

CO₂ adsorption on green zeolite

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ABSTRACT: 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 can be used to prepare an adsorbent material such as zeolite. In this work, the CO₂ adsorption process was applied and compared in synthesized zeolite (SZ) using sugarcane bagasse ash and a commercial zeolite (CZ). The CO₂ adsorption isotherms were measured at 293, 303, and 313 K, and the data were fitted by Toth and Freundlich equations. The adsorption process was well fitted with the Toth model, and the maximum uptake of CO₂ at 298 K was 5.05 and 5.13 mmol/g for SZ and CZ, respectively, indicating a potential application of the SZ in the CO₂ adsorption process.

KEYWORDS: Gas capture; Microporous materials; Sugarcane bagasse.

1. INTRODUCTION.

Greenhouse gases are considered the cause of the global temperature increase, and this has attracted attention to the need to develop strategies to decrease carbon dioxide (CO₂) emissions (Nugent *et al.*). The most commonly used techniques for CO₂ capture and separation from fuel gases include the ammonium absorption process (Yeh *et al.*, 2005), the dual-alkali absorption (Huang *et al.*, 2001), the membrane separation process (Ahmad *et al.*, 2012; L. Zhao *et al.*, 2008), and adsorption on solid adsorbents (Yan *et al.*, 2013; Witoon and Chareonpanich, 2012; Park *et al.*, 2012; Liu *et al.*, 2011; C. Lu *et al.*, 2008). Intense research is currently focused on the design of new and effective CO₂ adsorbents. The main challenge for greenhouse gas adsorption is to find a way to decrease the cost of the process and to make it more attractive than other market technologies. Therefore, CO₂ capture based on cheap technology with great potential for reducing the global cost of the sorbents is a very promising

alternative for the future (M. Olivares-Marin *et al.*, 2011; Sjoström and Krutka, 2010).

One of the promising strategies to prepare low-cost sorbents is the replacement of commercial chemicals with the waste products as the starting precursor (Lin and Bai, 2012). Consequently, the disposal of large amounts of sugarcane bagasse ash has become a serious environmental problem. Considering this, zeolite synthesis can be adopted as a promising technique for recycling this waste and has received extensive attention over the last decade.

In the present study, we have applied a low-cost zeolite A synthesized using sugarcane bagasse ash as the silicon source to the CO₂ adsorption process by the gravimetric method at high pressure, and compared its adsorbed amount with that of a commercial zeolite A

2. Experimental

2.1. Materials: Sugarcane bagasse ash (SCBA) for zeolite synthesis was collected from the sugarcane industry located in the region of Maringá City, Paraná, Brazil. The synthesis and



characterization methods adopted were described in our prior work (Moisés *et al.* 2013). However, the materials used crystallized in 160 hours. The commercial zeolite A was obtained from the Zeolyst Company® (USA) and used as received. The gases CO₂ carbon dioxide and helium were obtained from LindeGroup at purities of 99.999% and 99.999%, respectively.

2.2. CO₂ adsorption by the gravimetric method.

Adsorption equilibrium studies were performed with SZ and CZ materials using a magnetic suspension balance from Rubotherm (Bochum, Germany). The adsorbents were degassed *in situ* at 573 K until no mass variation was observed in the system. After that, the measuring chamber was cooled down to the experiment temperature (293, 303, and 313 K), and the gas pressure (CO₂) was increased stepwise (until 25 bar). The mass variation at equilibrium (*m*) was recorded for each pressure step. For each sample, a 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 the adsorbed volumes) may be calculated according to equation 1 (Dreisbach *et al.*, Oct, 2002; Dreisbach *et al.*, Aug, 2002; Dreisbach *et al.*, May, 1999).

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

where *m_{ex}* is the excess uptake (g/g sample), Δm is the mass difference sensed by the equipment (g/g sample), *V_b* is the specific volume of the balance-suspended components (cm³/g sample), *V_s* is the specific volume of the sample solid phase (cm³/g sample), ρ is the gas density (g/cm³), *P* is the pressure (bar), and *T* is the temperature (K).

