

LTA zeolite shaped with bentonite for CO₂ storage: characterization and performance studies

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Abstract

Climate change has worsened due to increased CO₂ emissions. Technologies to mitigate this, such as CO₂ capture using porous solids like zeolites, are promising, with efficiency depending on the adsorbent's properties. This work studies the properties of LTA pellets, comparing them to their commercial powder and shaping forms. It examines mechanical properties (rupture resistance), thermal properties (thermogravimetric analyses - TG/DTG), and textural properties (CO₂ isotherms at 0 °C under low pressures). Additionally, it evaluates adsorption capacity under post-combustion conditions (CO₂ isotherms at 25, 50, and 70 °C up to 5 bar). Compressive strength tests revealed that the increase in the percentage of bentonite did not result in a proportional increase in mechanical resistance. The TGA/DTG analyses show that the LTABEN20 pellet improves the thermal stability of the LTAc_{powder} sample. However, in CO₂ adsorption studies simulating a post-combustion scenario (high pressures and temperatures), the pellet studied presented adsorption capacity similar to the commercial LTA pellet. Thus, this study highlights the potential of LTA zeolite and bentonite composites for effective CO₂ capture and storage.

Keywords: CO₂ adsorption; LTA zeolite; Bentonite; Shaping; Storage.

1. Introduction

In recent decades, climate change has intensified due to rising greenhouse gases, particularly CO₂, contributing to global warming, rising sea levels, and melting polar ice caps. To face these challenges, technologies like CO₂ capture via adsorption in porous solids such as zeolites have been developed. The efficiency of this method depends on the adsorbent's properties, including high adsorption capacity, CO₂ selectivity, fast kinetics, low cost, and stability [1, 2].

This study focuses on investigating the thermal and mechanical stability of LTA zeolite pellets with bentonite for effective CO₂ capture and storage in post-combustion scenarios.

2. Materials and Methods

2.1. Materials

A commercial zeolite powder Linde-type A (LTAc powder, Sigma Aldrich) was used as an

active precursor phase for the shaped adsorbent samples. In order to shape the zeolite powder into pellets, the inorganic clay bentonite (BEN), supplied by T-Minas LTDA (Brazil), was used as a binder. A commercial LTA zeolite pellets (LTAc pellet, molecular sieves, 4 Å, 1.6 mm in diameter, Sigma-Aldrich) were tested only to compare with self-manufactured pellets.

2.2 LTA zeolite shaping

Three different pellet compositions were formulated using LTAc powder with 10, 20 and 25 wt% of bentonite. The samples were labeled as LTABEN10, LTABEN20, and LTABEN25, respectively. Pure bentonite pellets (BEN pellet) were also produced and tested.

For each shaping procedure, first, LTAc powder and bentonite were mixed evenly at room temperature. Distilled water was added dropwise and each mixture was kneaded until obtain a slurry with sufficient plasticity for extrusion. A cylindrical extruder (Multi Lab extruder, Caleva Process Solutions), with a 2 mm diameter matrix, was used.

The pellets formed were dried naturally for 2 h. These were then dried in an oven at 100 °C for 48 h and calcined in a muffle furnace at 400 °C for 24 h to gain permanent shape and resistance.

2.3 Characterization techniques

The shaped samples were characterized for their mechanical resistance using a Durometer HDP-20CP equipment (DUROControl®). This equipment measures the force applied to the cross section of the sample until its first rupture (maximum value). The methodology used for this test was based on the ASTM D6175 standard [3]. Around 15 tests were carried out for each type of sample.

In order to study the thermal stability of the shaped samples, thermogravimetric analyses (TG and DTG) were carried out. For this study, a Skimmer™ QMS STA 309 CD/403/5/G equipment (Netzsch) was used. Samples of approximately 20 mg were heated up to 800 °C in a nitrogen atmosphere at a flow rate of 20 mL.min⁻¹ and a heating rate of 10 °C.min⁻¹.

2.4 CO₂ isotherms

To evaluate adsorption capacity of the shaped materials at higher temperatures and pressures (post combustion scenario), adsorption isotherms of CO₂ were measured in a magnetic suspension balance (Rubotherm, Germany) for the temperatures of 25, 50 and 70 °C and pressure range of 0 – 5 bar. Before each analysis, the sample was degassed at vacuum (10⁻³ bar) and 300 °C for 12 h to remove any previously adsorbed species. The outgassed samples were exposed to stepwise increases of the pure gas pressure at constant temperature. The change in weight of the samples after each pressure step was measured continuously until equilibrium was reached [4].

