

Kinetics of CO₂ adsorption by temperature swing adsorption on KOH-impregnated activated carbon in powder and pellets

Lourdes Oliveira Galvão^{1,2}, Vanessa de Jesus Silva², Yanier Sánchez Hechavarria², Artur José Santos Mascarenhas^{1,2*}, Rildo Alves Fiuza Junior^{1,2}, Karen Valverde Pontes^{1,2,3}, Silvio Alexandre Beisl Vieira Melo^{1,2,3}

¹Programa de Pós-Graduação em Energia e Ambiente (PGENAM), Escola Politécnica, Universidade Federal da Bahia, R. Prof Aristides Novis, 2, Federação, 40120-910, Salvador-BA.

²Laboratório de Catálise e Materiais – LABCAT, Departamento de Química Geral e Inorgânica, Instituto de Química, Universidade Federal da Bahia, Travessa Barão de Jeremoabo, 147, Campus Ondina, 40170-280, Salvador – BA.

³Laboratório de Captura de CO₂ – LABCO2, CIENAM, Campus de Ondina, Universidade Federal da Bahia, Salvador-BA, 40170-115, Brasil.

*E-mail: artur@ufba.br

Resumo/Abstract

RESUMO - Neste trabalho, foi realizado um estudo preliminar sobre o desempenho de adsorção de CO₂ para carvões ativados com KOH na forma de pellet e pó. As morfologias dos materiais foram avaliadas por microscopia eletrônica de varredura. As propriedades texturais foram obtidas por fississorção de nitrogênio, numa faixa de pressão de $P/P_0 = 10^{-6} - 1,0$. Estudos de adsorção por modulação de temperatura foram realizados por termogravimetria dos adsorventes. A capacidade de adsorção de CO₂ obtida a 30°C, foi de 85,88 mg g⁻¹ para o carvão ativado de semente de cajá com KOH em uma razão de massa 1:1 e 57,77 mg g⁻¹ para o pellet, evidenciando uma maior capacidade de adsorção do adsorvente na forma de pó, o que pode estar relacionado com as propriedades texturais dos adsorventes. A cinética de adsorção investigada mostrou correlações mais precisas com o modelo de pseudo-primeira ordem para o carvão ativado tanto na forma de pó quanto em pellets ($r^2 = 0,9578$ e $0,9510$, respectivamente). Estudos de adsorção ciclica foram realizados e a captura de CO₂ se manteve estável após 5 ciclos de adsorção.

Palavras-chave: captura de CO₂, TSA, cinética, carvão ativado.

ABSTRACT- In this work, a preliminary study was conducted on the CO₂ adsorption performance of KOH-activated carbons in pellet and powder form. The morphologies of the materials were evaluated by scanning electron microscopy. The textural properties were obtained by nitrogen physisorption in a pressure range of $P/P_0 = 10^{-6} - 1.0$. Temperature-programmed adsorption studies were performed by thermogravimetry of the adsorbents. The CO₂ adsorption capacity obtained at 30°C was 85.88 mg g⁻¹ for biochar from yellow mombin seed activated with KOH in a mass ratio of 1:1 and 57.77 mg g⁻¹ for the pellet, hence the powder form resulted in a higher adsorption capacity, which may be related to the textural properties of the adsorbents. The adsorption kinetics were investigated and showed more precise correlations with the pseudo-first-order model for the activated carbon, both in powder and pellet forms ($r^2 = 0.9578$ and 0.9510 , respectively). Cyclic adsorption studies were performed, and CO₂ capture remained stable after 5 adsorption cycles.

Keywords: CO₂ capture, TSA, adsorption kinetics, activated carbon.

Introduction

The high atmospheric concentration of greenhouse gases, particularly carbon dioxide (CO₂), associated with using fossil fuels and their impacts on climate change have become a global concern in recent years. In this sense, various existing CO₂ adsorption technologies have been improved, and new technologies are being tested to contribute to the advancement of greenhouse gas mitigation.

Fossil fuels will continue to be a predominant energy source. However, studies aimed at reducing CO₂ emissions

are indispensable. In this context, carbon capture and storage (CCS) is one of the most promising solutions (1).

Cyclic adsorption processes such as Pressure Swing Adsorption (PSA), Vacuum Swing Adsorption (VSA), and Temperature Swing Adsorption (TSA) have been studied over the years for CO₂ capture. Recent studies have sought to improve Electrical Swing Adsorption (ESA) processes. This technology is a potential next-generation adsorption process (1,2).

