

CO₂ capture in fixed bed from pelletized 13X Zeolite

Tamille A. Souza^{a,b}, Geovana C.S. Ferreira^{a,b}, Rodrigo I.P. Vêras^a, Raildo A. Fiuza Jr^b,
Karen V. Pontes^a

^a Energy Laboratory (LEN), Federal University of Bahia (UFBA), Rua Professor Aristides Novis 02,40210-630 Salvador,BA,Brazil

^b Catalyst and materials laboratory -LABCAT,Federal University of Bahia (UFBA),Trav. Barão de Jeremoabo 147,40170-280,
Salvador,BA, Brazil

Abstract

Zeolites are commonly used as carbon dioxide adsorbents mainly because they have high selectivity do CO₂ due to the uniform pore distribution and the presence of charge compensating cations that interact more strongly with molecules of higher quadrupole moment. Zeolite 13X is the most studied for CO₂ capture, with most studies using the material in powder form, while studies with pellets are little explored. The objective of this work was to evaluate the breakthrough time and the adsorption capacity of CO₂ from 13X Zeolite in pellet form in a fixed bed, at different CO₂ concentrations. Scanning electron microscopy and textural analysis of the pellets were performed. The maximum value of CO₂ adsorption capacity was 1.32 mmol.g⁻¹ reached at a concentration of 50% CO₂. The results show that the breakthrough time reduces with the increase in CO₂ concentration, while the CO₂ adsorption capacity is directly proportional to the concentration.

Keywords: CO₂ capture; Fixed bed; Breakthrough curve; zeolite 13X

1. Introduction

Zeolites are microporous crystalline aluminosilicates. Its structure consists of an assemblage of SiO₄ and AlO₄ tetrahedra, joined together in regular arrangements through shared oxygen atoms, to form an open crystal lattice containing uniform pores of molecular dimensions [1].

The use of zeolites as carbon dioxide (CO₂) adsorbents occurs mainly because they present high selectivity to CO₂. This is attributed to the uniform pore distribution of these materials and the presence of charge-compensating cations that interact more strongly with molecules with a higher quadrupole moment. Thus, preferential adsorption of CO₂ can be satisfactorily applied in carbon dioxide capture processes in post-combustion process effluents or in natural gas beneficiation. [2].

Zeolite 13X is the most studied for CO₂ capture, with most studies using the material in powder form, while studies with pellets are little explored. However, the adsorbent in pellet form is more suitable for industrial application, especially in units that require reduced spaces. A recent article reports the CO₂ adsorption capacity of 2.97 mmol.g⁻¹ of zeolite 13X in pellet format [3]. Other articles have presented the same order of magnitude of CO₂ adsorption from pelletized zeolite 13X, of 2.47 mmol.g⁻¹ [4] and 2.49 mmol.g⁻¹ [5]. However, the

literature still presents few studies with zeolites in different formats of powder or granules.

In order to understand the adsorption kinetics of CO₂ in 13X zeolites in pellet format, the adsorbent breakthrough curves were developed. From the breakthrough curves, it was possible to obtain two parameters for investigating the extent of adsorption: the breakthrough time in minutes and the adsorption capacity of the adsorbent in terms of amount of CO₂ matter per mass of adsorbent (mmol g⁻¹). The objective of this work was to evaluate the breakthrough time and the adsorption capacity of CO₂ in pelletized 13X zeolite in a fixed bed, at different CO₂ concentrations.

2. Experimental

2.1 Adsorbent and characterization

The adsorbent used in the tests was the commercial 13X zeolite in pellet format provided by COPENE (Northeast Petrochemical Company), currently BRASKEM S.A. to the Catalysis and Materials Laboratory (LABCAT) of UFBA.

The micrographs were collected on Hitachi model S-3400N equipment at different magnifications. The most representative image of the sample was selected.

N₂ physisorption isotherms were obtained using a Micromeritics equipment (model ASAP 2020). The surface area measurement was calculated using

the nitrogen adsorption method developed by Brunauer, Emmett and Teller (BET), micropore area and micropore volume using the Dubinin-Astakhov (DA) method and the mean pore diameter using the Horvath-Kawazoe method.