The Sips model was used to fit the experimental data for CO₂, as shown in Eq. 1. This model is an extension of the Langmuir model in which it is assumed that the adsorbent surface is heterogeneous or that the adsorbent-adsorbate system has adsorption sites of different types.

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

Where q is the quantity of gas adsorbed at a T and P fixed, q_m is the maximum adsorbed, b is the adsorbate-adsorbent affinity parameter, and n is the heterogeneity parameter.

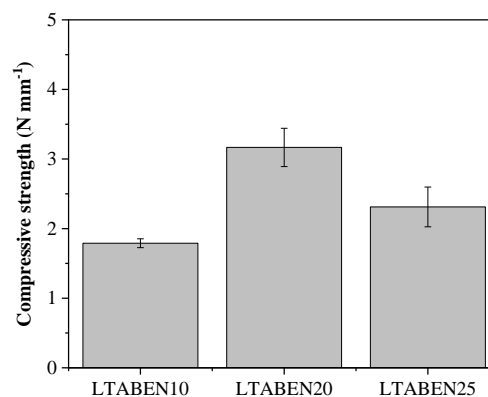
The adsorption equilibrium was modeled using Sips isotherms. Model parameters were calculated using the Solver Add-in in Microsoft Excel through non-linear regression.

3. Results

3.1. Mechanical resistance

Compressive strength tests (Fig. 1) showed that increasing bentonite percentage did not proportionally increase mechanical strength. Although bentonite is expected to act as a binder, its efficiency may be limited due to the formation of undesired fractures and heterogeneity in the matrix [5].

Fig. 1. Compressive strength of shaped samples.



The increase in the percentage of bentonite from 10% wt (LTABEN10) to 20% wt (LTABEN20) results in a significant increase in compressive strength. However, when the bentonite percentage is increased to 25% wt (LTABEN25), the compressive strength decreases. This suggests that excessive amounts of bentonite may introduce heterogeneities into the matrix, leading to the formation of undesirable fractures. Additionally, the chemical interaction between bentonite and zeolite can be optimized, resulting in stronger bonds, as suggested by the results of LTABEN20. The best composition, based on the information provided, is the one that contains 20% wt bentonite, making LTABEN20 the chosen sample for further analyses compared to commercial LTA and bentonite samples.

3.2. Thermogravimetric analyses

Analyzing Fig. 2, it can be observed that all samples show a significant mass loss (0.9 – 15%) when heated from 25 °C to approximately 200 °C.

This generally indicates the loss of weakly adsorbed external water, while losses at higher temperatures are related to more strongly adsorbed molecules. After 200 °C, all samples remain relatively stable in terms of mass, suggesting that the main mass loss occurs before this temperature. This is crucial for applications that require thermal stability up to 300 °C, such as in the regeneration of zeolites for CO₂ capture. In addition, according to Moreno *et al.* (2024) [6], between 300 and 400 °C, it is common for compensation cations in zeolites to begin to destabilize or displace within the zeolite structure, which can affect the stability of the crystal lattice.

Fig 2. Thermogravimetric analyses: TG (continuous line) and DTG (dotted line).

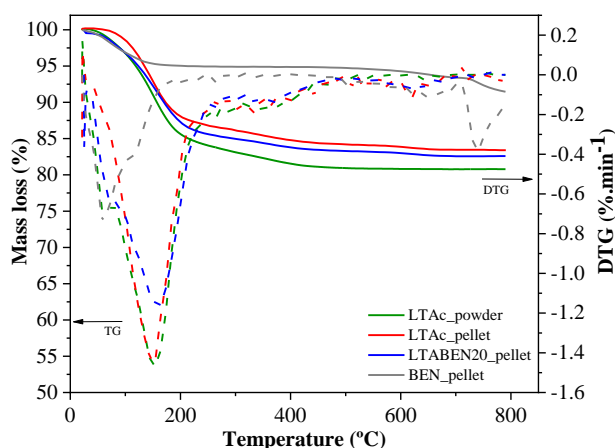


Table 1 presents the percent mass loss in each temperature range. Thus, the results show that the addition of 20% wt bentonite improves the thermal stability of LTA compared to the powder LTA samples (100 – 300 °C). This indicates that LTABEN20 is a viable choice for applications requiring thermal resistance, such as in the regeneration of adsorbents used for CO₂ capture, which involve temperatures up to 300 °C.

Table 1. Mass loss of the samples.