TSA is an important and effective method to reduce carbon dioxide emissions and achieve carbon neutrality.

However, the application of TSA to CO₂ capture is in its initial stages (3). The first reason for the lag in developing TSA processes for CO₂ capture is the need for large volumes of direct hot non-adsorbing purge gas to regenerate the bed, which leads to dilution in the recovered CO₂. The second reason is that conventional TSA cycles need long heating/cooling steps that lower the productivity for a given bed volume (2-4).

TSA processes offer an additional advantage over PSA/VSA. Firstly, the large flue gas released near ambient pressure does not need pressurization (5). Secondly, waste heat can supply the energy required for the temperature swing (6).

Although powdered adsorbents have been successfully applied in diverse CO₂ adsorption methods, industrial-scale gas separation commonly favors adsorbents in forms like spheres, pellets, granules, or monoliths (5). Extrusion is a significant technique for shaping materials (7). It entails blending powdered adsorbents with inorganic and organic additives to produce a consistent suspension or paste, then passing it through a shaped die. Subsequent drying and thermal processing remove some additives, producing a mechanically stable final product.

One of the important parameters that must be evaluated is the regeneration of the adsorbent, as this is a fundamental step in the adsorption/desorption process since it largely determines its energy costs and efficiency (1-3). Multiple reuses of the adsorbent material increase the efficiency of the entire process and, therefore, its industrial viability.

The main objective of this work was to preliminarily evaluate the CO₂ adsorption performance of activated carbons derived from yellow mombin seeds, in both pellet and powder forms, using the thermogravimetric technique to simulate TSA conditions.

Experimental

Synthesis of the adsorbents

To produce activated carbon in powder form, yellow mombin seeds were collected, washed, and dried for three days at 100°C and ground in a knife mill. Subsequently, the biomass was sieved using a 100-mesh sieve. The biomass was pyrolyzed at 400°C in an inert atmosphere with a nitrogen flow rate of 150 mL min⁻¹ and a heating rate of 10 °C min⁻¹ and then impregnated with KOH in an aqueous solution at a mass ratio of 1:1. Following this, the impregnated material was pyrolyzed at 750°C in an inert atmosphere with a nitrogen flow rate of 150 mL·min⁻¹ and a heating rate of 10 °C min⁻¹. Finally, the activated carbon was washed with distilled water until the pH was approximately 7.0 and dried in an oven at 100°C for 24 hours.

After preparation, the activated carbon was pelletized using a Caleva Multi Lab (MLC) pelletizing extruder. A

mixture of isopropyl alcohol and carboxymethylcellulose was combined with the activated carbon in a mass proportion of 1:0,5:1 to produce an extrudable material. The yellow mombin seed powder activated carbon was identified by the acronym YMCOH1:1, and the pelletized form as pellet100%AC.

Characterization of the adsorbents

The adsorbents were characterized by powder X-ray diffraction (XRD) in a Shimadzu XRD6000, operating with CuK α radiation. The thermal stability was determined by thermogravimetric analysis (TGA) using Shimadzu equipment, DTG-60H. The morphology of the adsorbents was analyzed by scanning electron microscopy (SEM) using a Hitachi S-3400H. The textural properties, such as surface area, micropore volume, and pore size distribution, were evaluated by N₂ physisorption using an ASAP 2020 Micromeritics instrument. Before the analysis, the sample surface was degassed for 10 hours, obtaining the following parameters: surface area by the BET method and surface area by the NLDFT method.

CO₂ adsorption

Adsorption studies were carried out using a Shimadzu DTG-60H thermogravimetric analysis (TGA) instrument. Cyclic adsorption studies were carried out following these steps: (i) Drying the material at 200°C for 30 minutes under a nitrogen flow (100 mL min⁻¹) to remove moisture and adsorbed gases; (ii) The adsorbent was cooled to 30°C under a nitrogen flow (100 mL·min⁻¹); (iii) Then, a gas mixture of CO₂:N₂ in a 1:1 ratio was introduced with a total flow rate of 100 mL min⁻¹ for 30 minutes for adsorption. (iv) The gas was switched back to N₂ at a 100 mL min⁻¹ flow rate, and the sample was heated to 150°C for 15 minutes for desorption. To verify the stability of the pellet100%AC adsorbent, the adsorption/desorption procedure was repeated five times.