2.2 CO₂ adsorption tests in fixed bed: breakthrough curves

The breakthrough curve tests were performed in a tubular reactor with 17.5 mm internal diameter. The gas flow was controlled by PID Eng&Tech flow meters and then analyzed at appropriate intervals and quantified in a Shimadzu GC17 gas chromatograph equipped with a Carboxen1010 capillary column. The procedures used for chromatographic analysis consisted of runs using nitrogen as carrier gas, TCD detector, including previous injections of standards under the same conditions.

The breakthrough curve tests were performed after pre-treatment of the adsorbent for 30 min at 350 °C in a nitrogen stream of 50 mL min⁻¹, to purge the adsorbent surface (removal of gases and moisture). After cooling the reactor to 35 ± 3 °C, the adsorption test was started by allowing the passage of a mixture containing 10% CO₂ and 90% N₂, then 30% CO₂ and 70% N₂, and finally 50% CO₂ and 50% N₂. The total flow of the reagents was 100 mL.min⁻¹ and the adsorbent mass (*W*) was 20 g.

The tests were conducted until the saturation of the adsorbent surface was reached, until the point at which the CO₂ concentration at the reactor outlet approached that of the inlet stream. To obtain the breakthrough curves, the ratio between the outlet and inlet concentration of the desired effluent (normalized concentration, *C/C*₀) was used as a variable, as a function of the reaction time. The breakthrough time (*t*_b) corresponds to the time in which the effluent outlet concentration reaches 5% of the bed inlet concentration [6,7]

The CO₂ adsorption capacity (*Q*) of the adsorbent at different concentrations was estimated from [8]:

$$Q = \frac{F \cdot C_0 \cdot t_q}{W} \quad (1)$$

where *F*, *C*₀ and *W* are the total flow rate (mL.min⁻¹), initial concentration (mmol.mL⁻¹) and weight of the adsorbent (g). The stoichiometric time (*t*_q) in minutes is calculated from [8]:

$$t_q = \int_0^{t_q} \left(1 - \frac{C}{C_0}\right) dt \quad (2)$$

3. Results and discussion

3.1. Adsorbent and characterization

Fig. 1 shows the micrograph of commercial zeolite 13X pellets. The pellets have a predominantly smooth surface with micro cavities, a diameter of 1.5 mm and an average length of 6.0 mm.

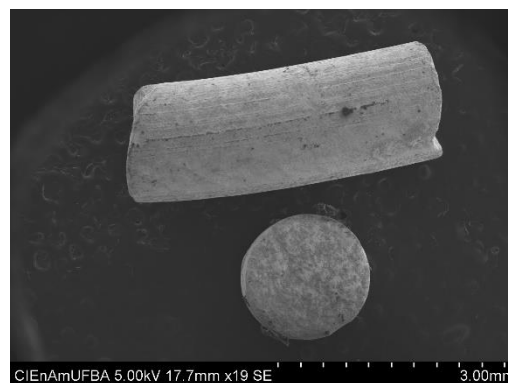


Fig. 1. Micrograph of pelletized 13X Zeolite

Fig. 2. shows the N₂ physisorption isotherm of zeolite 13X. The isotherm is classified as type I, typical of microporous materials. With increasing relative pressure, the isotherm acquires characteristics of type IV isotherm. Additionally, the hysteresis loop observed for the zeolite can be classified as type H1, which represents a narrow band of uniform mesopores. A marked adsorption of N₂ can be observed at low *P/P*₀ values, indicating high adsorption in micropores. Moreover, a very pronounced inflection point can be noted at low relative pressures, suggesting the formation of a monolayer and the complete filling of the micropores.

