

# Unprecedented Low-Cost Hybrid Material for CO<sub>2</sub> and CH<sub>4</sub> Separation

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**Abstract:** The zeolite synthesis using waste as silicon source is a promising low-cost process. Sugarcane bagasse ash is a hazardous solid waste generated in large amounts in the sugar industry. Thus, development of new procedures for its productive reuse is relevant. Therefore, this waste was used to prepare a new ZCNT (zeolite/carbon nanotube material). In this work, ZCNT was applied in a CO<sub>2</sub>/CH<sub>4</sub> separation. The adsorption took place at 303 K under pressure of 0.1 until 20 bar and the data were fitted by Langmuir, Toth and Freundlich equations. The adsorbed amount at 20 bar found was 4.7 mmol of CO<sub>2</sub>/g and 4.1 mmol of CH<sub>4</sub>/g; at 3 bar the adsorbed amount was 4.1 mmol of CO<sub>2</sub>/g and 1.2 mmol of CH<sub>4</sub>/g. This result indicates that ZCNT has potential application in CO<sub>2</sub>/CH<sub>4</sub> separation at low pressures.

**Key words:** Gas adsorption, biogas purification, porous materials.

## 1. Introduction

Greenhouse gases are considered as one cause of the global temperature increase, and this has attracted attention to the need to develop strategies to decrease CO<sub>2</sub> (carbon dioxide) emissions [1]. CO<sub>2</sub> causes serious environmental problems as well as impurity in natural gas. CO<sub>2</sub> separation from natural gas is an important concern in the chemical industry because it reduces the energy content of natural gas, and in the presence of water vapor, it becomes corrosive to equipment and pipelines [2]. The most commonly used techniques for CO<sub>2</sub> capture and separation from fuel gases include ammonium absorption [2], dual-alkali absorption [3], membrane separation [4], and solid adsorbents [5].

Intense research is currently focused on the design of new and effective CO<sub>2</sub> adsorbents. The main

challenge for greenhouse gas adsorption is to find a way to decrease its cost and make it more attractive than other market technologies. Therefore, CO<sub>2</sub> capture based on cheap technology with great potential for reducing the global cost of sorbents is a very promising alternative for the future [6].

One of the most promising strategies to prepare low-cost sorbents is the replacement of commercial chemicals with waste products as the starting precursor [7-13]. The disposal of large amounts of SCBA (sugarcane bagasse ash) has become a serious environmental problem. Therefore, this solid waste can be used to prepare zeolite [14]. On the other hand, CNTs (carbon nanotubes), due to their distinctive chemical and physical properties can be applied in gas separation process. Considering this, low-cost zeolite/CNT synthesis is a promising technique for recycling SCBA and separate CO<sub>2</sub> from natural gases.

In the present study, the authors have applied a low-cost zeolite A, synthesized using sugarcane

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bagasse ash as the silicon source and carbon nanotubes, to the CO<sub>2</sub> and CH<sub>4</sub> adsorption process by the gravimetric method at high pressure.

## 2. Experimental Sections

### 2.1 Materials

SCBA for zeolite synthesis was collected from the sugarcane industry located in the region of Maringa City, Parana, Brazil. The authors used sodium hydroxide (Across), sodium aluminate (Sigma Aldrich) and MWCNT (multiwall carbon nanotubes) from CNT Co. Ltd. (Incheon, Korea). The gases CO<sub>2</sub>, CH<sub>4</sub> and helium were obtained from Linde Group at purities of 99.999%.

### 2.2 Porous Material Preparation

For the material synthesis, 3 g of SCBA treated at 873 K by 4 h was homogeneously mixed with NaOH in a 1.5 ratio (4.5 g of NaOH). Then, the mixture was heated in a nickel crucible at 823 K for 40 min. The resultant fused mixture was dissolved in 100 mL of distilled water (Solution 1). Soon after, an amount of 100 mL of sodium aluminate solution 0.48 mol·L<sup>-1</sup> (Sigma Aldrich) and 1 g of CNT was added to Solution 1. The gel was transferred to polypropylene reactor (250 mL) and kept at 353 K for 148 h. Then, the solid was separated by filtration, washed with distilled water and dried overnight at 100 °C.

