfaction experimental data. It can be expressed as

$$\text{Log } q_e = \log K + \frac{1}{n} \log C_e$$

Table 6 and Figure 5 show Freundlich model of carbon dioxide adsorption on CZC. The values of K and n were obtained by plotting logarithms of adsorption capacity against logarithms of equilibrium concentration. Estimated adsorption parameters by the Freundlich model are shown in Table 6.

High levels of K and n values greater than 1 from the Freundlich isotherm suggests that the adsorption capacity of carbon dioxide on CZC. Also high values of n show that forces which are exerted on the surface of CZC during carbon dioxide adsorption are weak forces, which are in order of CZC. The square of correlation coefficients (R^2) for Freundlich isotherm are 0.966 representing a good fit ($R^2 \geq 0.95$) of the observed data. The values of R^2 also indicated that Freundlich isotherm describes adsorption of carbon dioxide on the adsorption capacities are in order of CZC.

The Temkin isotherm is an empirical relationship which often gives a more satisfactory model of experimental data (Saswati and Ghosh, 2005). It can be expressed as;

$$q_e = B \ln A + B \ln C_e$$

The values of A and B were obtained by plotting of adsorption capacity against equilibrium concentration. Estimated adsorption parameters by the Temkin model are shown in Table 7. The values of A and B from the Temkin isotherm (Table 8) suggests that the adsorption capacity of CZC was high and that any large change in the equilibrium concentration of carbon dioxide. The correlation coefficients R^2 is 0.9133 representing an average fit ($0.5 < R^2 < 0.75$ and $0.75 < R^2 < 0.95$) of the observed data. From the resulting data, CO_2 adsorption by carbon-zeolite

composite capacity was found to be in order with three isotherms, Langmuir, Freundlich and Temkin isotherms.

Table 5 Langmuir Isotherm for Carbon Dioxide by Carbon Zeolite Composite

Dosage (g)	C _i (mg)	C _e (mg)	X (mg)	q _e (mg g ⁻¹)	$\frac{1}{C_e}$	$\frac{1}{q_e}$
0.5	0.313	0.237	0.076	0.152	4.219	6.579
1.0	0.313	0.174	0.139	0.139	5.747	7.194
1.5	0.313	0.118	0.195	0.130	8.474	7.692
2.0	0.313	0.102	0.211	0.105	9.804	9.524
2.5	0.313	0.099	0.214	0.086	10.101	11.628

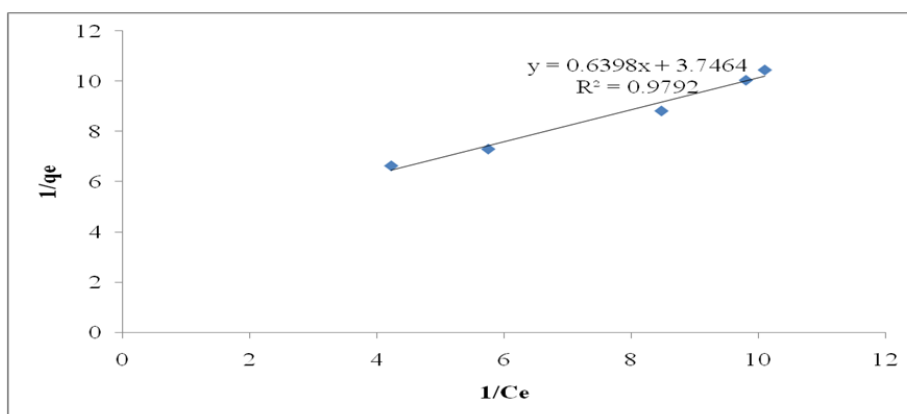


Figure 4 Langmuir adsorption isotherm for carbon-zeolite composite

Table 6 Freundlich Isotherm for Carbon Dioxide by Carbon- Zeolite Composite

Dosage (g)	C _i (mg)	C _e (mg)	X (mg)	q _e (mg g ⁻¹)	Log C _e	Log q _e
0.5	0.313	0.237	0.076	0.152	-0.625	-0.818
1.0	0.313	0.174	0.139	0.139	-0.759	-0.857
1.5	0.313	0.118	0.195	0.130	-0.928	-0.886
2.0	0.313	0.102	0.211	0.105	-0.991	-0.979
2.5	0.313	0.099	0.214	0.086	-1.004	-1.065