Adsorption kinetics

The adsorption kinetics was evaluated using pseudo-first-order and pseudo-second-order models. All fits were performed using nonlinearized equations, which are superior to linearized fits. The correlation coefficients (R²) agreed with the experimental data and the values calculated by the model.

Results and Discussion

Characterization of the adsorbents

The XRD patterns of the adsorbents are shown in Figure 1. As seen in the figure, the activated carbon derived from yellow mombin seeds in powder and pellet form exhibits an amorphous halo with broad peaks at 23.5° and 43.4° , corresponding to the (002) and (100) planes of amorphous graphitic carbon, indicating a material with an amorphous structure and disordered graphitic planes (6). Therefore, it can be concluded that the binder used in the preparation of pellets did not cause modifications in the carbon structure.

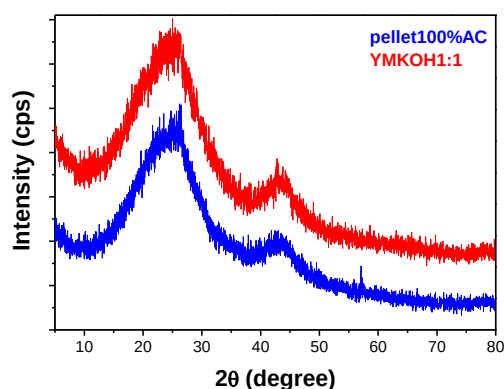


Figure 1. X-ray diffraction patterns of the adsorbents.

The micrographs of the adsorbents are shown in Figure 2. The adsorbents in powder and pellet forms exhibit a rough and porous surface, similar to that found in the original lignocellulosic biomass. However, it is possible to observe significant changes in the morphology of the pelletized sample when compared to the powder adsorbent.

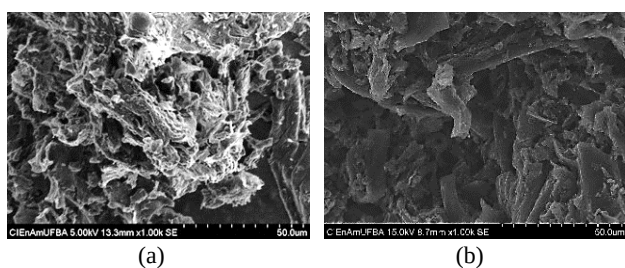


Figure 2. Scanning electron microscopy of the activated carbons: (a) YMKOH1:1; (b) pellet100%AC.

Figure 3 and Table 1 present the results of the adsorbents' textural analysis. Figure 3 shows the nitrogen (N_2) adsorption isotherms of the YMKOH1:1 carbon in powder form and the pellet100%AC. According to the IUPAC classification, the adsorbents exhibited a type I(a) adsorption isotherm, common in microporous materials, showing a type H4 hysteresis loop at $P/P_0 \approx 0.4$, typical of microporous materials with the presence of small mesopores (7).

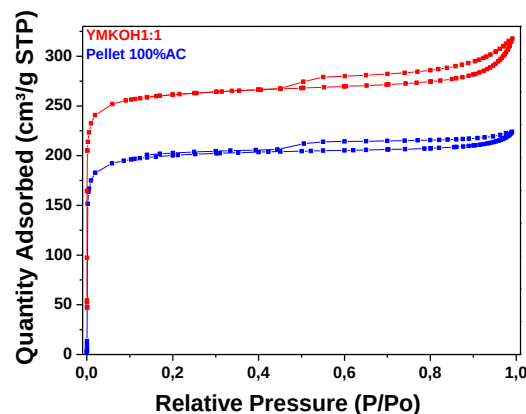
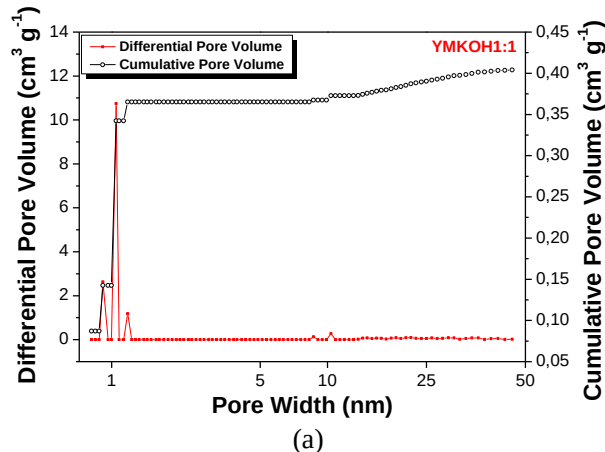
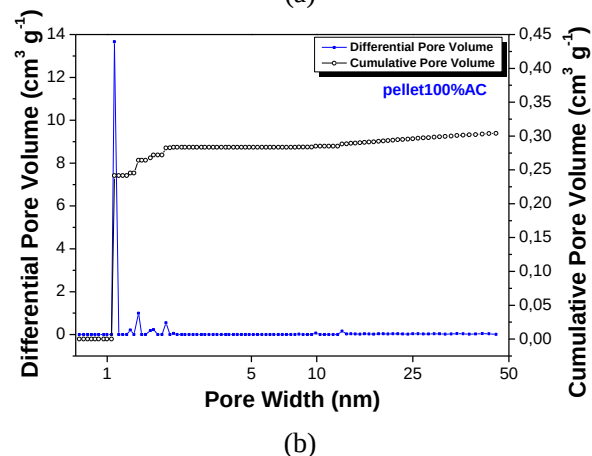