### 2.3 Characterization

The synthesized zeolite/CNT was characterized by FTIR (Fourier transform infrared spectrometry) (Bomem-Michelson MB-100 with a resolution of 4 cm<sup>-1</sup> using a KBr disc method), XRD (X-ray diffraction) analysis (Shimadzu, model XRD-6000 X-ray operated at 40 kV and 40 mA, with Cu K $\alpha$  as the radiation source, diffraction angle 2 $\theta$  in the range 10°-60°). The specific surface area was determined by N<sub>2</sub> physisorption at 77 K (Micromeritics ASA 2020) using BET method, SEM (scanning electron microscopy, Shimadzu SSX-550 Superscan), and TEM

(transmission electron microscopy, JEOL JEM 1400).

### 2.4 CO<sub>2</sub> Adsorption by the Gravimetric Method

Adsorption equilibrium studies were performed using a magnetic suspension balance from Rubotherm (Bochum, Germany). The adsorbent was degassed in situ at 573 K until no mass variation was observed in the system. After that, the measuring chamber was cooled down to 303 K, and helium gas pressure was increased stepwise (up to 20 bar). Then, the CO<sub>2</sub> gas was added in the chamber and mass variation at equilibrium ( $m$ ) was recorded for each pressure step (until 20 bar). The previous experiment with helium was carried out to determine the specific volume of the solid phase of the sample and the sample container volume, characteristic of the suspended parts inside the chamber. The sum of these volumes was used to account for the buoyancy effects on measurements with adsorbing gases. For a given gas pressure  $P$ , the excess adsorbed phase concentration (disregarding adsorbed volumes) may be calculated according to Eq. (1) [15-17]:

$$m_{ex(P,T)} = \Delta m_{(P,T)} + (V_b + V_s) \cdot \rho_{(P,T)} \quad (1)$$

where,  $m_{ex}$  is the excess uptake (g/g sample),  $\Delta m$  is the mass difference sensed by the equipment (g/g sample),  $V_b$  is the specific volume of the balance-suspended components (cm<sup>3</sup>/g sample),  $V_s$  is the specific volume of the sample solid phase (cm<sup>3</sup>/g sample),  $\rho$  is the gas density (g/cm<sup>3</sup>),  $P$  is the pressure (bar), and  $T$  is the temperature (K).

To clearly describe the CO<sub>2</sub> and CH<sub>4</sub> adsorption behavior on the synthesized zeolite/CNT, the Langmuir, Toth, and Freundlich equations were used to fit the isotherms using the software Origin 7.0<sup>®</sup>.

The adsorption selectivity of CO<sub>2</sub> and CH<sub>4</sub> was calculated with Eq. (2):

$$\frac{\alpha(\text{CO}_2)}{(\text{CH}_4)} = \frac{n(\text{CO}_2)}{n(\text{CH}_4)} \quad (2)$$

Where absolute adsorbed amount ( $n$ ) of CO<sub>2</sub> and CH<sub>4</sub> (mmol/g) and temperature of 303 K.

### 3. Results and Discussion

Fig. 1 displays the XRD patterns and FTIR spectra to standard zeolite X/A and ZCNT as well as N<sub>2</sub> physisorption results for CNT and ZCNT materials. In the XRD results for ZCNT material (Fig. 1a), the diffraction peaks were indexed to zeolite types X and A (ZX and ZA respectively). These zeolites exhibit Pm-3m and Fd-3 space groups respectively (standard pattern number 71-0784 and 85-2064 in the ICDD database and standard pattern of IZA (international zeolite association)).

