MACEIÓ - ALAGOAS
EBA 15
15° ENCONTRO BRASILEIRO SOBRE ADSORÇÃO
15th Brazilian Meeting about Adsorption

CO_2 adsorption from post-combustion gases stream

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Abstract

The increasing release of CO_2, the primary greenhouse gas, along with other contaminants, from post-combustion gases, poses a significant challenge. Adsorption processes, particularly through Moving Bed Temperature Swing Adsorption (MBTSA), may offer a viable solution to mitigate CO_2 emissions, using zeolite 13X, in a process primarily governed by physisorption, in which the adsorbed amount of CO_2 decreases with increasing temperature. In this study, breakthrough experiments were performed to evaluate CO_2 adsorption behaviour at dynamic conditions. The experimental results agree with previously published gravimetric measurements, showing symmetrical breakthrough curves which may be used to further scale-up the MTBSA process.

Keywords: CO_2 capture; Breakthrough curve; post-combustion

1. Introduction

Post-combustion emissions pose significant concerns for mankind, due to high CO_2 levels contributing to the greenhouse effect [1], alongside hazardous contaminants like SO_2 and NO_2, which endanger human health [2]. Levels over 5 μg m^{-3} of SO_2 over a short-term exposure and not exceeding 10 μg m^{-3} of NO_2 also pose health risks to humans [3,4]. To tackle these environmental gas pollutants, increasing research is dedicated to techniques for mitigating these gases from the atmosphere. Adsorption processes are particularly promising due to their low energy requirements and high efficiency [5].

Understanding CO_2 adsorption is critical for industrial cyclic processes, where temperature fluctuations are required due to the strong affinity between CO_2 and commonly used adsorbents. The Moving Bed Temperature Swing Adsorption (MBTSA) process has been proposed for capturing specific gases within an adsorbent column. However, the impact of gas contaminants requires thorough analysis due to potential side effects on process efficiency. This research aims to investigate the CO_2 adsorption behavior using dynamic fixed bed experiments. Essential parameters such as bed porosity and the diameter of adsorbent particles were taken into account.

2. Methodology: materials and equipment

The adsorbent was a 13X zeolite sample (CAS: 63231-69-6, Shanghai Hengye Chemical Industry®, China). Gases were CO_2 (purity: 99.8%, White Martins Prx ®, Brazil), N_2 (purity: 99.999%, White Martins Prx ®, Brazil) and He (purity: 99.999%, White Martins Prx ®, Brazil). Static equilibrium measurements were conducted using a Magnetic Suspension Balance®, (Rubotherm, Germany). Dynamic experiments were performed

with mixSorb® (3P Instruments, Germany) which features in-situ sample regeneration and preparation. It includes four high-precision mass flow controllers — two with a range up to 1 mL min^{-1} and two with a range up to 10 mL min^{-1} — as well as the capability to measure inlet and outlet gas compositions (see simplified scheme in Figure 1). Additionally, the system is equipped with a built-in Thermal Conductivity Detector (TCD) and an interfaced mass spectrometer. The adsorbent average diameter was 0.5075 mm, and the column dimensions are: diameter (6.35 mm) and heigh (40.0 mm).

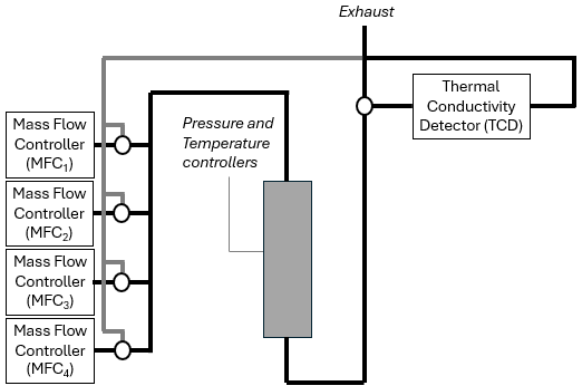

Figure 1. Mixsorb simplified scheme.

Prior to the experiments, the adsorbent was pretreated at 573 K for 10 hours (heating rate: 1 K min^{-1}) under vacuum or inert gas flow. Adsorbent textural properties were determined using nitrogen isotherms at 77 K and helium isotherms at 298 K. In the case of breakthrough curves, the chosen gas was fed through the bed at an average flow rate of 10 mL min^{-1} and temperatures ranging from 323 to 363 K. The stoichiometric times for a specific experiment were determined by integrating the relative concentration (C/C_o) over time (Eq. 1).

$$t_{st} = \int_0^{te} \left(1 - \frac{C_i}{C_{io}}\right) dt \qquad \text{Eq. 1}$$

where, t_{st} is the stoichiometric time; t_e is the equilibrium time; C_i is the actual concentration and C_{io} is the feed concentration. Additionally, adsorption capacity data from fixed bed experiments must account for the gas molecules that are not adsorbed but are simply compressed into the void spaces of the column. Thus, the total porosity of the bed (Eq. 2), plays a crucial role and is determined by the sum of particle porosity (Eq. 3) and bed porosity (Eq. 4).

$$\varepsilon_t = \varepsilon_b + (1 - \varepsilon_b) \cdot \varepsilon_p \qquad \text{Eq. 2}$$

$$\varepsilon_p = 1 - \frac{V_s}{V_s + V_p} \qquad \text{Eq. 3}$$

$$\varepsilon_b = 1 - \rho_{pck} \cdot (V_s + V_p) \qquad \text{Eq. 4}$$

where, ε_t is the total porosity; ε_b is the bed porosity; ε_p is the particle porosity; V_s is the solid volume; V_p is the pore volume and ρ_{pck} is the packing density.