Figure 3. N_2 physisorption isotherms of the adsorbents.

The analysis of the pore size distribution by NLDFT, as shown in Figures 4(a) and (b), confirms that the adsorbent materials are essentially microporous, with insignificant mesoporosity contribution, indicating that the mesopores are secondary, i.e., formed by pilling of small adsorbent particles.



(a)



(b)

Figure 4. Pore size distribution of the adsorbents (a) YMKOH1:1 and (b) pellet100%AC.

Textural analysis presented in Table 1 indicates that the activated carbon YM KOH1:1 exhibits a micropore volume of $0.1424 \text{ cm}^3 \text{ g}^{-1}$ (0.7–1.0 nm) and $0.2226 \text{ cm}^3 \text{ g}^{-1}$ (1.0–1.5 nm), with a total volume of $0.3650 \text{ cm}^3 \text{ g}^{-1}$. On the other hand, the pellet100%AC displays a smaller total micropore volume ($0.2825 \text{ cm}^3 \text{ g}^{-1}$), distributed in the ranges of 1.0–1.5 nm ($0.2642 \text{ cm}^3 \text{ g}^{-1}$) and 1.5–2.0 nm ($0.0183 \text{ cm}^3 \text{ g}^{-1}$).

Table 1. Textural properties of the prepared adsorbents.

Textural properties	YM KOH1:1	pellet100%AC
S_{BET} ($\text{m}^2 \text{ g}^{-1}$)	924	708
S_{micro} ($\text{m}^2 \text{ g}^{-1}$)	1082	821
V_{micro} ($\text{cm}^3 \text{ g}^{-1}$)		
(0.7–1.0 nm)	0.1424	-
(1.0–1.5 nm)	0.2226	0.2642
(1.5–2.0 nm)	-	0.0183
V_{meso} ($\text{cm}^3 \text{ g}^{-1}$)	0.0389	0.0213
$V_{\text{total micro}}$ ($\text{cm}^3 \text{ g}^{-1}$)	0.3650	0.2825

^a S_{BET} , surface area calculated by the BET equation at $P/P_0 = 0.05–0.2$.

^b S_{micro} , micropore surface area calculated by the Dubinin-Astakhov method.

^c Distribution pore volumes calculated by NLDFT method assuming slit pore model.

Table 1 also reveals that the powdered activated carbon YM KOH1:1 exhibits higher BET surface area ($924 \text{ m}^2 \text{ g}^{-1}$) and micropore area ($1082 \text{ m}^2 \text{ g}^{-1}$) compared to the 100%ACpellet, which has a BET surface area of $708 \text{ m}^2 \text{ g}^{-1}$ and a micropore area of $821 \text{ m}^2 \text{ g}^{-1}$. This decrease in BET surface area, surface area, and microporosity can be attributed to the extrusion process, where carboxymethylcellulose was used as a binder in a proportion of 5%.