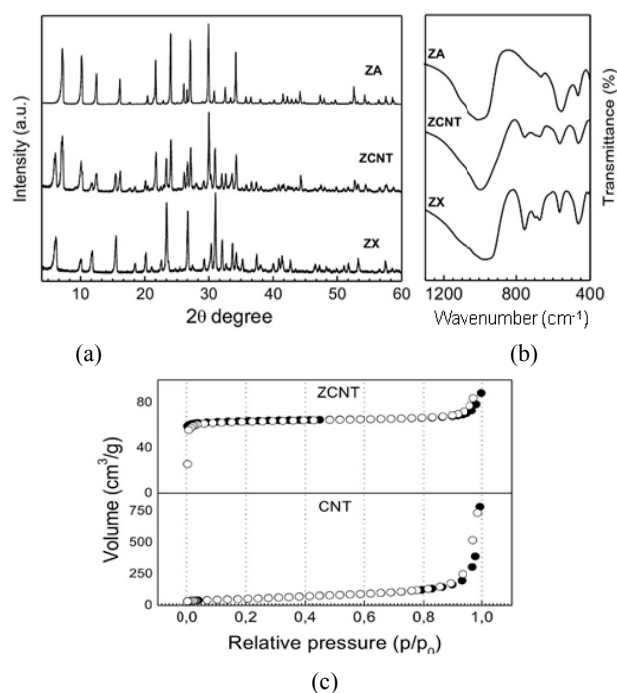
The FTIR spectras (Fig. 1b) of the synthesized zeolite reveals the existence of zeolite A and X. Peaks in the lattice region of 1,300-400 cm<sup>-1</sup> suggests this. The spectrum of zeolite X illustrates the presence of absorptions at 458, 559, 666, 746 and 974 cm<sup>-1</sup>. The 974 cm<sup>-1</sup> band is due to the Si-O-Al asymmetric stretching vibration mode of T-O bonds, (where T = Si or Al). The band at 746 cm<sup>-1</sup> is due to the S4R T-O-T symmetric stretching, while the absorption at 559 cm<sup>-1</sup> is attributed to D6R T-O-T symmetric stretching and very close to external vibration of double four-rings (D4R) in for zeolite A framework localized in 557 cm<sup>-1</sup>. The two bands at 666 and 458 cm<sup>-1</sup> are assigned to the Si-O-Al symmetric stretching and S4R symmetric bending modes, respectively.

The specific surface area of ZCNT and CNT was measured by nitrogen adsorption-desorption isotherms at 77 K. The BET method obtained the total specific surface area (the authors chose the linear region in the range 0.05 < P/P<sub>0</sub> < 0.3) was 201.78 m<sup>2</sup>/g and 188.56 m<sup>2</sup>/g, respectively. The measured surface areas for as-produced CNTs generally range from 10 to 500 m<sup>2</sup>/g in experiments [18]. The N<sub>2</sub> isotherm at 77 K for ZCNT material is classified as type I, characteristic of microporous material, as zeolite X and A; on the other hand, the CNT presents type III isotherm characteristic of nonporous material [19, 20]. However, this fact points to a potential application of this green material in gas separation, because zeolite X has a large pore size (7.3 Å) [21-23] and CNTs

present diameters from 10 to 40 nm [24] and lower polarity than zeolite. This size pore distribution makes this new material interesting in molecular sieve application.

The SEM and TEM observations are shown in Fig. 2. SEM images indicate the external morphology of synthesized zeolite. A well-defined octahedral and cubic morphology is typical of zeolite X and A, respectively [25, 26], indicating the mixture. This evidence corroborates XRD and FTIR results. Therefore, TEM micrographs reveal that CNTs are localized inside materials, making the synthesized materials not only composite but a new low-cost hybrid material, and study of its properties is relevant to apply in adsorption and separation.

Fig. 3a shows the experimental CO<sub>2</sub> adsorption isotherm and the adjustment with the three models at 303 K in the pressures between 0 and 20 bar. The maximum adsorbed amount of CO<sub>2</sub> on the zeolite sample is close to 5 mmol/g. However, this amount is achieved up to 3 bar pressure indicating a fast saturation of the porous structure. This behavior at low pressure can be explained by the strong interaction