3. Results

3.1. Fixed-bed adsorption column

Some information of the fixed-bed adsorption column used in the dynamic experiments is detailed in Table 1.

Table 1. Bed porosities.

ε_t	ε_b	ε_p
0.70	0.53	0.35

3.2. Mono-components isotherms

Equilibrium adsorption isotherms for CO_2 at three different temperatures (323 K, 343 K, and 363 K) up to 1 bar, measured in the Magnetic suspension balance, are shown in Figure 2. The 13X zeolite sample showed strong adsorbent-adsorbate interactions for CO_2, mainly in the low-pressure region (up to 0.2 bar). The experimental data were fitted using the Langmuir equation (Eq. 5), where q_{max} and b are the fitting parameters, as shown in

Table 2. It may also be noted that the isotherms displayed a Type 1 adsorption behavior [6].

$$q_{eq} = \frac{q_{max} \cdot b \cdot P}{1 + b \cdot P} \qquad \text{Eq. 5}$$

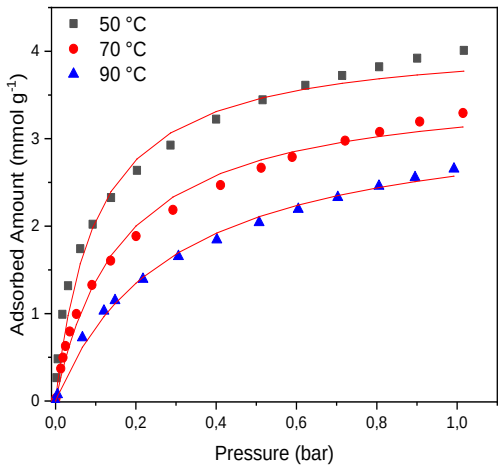

Figure 2. Equilibrium experimental data for CO_2 on the 13X zeolite sample at 323, 343 and 363 K. Lines represent the Langmuir fitting.

Table 2. Langmuir parameters for CO_2 equilibrium on the 13X zeolite sample.

	323 K	343 K	363 K
q_{max} [mmol g^{-1}]	4.147	3.642	3.338
b [bar^{-1}]	9.897	6.155	3.379

3.3. Breakthrough curves for pure CO_2

The breakthrough curves for pure CO_2, at three temperatures (323, 343, and 363 K), using flow rates of 2 mL min^{-1} of CO_2 and 8 mL min^{-1} of He, at NTP (partial pressure = 0.2 bar), are shown in Figure 3. As already observed from the gravimetric static measurements, the adsorption capacities clearly decreased with increasing temperature. The CO_2 adsorbed amounts at 0.2 bar show similar values to those obtained from the equilibrium static measurements (see Table 3).

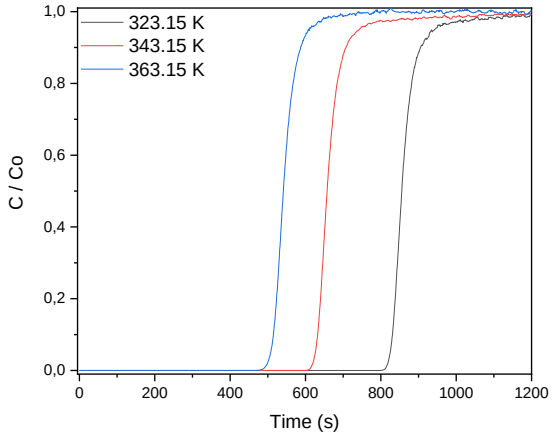

Figure 3. Breakthrough curves for CO_2 on zeolite 13X at 323, 343 and 363 K.

Table 3. Carbon dioxide adsorbed amounts @ 0.2 bar [mmol g^{-1}].

	323 K	343 K	363 K
gravimetry	2.64	2.00	1.35
bkt curves	2.69	2.11	1.71

4. Conclusion

Static and dynamic adsorption experiments were performed for CO_2 adsorption in a 13X zeolite sample, showing its effective adsorptive capacity for CO_2 gas capture. Further dynamic measurements with other gases present in the post-combustion streams shall bring better understanding of the adsorption capture process in industrial scenarios.

Acknowledgements

The authors acknowledge financial support received from ENEVA (Rio de Janeiro, Brazil, Programa P&D ANEEL código PD-06981-0222/2022) and CNPq (Brasilia, Brazil). Technical and scientific collaboration with SATC (Criciuma, Brazil) is also gratefully acknowledged.

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