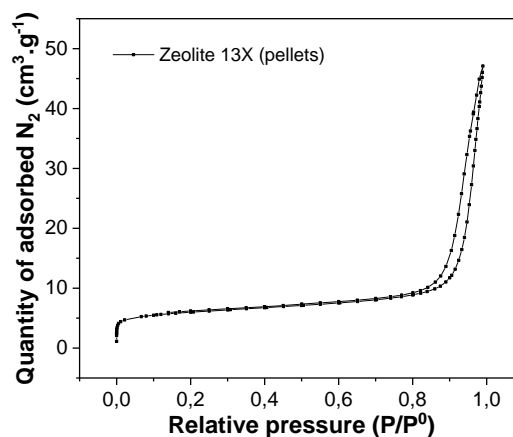


Fig. 2. N₂ physisorption isotherm of pelletized 13X zeolite

The textural properties of zeolite 13X are presented in Table 1. The commercial zeolite 13X of the present work presented low surface area (BET) compared to the commercial pelletized zeolites 13X observed in the literature, 802 m².g⁻¹ [6], 544 m².g⁻¹ [7]. This small surface area and especially the micropore area can reduce the CO₂ adsorption capacity.

Table 1. Textural properties of pelletized 13X Zeolite.

Textural properties	Zeolite 13X(pellets)
S _{BET} ^a (m ² .g ⁻¹)	21.17
S _{mic} ^b (m ² .g ⁻¹)	24.77
V _{micro} ^b (cm ³ .g ⁻¹)	0.0106
Dp ^c (nm)	0.72

^aS_{BET}, surface area calculated by BET

^bS_{mic}, surface area calculated by Dubinin-Astakhov method

^bV_{micro}, volume de microporos by Dubinin-Astakhov method

^cDp, mean pore diameter by Horvath-Kawazoe

3.2. CO₂ adsorption tests in fixed bed: breakthrough curves

Fig. 3. shows the results of the breakthrough curves (A) and the adsorption capacity (B) of CO₂ at different concentrations. The breakthrough time reduces as CO₂ concentration increases. Concentrations of 30 and 50% saturates at nearly the same time, around 10 minutes, while the breakthrough time for 10% CO₂ is 35 minutes. This indicates that the increase in CO₂ concentration leads to a faster saturation of the adsorptive bed. At low concentrations, there is less interaction between the adsorbate (CO₂) and the adsorbent (zeolite 13X), in addition to the greater incidence of diffusional effects in the bed, leading to a slower saturation of the adsorbent.

However, regarding the CO₂ adsorption capacity (Fig. 3-B), an increase in *Q* is observed with the increase in the concentration of the adsorbate in the stream. The trend curve of the CO₂ adsorption capacity continues to increase with the increase in concentration, indicating that the adsorbent may present a greater adsorption capacity at concentrations greater than 50% CO₂, until reaching a plateau; however, the increase in concentration also reduces the rupture time (bed saturation).

The maximum value of the CO₂ adsorption capacity was 1.32 mmol.g⁻¹, reached at the concentration of 50% CO₂. This result is consistent with the literature, despite the low surface area of the 13X zeolite in the present work, in which the CO₂ adsorption capacity of the 13X zeolite pellets

was between 2.4 and 3.0 mmol.g⁻¹, with a CO₂ concentration of 100% [3,4,5].