**Fig. 1** X-ray diffraction patterns (a), FTIR spectra (b) and N<sub>2</sub> isotherm at 77 K (c).

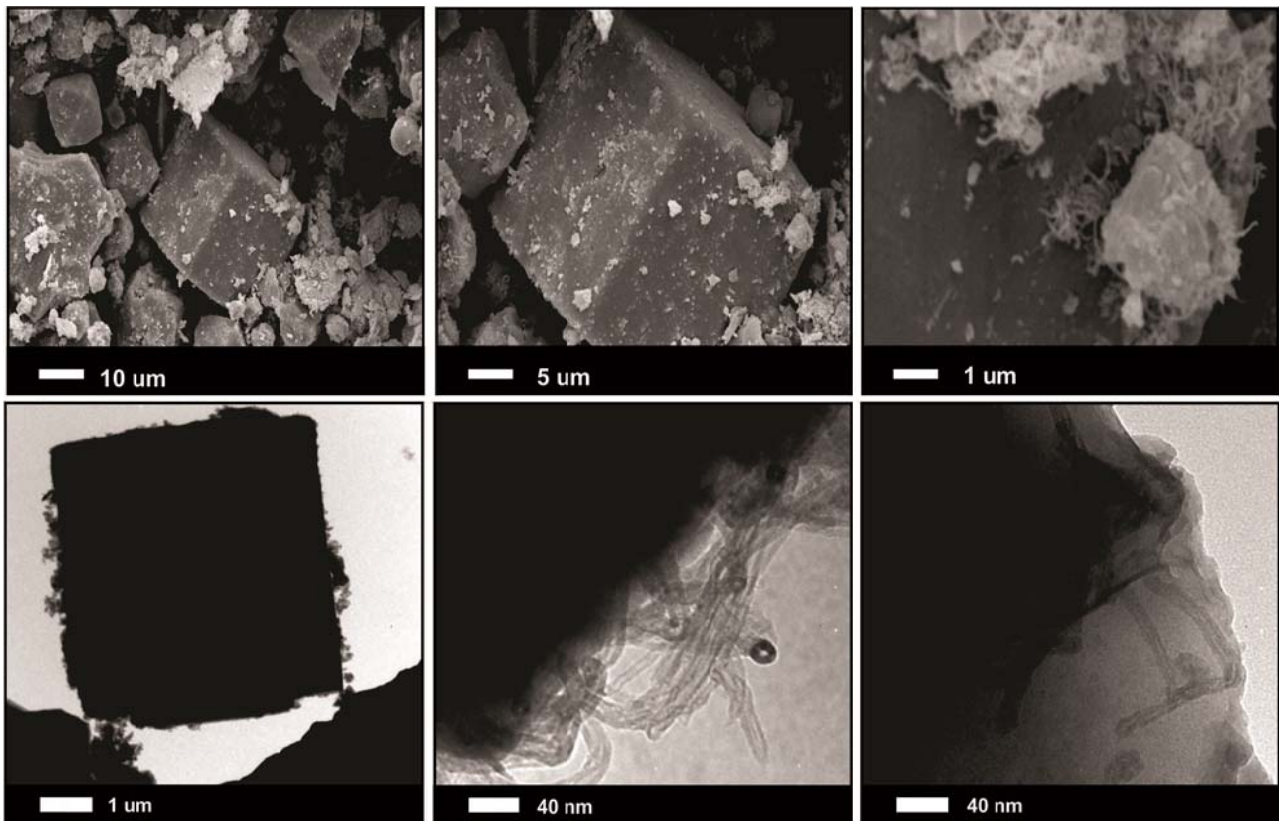


Fig. 2 SEM and TEM micrographs for ZCNT materials.

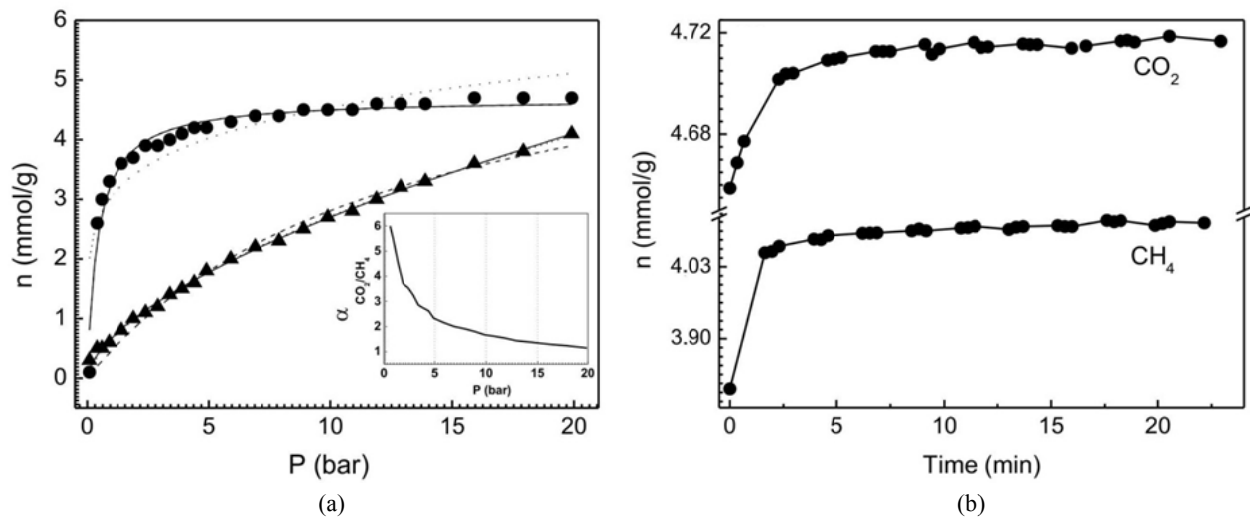


Fig. 3 CO<sub>2</sub> (circles) and CH<sub>4</sub> (triangle) adsorption isotherms and the adjustment with the Langmuir (full), Toth (dash) and Freundlich (dot) models at 303 K and selectivity inset (a) and Kinetic of CO<sub>2</sub> and CH<sub>4</sub> uptake by the ZCNT at 303 K and about 20 bar of pressure (b).