CO₂ adsorption by TG

The curves obtained in the study of the CO₂ adsorption-desorption capacities of the synthesized adsorbents are shown in Figure 5. In the adsorption process, the YM KOH1:1 activated carbon showed an adsorption capacity of around $9.5 \pm 0.05\%$, indicating that the concentration of narrow micropores in the 0.7–1.0 nm range ($0.1424 \text{ cm}^3 \text{ g}^{-1}$) was beneficial for CO₂ adsorption. The decrease in surface area and, fundamentally, in the total micropore volume influenced the lower adsorption capacity of pellet100%AC, as observed in Figures 5 and 6.

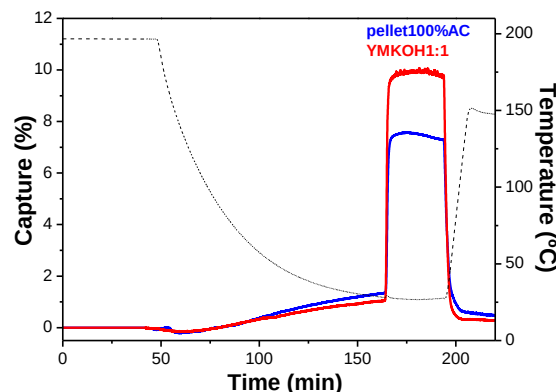


Figure 5. CO₂ adsorption-desorption curves of the synthesized adsorbents through TSA.

Figure 6 illustrates that the powdered activated carbon YM KOH1:1 possesses a significantly higher CO₂ adsorption capacity (85.88 mg g^{-1}) than the 100%ACpellet (57.77 mg g^{-1}). This lower capacity in the pellet may be related to the decrease in surface area and microporosity resulting from the extrusion process, where the material is compacted after incorporating the binding agent (8). Despite its lower adsorption capacity, the performance of the 100%ACpellet was evaluated in cyclic CO₂ capture at 30°C, aiming at its potential application in large-scale CO₂ capture processes that require pelletized activated carbon (8). Five CO₂ capture cycles were conducted (Figure 7) using TSA adsorption with a desorption temperature of 150 °C.

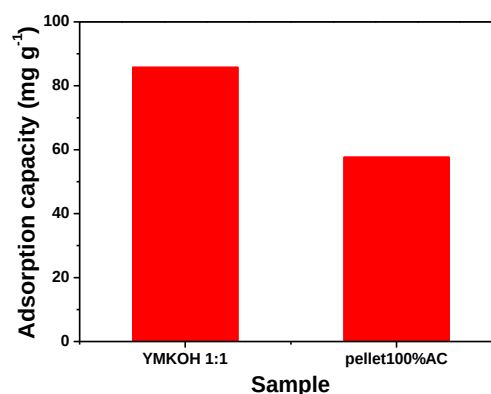


Figure 6. Adsorbent capacity through TSA for CO₂ capture.

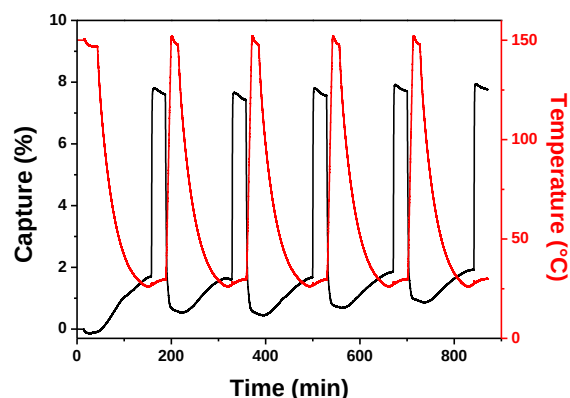


Figure 7. CO₂ adsorption cycles of pellet100%AC at a temperature of 30°C and a pressure of 1 bar.

The loss of adsorption capacity of the 100%ACpellet was only 0.56% after 5 CO₂ capture cycles (Figure 8). This suggests a stable adsorption capacity that can be successfully used for CO₂ adsorption at a low temperature and ambient pressure, highlighting its potential for large-scale applications.

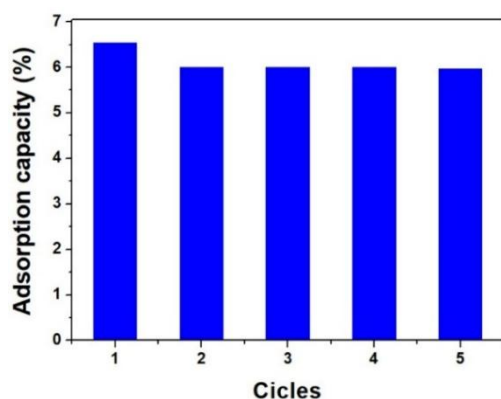


Figure 8. CO₂ adsorption capacity of pellet 100% AC obtained by TSA at a temperature of 30°C and a pressure of 1 bar.