To describe the CO₂ adsorption behavior on the synthesized zeolite clearly, the Toth and Freundlich equations were used to fit the isotherms using the software Origin 7.0®. The Toth isotherm model is a three-parameter equation derived by Langmuir equation. This model assumes a quasi-Gaussian energy distribution and is a successful isotherm in representing the adsorption of gases at both low and high pressure on heterogeneous surfaces (Kumar *et al.*, 2011). This model was

chosen because it takes the energetic heterogeneity of the active sites of sorbent and is represented as described in equation 2 (Toth, 1995).

$$q = q_m \frac{bp}{(1 + (bp)^n)^{1/n}} \quad (2)$$

where *q_m* is the maximum adsorbed amount (mmol/g), *b* is the Toth factor (bar⁻¹), *p* is the pressure (bar), and *n* indicates the heterogeneity of the active sites of the sorbent.

The Freundlich isotherm model was the earliest known equation describing the adsorption process. It is an empirical equation used for non-ideal sorption that involves heterogeneous sorption. The Freundlich isotherm is commonly given by the nonlinear equation 3:

$$q = kp^{1/n} \quad (3)$$

where *k* is the Freundlich constant (mmol/g), whereas *1/n* is the heterogeneity factor and an indicator of adsorption capacity, becoming more heterogeneous as its value gets further from one (Zhou *et al.*, 2012).

The heat of adsorption (*Q*) is used to achieve an energetic heterogeneity of the surface of an adsorbent; in other words, it is an indicator of the regenerability of an adsorbent and as a function of surface loading can be determined by the Clausius–Clapeyron relationship as described in equation 4 (Yuan *et al.*, 2013).

$$Q = -RT^2 \left(\frac{\partial \ln P}{\partial T} \right)_q \quad (4)$$

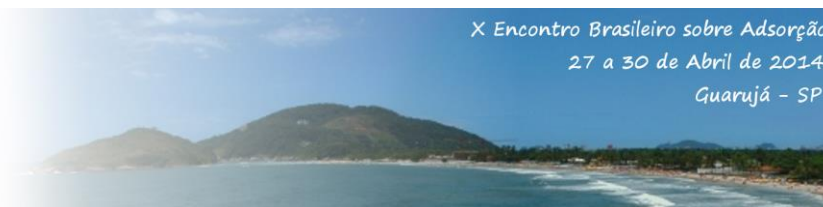
where *Q* is the heat of adsorption (kJ/mol), *R* is the gas constant, *q* is the adsorbed amount (mmol/g), and *T* is the temperature of the adsorption process (K). The isosteric heat was determined by plotting $\ln P$ and $1/T$, and the slope was $-(\Delta H/R)$. The integration of equation 4 gives equation 5:

$$\ln P = \left(\frac{Q}{RT} \right) + \text{constante} \quad (5)$$

The isosteric heat was calculated using slopes of linear plots of $\ln P$ and $1/T$ (Yuan *et al.*, 2013)

3. RESULTS AND DISCUSSION

Figure 1 (a and b) shows the isotherms of CO₂ on the CZ and SZ sample at 293, 303, and 313 K in a range of pressures from 0.1 to 25 bar. It can be seen that the adsorbed amounts of CO₂ on the samples decreased with temperature increase, as was found by many researchers (Yuan *et al.*, 2013;



Shao *et al.*, 2009; Maghsoudi *et al.*, 2013). If temperature increases, adsorbed gases will have sufficient energy to overcome the Van der Waals' attraction on the sorbent surface and migrate back to the gas phase (Zhou *et al.*, 2012). Figure 1c illustrates the relationship between the amounts adsorbed on CZ and SZ zeolite materials. This mathematical treatment is done to evaluate the adsorbate-adsorbent interaction with increased gas pressure. In fact, the nCZ:nSZ ratio reveals in which low pressure this ratio is large (*ca.* 9%) and decreases when the pressure increases. This behavior at low pressure can be explained by the strong interaction between CO₂ molecules and the CZ surface. In fact, the high-energy sites are first occupied by CO₂ molecules (Dreisbach *et al.*, 2002). On the other hand, at high pressure (up to 5 bar and *ca.* 4.5 mmol), the repulsion between CO₂ molecules is greater, and the energy surface of the zeolite generates little influence in the amount adsorbed, causing the adsorption process to be dependent only on CO₂ molecules (Cavenati *et al.*, 2004; Bae *et al.*, 2013).