between CO<sub>2</sub> molecules and the ZCNT surface. Other authors found similar results for CO<sub>2</sub> adsorbed in porous materials [11, 27-29]. On the other hand, the maximum adsorbed amount of CH<sub>4</sub> on the zeolite

sample is close to 4 mmol/g. However, this amount is achieved up to 15 bar pressure, indicating a slow saturation of the porous structure, explained by higher kinetic diameter ( $dk_{[\text{nm}]} 0.38/0.33$ ) and methane

molecules lesser polarity than CO<sub>2</sub> that decrease the methane diffusion on ZCNT pores structure. In fact, this properties difference can be used in the CH<sub>4</sub>/CO<sub>2</sub> separation process because at low pressures, the selectivity value for CO<sub>2</sub> is close to 6 (Fig. 3a). Therefore, these results indicate that ZCNT obtained from SCBA is a promising low-cost sorbent and has potential as an efficient gas-separation process at low pressures.

Table 1 shows the maximum values for the adsorption amount ( $q_m$ ), the correlation coefficient ( $r^2$ ) of fitted curves, and the other parameters for adjusted equations (supplementary material).

The CO<sub>2</sub> adsorption on adsorbents can be better fitted by the Langmuir adsorption equation. The Langmuir isotherm assumes that adsorption occurs on a homogeneous surface containing sites with equal energy. The CH<sub>4</sub> adsorption can be explained by the Freundlich equation. This equation indicates an adsorption on heterogeneous surface. In fact, the hybrid material ZCNT exhibits polar and nonpolar structure and becomes hydrophilic zeolite and CNT respectively. Therefore, the new material prepared in this work exhibits potential as an adsorbent and molecular sieve.

Fig. 3b shows the kinetics of CO<sub>2</sub> and CH<sub>4</sub> uptake by the ZCNT at 303 K and 20 bar of pressure. The adsorption kinetics of two gases consisted of an initial rapid step and a second slow step (where equilibrium uptake was obtained). The equilibrium time was 7 min

**Table 1 Parameters for adjusted equations.**

Equations		CO <sub>2</sub>	CH <sub>4</sub>
Toth	$q_m$ (mmol/g)	4.69 ± 0.12	6.77 ± 3.53
	$b$ (bar <sup>-1</sup> )	2.32 ± 0.61	0.16 ± 0.02
	$n$	0.10 ± 0.17	0.62 ± 0.29
	$r^2$	0.95708	0.97558
Freundlich	$n$	0.17 ± 0.02	0.61 ± 0.01
	$k$	3.05 ± 0.15	0.67 ± 0.01
	$r^2$	0.77641	0.9979
Langmuir	$q_m$ (mmol/g)	4.69 ± 0.06	6.40 ± 0.37
	$b$ (bar <sup>-1</sup> )	2.32 ± 0.24	0.08 ± 0.01
	$r^2$	0.95903	0.98488

for CO<sub>2</sub> and 3 min for CH<sub>4</sub>. The relatively fast adsorption of CH<sub>4</sub> on the ZCNT reflected the existence of easier accessibility of adsorption sites on the adsorbent, probably due to low polarity of CNT that interacts more with CH<sub>4</sub> than CO<sub>2</sub>. This fact indicates that at higher pressure (20 bar), the hydrophilic zeolite structure was saturated with CO<sub>2</sub> but CNT pores were still absorbing nonpolar molecules of CH<sub>4</sub>.

## 4. Conclusions

In this work, it was observed that the unprecedented ZCNT material exhibited higher selectivity for CO<sub>2</sub> than CH<sub>4</sub>, close to 6 units. This reveals a new green and low-cost material for gas separation, doubly beneficial to environmental management due to decreased contamination of hazardous waste as bagasse ash and easy capturing and low separation costs for greenhouse gases.

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