Adsorption kinetics

The pseudo-first-order kinetic model is frequently used to study the gas-solid adsorption process, especially when it is controlled by diffusion on the surface. This model is effective in predicting the physisorption behavior of CO₂ between the adsorbent and the gas (8-10). On the other hand, the pseudo-second-order model assumes that the chemical reaction at the gas-solid interface is the rate-controlling step in the adsorption process and, therefore, is suitable for predicting the CO₂ adsorption behavior involving chemical interactions (9-10).

To identify the model that best fits the adsorption processes in this study, an evaluation was performed based on the correlation coefficient (R^2) of the pseudo-first-order (PFO) and pseudo-second-order (PSO) kinetic models.

Figure 9 displays the obtained data and correlations. The comparison of the correlation coefficients (R^2) for CO₂ adsorption at 30°C on the different adsorbents demonstrates a better fit of the pseudo-first-order (PFO) model for YM KOH1:1 and pellet100%AC (0.9578 and 0.9510, respectively) compared to the pseudo-second-order (PSO) model (0.8659 and 0.8315, respectively). This observation suggests that physisorption is the predominant mechanism in CO₂ adsorption by temperature variation in powdered activated carbon YM KOH1:1 and pelletized activated carbon pellet100%AC. According to the pseudo-first-order kinetic model, the adsorption rate is directly proportional to the concentration of unoccupied active sites on the adsorbent surface (9).

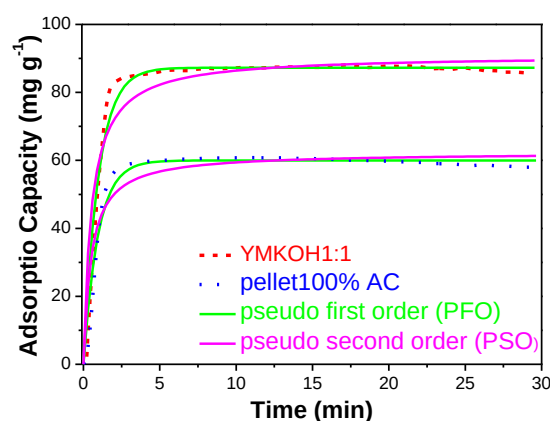


Figure 9. Non-linear kinetic fitting of the CO₂ adsorption curves of the adsorbents.

Conclusions

The powder and pellet adsorbents exhibited amorphous and disordered structures common in activated carbons. The adsorbents displayed a type I(a) adsorption isotherm, typical of microporous materials, showing a type H4 hysteresis loop at $P/P_0 \approx 0.4$, characteristic of microporous materials with small mesopores. The adsorbents are microporous, with a micropore volume of 0.1424 cm³ g⁻¹ (0.7-1.0 nm) and 0.2226 cm³ g⁻¹ (1.0-1.5 nm) for YM KOH1:1, and 0.2642 cm³ g⁻¹ (1.0-1.5 nm) and 0.0183 cm³ g⁻¹ (1.5-2.0 nm) for pellet100%AC.

The CO₂ adsorption of the YM KOH1:1 and pellet100%AC adsorbents reached 85.88 mg g⁻¹ and 57.77 mg g⁻¹, respectively, demonstrating that the powdered adsorbent has a higher adsorption capacity. This is related to the textural properties of the adsorbent, such as surface area and micropore volume. However, the use of solid materials in pellet form is more suitable than powder for large-scale processes due to low pressure drop and convenience in transportation and storage, which represents an advantage of the pellet100%AC when compared to

YMKOH1:1. The pseudo-first-order and pseudo-second-order models were used to examine the kinetics of CO₂ adsorption. The pseudo-first-order model provided the most accurate prediction of CO₂ adsorption for both adsorbents, indicating that the physisorption mechanism dominates the process.

The cyclic adsorption investigation of the adsorbent in pellet form showed that after five adsorption cycles, the adsorbent remained stable, which is promising for large-scale applications.

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