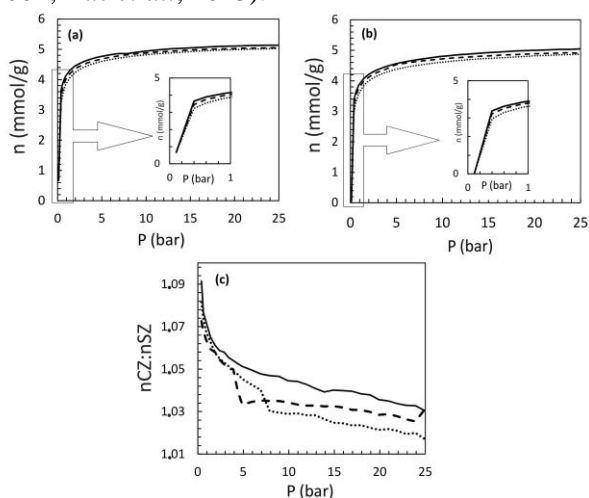


Figure 1. Isotherms of CO₂ adsorption at a 293 K (solid line), 303 K (dash line) and 313 K (dot line) on the commercial zeolite (a) synthesized zeolite (b) and adsorbed amount ratio between CZ and SZ materials (c).

These comparisons suggest that the energy on the surface of the SZ zeolite is lower than on the CZ zeolite. It is important to mention that the energy of the surface is related to the cation exchangers. The CZ material has only a small cation, Na⁺, as ion exchanger in its structure, which interacts with CO₂ molecules to cause a high polarization effect in CO₂. Since the polarization

effect is greater in the CZ zeolite, a larger amount of CO₂ is adsorbed on this material.

Unlike the SZ zeolite, other larger ion exchanging metals such as K⁺ and Ca²⁺ are present in the surface, and these cations are responsible for the lower energy on the surface, causing less polarization in CO₂ and decreasing the amount of CO₂ in the SZ zeolite. These ions are present in the sugarcane bagasse ash described in the previous publication (Moisés *et al.*, 2013) and are probably present in the SZ structure.

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. The CO₂ adsorption on adsorbents can be better fitted by the Toth adsorption equation. The Toth isotherm assumes that adsorption occurs on a heterogeneous surface containing sites with different energy and available for adsorption (Dreisbach *et al.*, Oct, 2002; Dreisbach *et al.*, Aug, 2002; Dreisbach *et al.*, May, 1999; Toth, 1995). In addition, when the affinity of Toth constant b is larger, there is a stronger affinity of adsorbate molecule toward the surface; in other words, the surface is covered by an organized layer of adsorbate molecules.

Table 1. Parameters adjusted to CO₂ adsorption experimentals on SZ and CZ materials at 293, 303 and 313 K

		Zeolite					
		CZ			SZ		
T (K)		293	303	313	298	303	313
q_{max} (mmol/g)		5.13	5.06	5.02	5.05	4.92	4.87
Parameters							
Toth	q_m (mmol/g)	5.06±0.06	4.97±0.06	4.97±0.05	4.94±0.08	4.88±0.06	4.90±0.06
	b (bar ⁻¹)	2.85±0.56	2.85±0.54	3.00±0.56	2.81±0.77	3.76±0.77	4.15±0.76
	n	1.27±0.18	1.19±0.16	1.05±0.12	1.11±0.19	0.95±0.10	0.83±0.07
	r^2	0.9440	0.9535	0.9636	0.93628	0.96536	0.97821
Freundlich	$1/n$	0.11±0.01	0.11±0.01	0.12±0.01	0.129	0.120	0.128
	r^2	0.6837	0.6952	0.7393	0.7009	0.7626	0.8055

The value found for SZ zeolite was higher than for the CZ material; however, due the different polarizability of cations on the surface, the adsorbed amount was less. In our zeolite, the fitted curve with the method of Toth presented higher r^2 than CZ. This indicated and confirmed which material has surface heterogeneity and which induces a less adsorbed amount. This result also corroborated with the nCZ:nSZ ratio results presented in Figure 1c. Toth results indicated that there was no statistical difference between maximum adsorbed amount (q_m) between SZ and CZ zeolites at the temperatures studied. The amounts of CO₂ adsorbed in studied temperatures



on the SZ sample is close to 5 mmol/g at 25 bar. Other authors in the literature found similar results for the amount of CO₂ adsorbed in porous materials (Araki *et al.*, 2012; Chandrasekar *et al.*, 2009; Walton *et al.*, 2006; M. Olivares-Marín *et al.*, 2011; Uibu *et al.*, 2009). Therefore, the results indicate that zeolite obtained from sugarcane bagasse ash is a promising low-cost sorbent and has potential as an efficient gas-adsorption process.