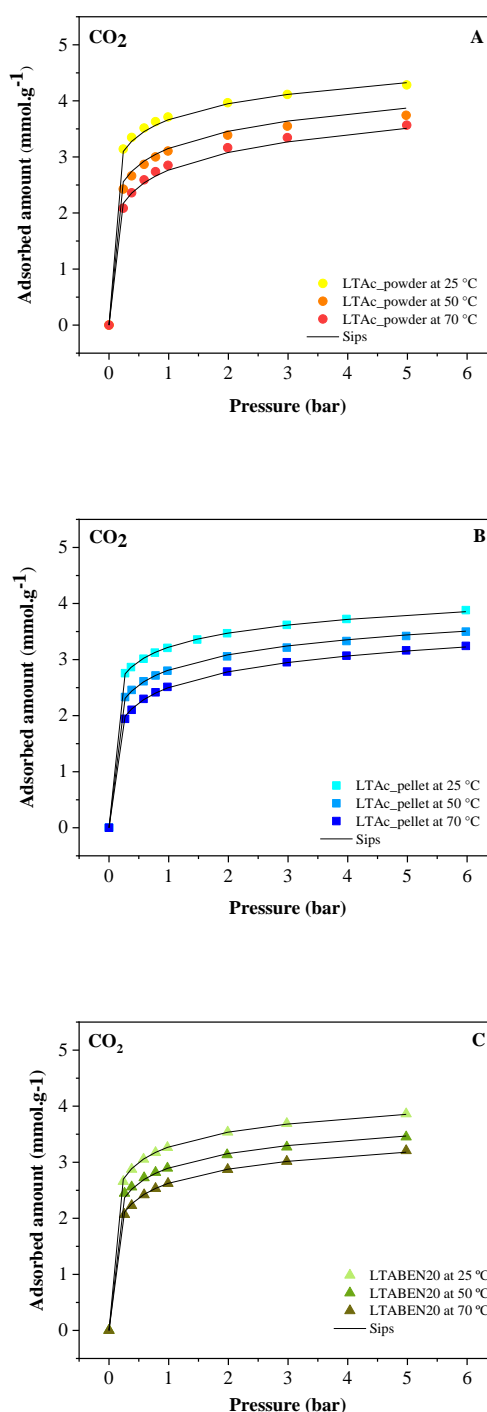
Shaped samples	Mass loss (%)		
	≤100 °C	100 – 300 °C	≥300 °C
LTAc_powder	2.63	16.76	19.03
LTAc_pellet	0.96	13.74	15.73
LTABEN20	2.67	14.96	16.66
BEN_pellet	2.81	5.09	5.22

3.3. CO₂ isotherms

This CO₂ adsorption isotherm test was carried out to compare the adsorption capacities of adsorbents under pressure and temperature

conditions close to the post combustion scenario. So, as shown in Fig. 3 and expected for a mechanism of physical adsorption, the capacity decreases with increasing temperature.

Fig. 3. CO₂ adsorption isotherms at 25, 50, and 70 °C. Fits to Sips model are also plotted.



It can be observed that samples shaped into pellets, LTAc_pellet and LTABEN20 present in the Fig. 3B and 3C, respectively, present similar CO₂ adsorption capacities, lower than that of LTAc_powder (Fig. 3A), at each temperature.

Additionally, the Sips model shows good agreement with experimental data for CO₂ adsorption. Table 2 shows the fitting parameters of the models used for the fit of the equilibrium data.

Table 2. Sips model parameters for CO₂ adsorption based on Eq. 1.

Adsorbent	T (°C)	q_m (mmol.g ⁻¹)	b (bar ⁻¹)	n	Error
LTAc powder	25	8.16	0.36	4.96	0.019
	50	7.89	0.17	4.35	0.060
	70	7.69	0.10	4.00	0.041
LTAc pellet	25	6.05	1.72	4.15	0.001
	50	5.77	0.83	3.68	0.003
	70	5.56	0.51	3.41	0.004
LTABEN20	25	5.32	4.59	3.23	0.002
	50	4.79	3.60	2.99	0.010
	70	4.40	3.04	2.85	0.004

The q_m data presented in Table 2 confirm the reduction in the maximum adsorbed quantity for the shaped samples. The adsorbent/adsorbate ratio (parameter b) presents higher values for the LTABEN20 sample, which is an advantage from the point of view of the use of LTA shaped with bentonite in the CO₂ capture and storage process, as it indicates a greater affinity between them. The heterogeneity parameter (n) decreases visibly with the presence of binder, this effect being more pronounced in LTABEN20, suggesting that the surface becomes more homogeneous when shaped.

4. Conclusions

The results indicate that the combination of LTA with bentonite can be a viable strategy to improve the thermal and mechanical stability of adsorbents in industrial applications. However, it is necessary to evaluate its composition to minimize the impacts of the binder on the adsorptive capacity of the pelletized adsorbent.

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