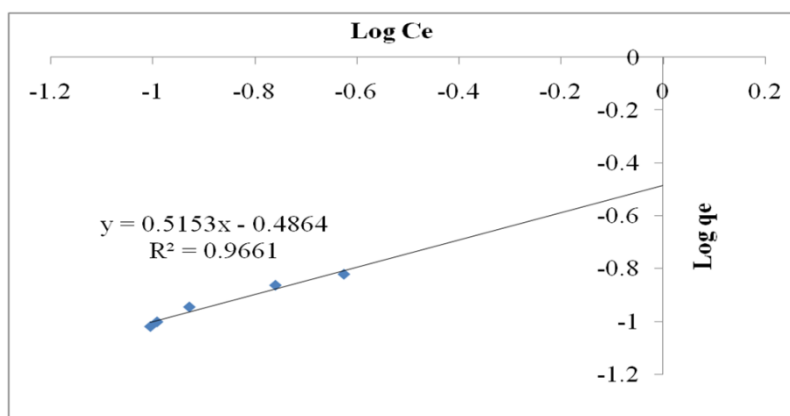
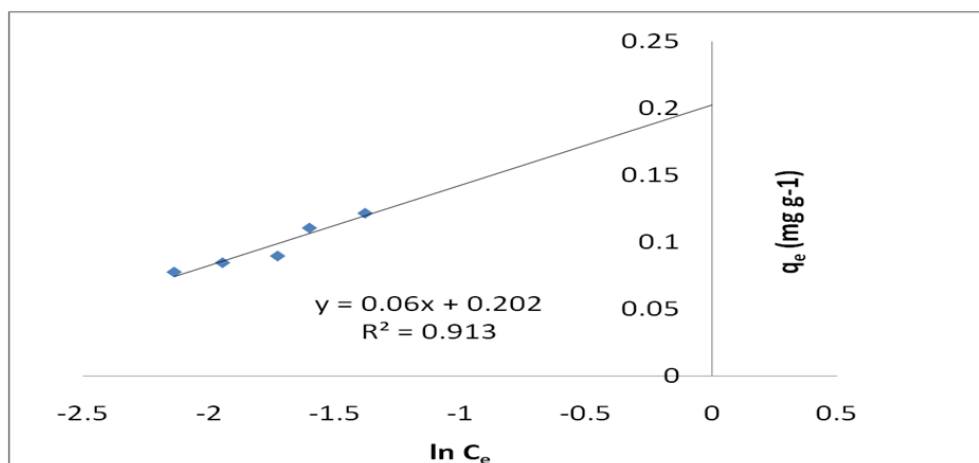


Figure 5 Freundlich adsorption isotherm for carbon- zeolite composite

Table 7 Temkin Isotherm for Carbon Dioxide by Carbon-Zeolite Composite

Dosage (g)	C_i (mg)	C_e (mg)	x (mg)	q_e (mg g ⁻¹)	$\ln C_e$
0.5	0.313	0.237	0.076	0.152	-1.439
1.0	0.313	0.174	0.139	0.139	-1.749
1.5	0.313	0.118	0.195	0.130	-2.137
2.0	0.313	0.102	0.211	0.105	-2.283
2.5	0.313	0.099	0.214	0.086	-2.313

**Figure 6** Temkin adsorption isotherm for carbon-zeolite composite**Table 8 Adsorption Parameters for Monolayer System by Carbon-Zeolite Composite**

Sample	Langmuir Model				Freundlich Model			Temkin Model		
	X_m (mg g ⁻¹)	b	R^2	R_L	K (mg g ⁻¹)	n	R^2	A (mg g ⁻¹)	B	R^2
CZC	0.267	5.855	0.9792	0.353	0.721	1.941	0.9661	28.982	0.060	0.913

Conclusion

From the overall results and data, it may be deduced that; carbon-zeolite composites were prepared by incorporating zeolite into a TEA solution. Preparations were carried out by various concentration of TEA solution and various pyrolysis temperatures. Among these results, equal amount of zeolite and TEA at 500°C. S₂ showed the highest surface area (807 m²/g), highest moisture content (2.92%), highest porosity (48%) and the lowest bulk density (0.81 gcm⁻³).

The characterization of carbon-zeolite composites were carried out by XRD, SEM and FTIR. From the X-ray diffractograms of zeolite and carbon-zeolite composite, the crystal structure zeolite was observed as zeolite A. In composite, it was observed that the zeolite structure was not destroyed during the heat treatment and embedded in the carbon matrix.

SEM images show the surface morphology of the carbon-zeolite composite and zeolite structure. White crystal indicates the zeolite molecular sieve crystals and black spots indicate the carbon domains. The zeolite crystals are well dispersed in carbon matrix.

From the FTIR spectrum of composite, Si-O-Al stretching was found at 710 cm^{-1} and then the organic compounds such as C = C stretching (1666 cm^{-1}) and C-H bending (1489 cm^{-1}) were observed.

The Langmuir isotherm shows that the attachment of carbon dioxide on carbon-zeolite composite was monolayer formation and stronger binding nature. The Freundlich isotherm also describe that the adsorption capacity of carbon dioxide on carbon-zeolite composite was observed and good fit attachment was formed. The Temkin isotherm suggests that the adsorption capacity was high and any large change in the equilibrium concentration of carbon dioxide.

Therefore, the carbon-zeolite composite parameters presented in this experiment have great potential for application in gas adsorption.

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