Figure 2 illustrates the linear plot $\ln P$ and $1/T$ and heat of adsorption to SZ (3a and 3b) and CZ (3c and 3d), respectively. The isosteric heat value is negative, indicating that the adsorption process is exothermic and value decreases to a value of -9.0 kJ/mol to -26.0 kJ/mol for the SZ zeolite and -5.0 kJ/mol to -28.0 kJ/mol for the CZ. Furthermore, for SZ material in the range of 0.1 to 2.5 mmol/g, a slight increase of the heat of adsorption was noticed, showing again the heterogeneity of the material's surface, as mentioned. The CZ material presents a homogeneous energy surface, but this increase was not observed; in fact, the heat was constant until 3.0 mmol/g. It has been reported that the heat adsorption of CO₂ on NaX zeolite presents a decreased adsorbed amount, which can be attributed to the interactions of Na⁺ ions with the quadrupole moment of carbon dioxide (Khelifa *et al.*, 2004). There is a strong effect of ion type on adsorption heat, with Na⁺ ions providing a stronger electric field (polarizability effect) than other large cations.

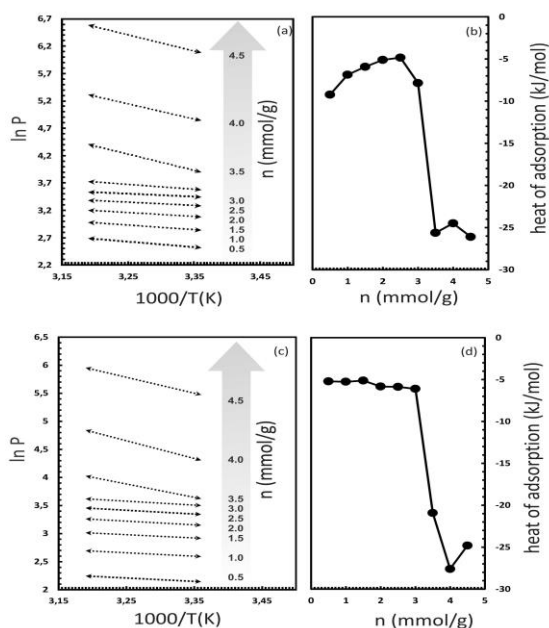


Figure 2. Linear plot $\ln P$ and $1/T$ and heat of adsorption to SZ (3a and 3b) and CZ (3c and 3d).

This explains the difference between heat adsorption for SZ (heterogeneity of cations from sugarcane bagasse ash) and CZ (Na⁺ cations) materials.

The heat of adsorption decreased in both materials, up to 2.5 mmol/g and 3.0 mmol/g for SZ and CZ materials, respectively. This indicates that quenching between CO₂ molecules in the zeolite framework is high; in fact, the surface material is completely covered by adsorbent molecules, and before this point, the CO₂ only occupies free spaces in the material. This result corroborates with the discussion in Figure 1c demonstrating that the adsorption phenomenon in high pressure is governed by gas properties, not energy surface.

In summary, the mechanism proposed for CO₂ adsorption of zeolite A indicates that this process mostly occurs in the cavities. Linear OCO-X⁺ complexes are formed (X⁺ is the cation) that also involve the perturbation of Si-O-Al bonds. Together, several different kinds of carbonate-like species form complex interactions where the adsorbate interacts with more cations, and the oxygen framework may be very relevant in zeolite adsorption chemistry (Montanari and Busca, 2008).

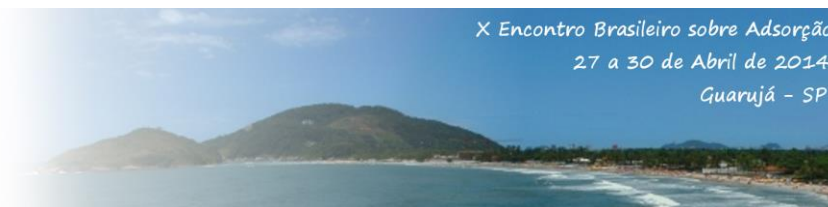
4. CONCLUSIONS

In this work, the CO₂ adsorption was studied on commercial zeolite A and a green zeolite synthesized using sugarcane bagasse ash as the silicon source. It was observed that the SZ material exhibited higher CO₂ adsorption capacity (5.05 mmol/g), and this value was comparable with commercial zeolite A (5.13 mmol/g). This reveals a new green and low-cost material for CO₂ capture, which is possibly doubly beneficial to environmental management because decreased contamination of hazardous waste as bagasse ash and greenhouse gases captures costs.

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