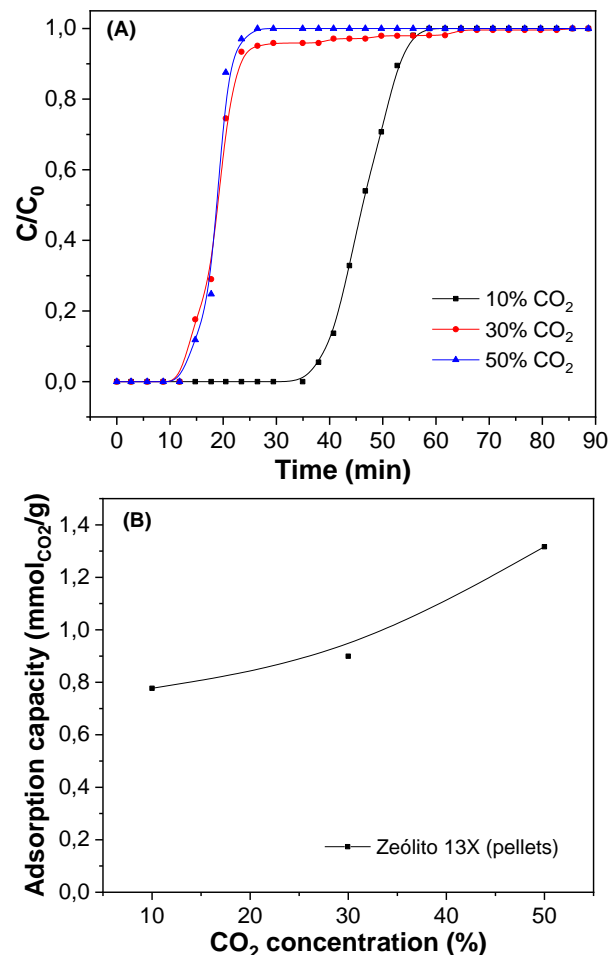


Fig 3. Breakthrough curves (A) and adsorption capacity (B) of CO₂ at different concentrations

5. Conclusion

This work presented the breakthrough time and the CO₂ adsorption capacity of 13X zeolite pellets in a fixed bed, at different CO₂ concentrations. The results show that the breakthrough time reduces with the increase in CO₂ concentration, while the CO₂ adsorption capacity is directly proportional to the adsorbate concentration.

6. References

- [1] KHALEQUE, A.; ALAM, M.M.; HOQUE, M.; MONDAL, S.; HAIDER, J.B.; XU, B.; JOHIR, M.A.H.; KARMAKAR, A.K.; ZHOU, J.L.; AHMED, M.B.; MONI, M.A. Zeolite synthesis from low-cost materials and environmental applications: A review. *Environmental Advances* 2, 2020
- [2] DA SILVA, JEFFERSON SANTOS. *Aproveitamento do catalisador de equilíbrio de*

- uma planta de refino de petróleo (fcc) na captura de co₂.** Tese apresentada ao Instituto de Química da Universidade Federal da Bahia como parte dos requisitos para obtenção do título de doutor em Química. Salvador, 2017.
- [3] CIORA, R.J.; SENGUPTA, B.; WANG, F.; LI, SHIGUANG.; YU, M. Direct modification of pelletized 13X zeolite by atomic layer deposition toward effective CO₂ capture from flue gas. **Chemical engineering journal**, 2024.
- [4] CHOUDHARY, V. R.; MAYADEVI, S.; SINGH, A. P. Sorption isotherms of methane, ethane, ethene and carbon dioxide on NaX, NaY and Na-mordenite zeolites. *Journal of the Chemical Society, Faraday Transactions*, 1995.
- [5] CAVENATI, S.; GRANDE, C.A.; RODRIGUES, A.E. Adsorption Equilibrium of Methane, Carbon Dioxide, and Nitrogen on Zeolite 13X at High Pressures. **Journal of Chemical & Engineering Data**, 2004.
- [6] SRIVASTAVA, V. C.; MALL, I. D.; MISHRA, I. M. Adsorption thermodynamics and isosteric heat of adsorption of toxic metal ions onto bagasse fly ash (BFA) and rice husk ash (RHA). **Chemi. Eng. J.**, 2007
- [7] GOEL, C., BHUNIA, H., BAJPAI, P. K. Mesoporous carbon adsorbents from melamine-formaldehyde resin using nanocasting technique for CO₂ adsorption. **J. Env. Sci.**, v. 32, 2015.
- [8] TOURZANI, A.A.; HORMOZI, F.; ASADOLLAHZADEH2, M.; TORKAMAN, R. Effective CO₂ capture by using poly (acrylonitrile) nanofibers based on the radiation grafting procedure in fixed-bed adsorption column. **Scientific Reports**, 2023.
- [9] SHIGAKI,N.; MOGI, Y.; HARAOKA, T.; FURUYA, E. Measurements and calculations of the equilibrium adsorption amounts of CO₂-N₂, CO-N₂, and CO₂-CO mixed gases on 13X zeolite. **SN Applied Sciences**, 2020.
- [10] LIMA, Y.S.; GUIMARÃES, P.R.B.; CARVALHO, L.S.; FAGUNDES, R.C.; SILVA, A.G.; LISBOA, D.O. Estudo da capacidade de adsorção de CO₂ em zeólita 13x para a separação de gases industriais. **4o PDPETRO**, Campinas, SP, 2007.