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

High-pressure adsorption of CO_2 and CH_4 on an impregnated activated carbon derived from cashew nut shell

Óscar Javier Fonseca-Bermúdez[a], Juliana A. Guimarães[b], Enrique Vilarrasa-Garcia[b], Moisés Bastos-Neto[b], Diana C. S. Azevedo[b], Liliana Giraldo[c], Rocío Sierra-Ramírez[a], Juan Carlos Moreno-Piraján[d]

[a] *Department of Chemical and Food Engineering, Universidad de Los Andes, Cra 1 Nº 18A – 12, 111711, Bogotá, Colombia*
[b] *Department of Chemical Engineering, Federal University of Ceará, 60440-900, Fortaleza, Brazil*
[c] *Department of Chemistry, Universidad Nacional de Colombia, Cra 30 N° 45 – 03, 111711, Bogotá, Colombia*
[d] *Department of Chemistry, SPCal,Universidad de Los Andes, Cra 1 Nº 18A – 12, 111711, Bogotá, Colombia*

Abstract

The depletion of global oil reserves and the escalating issue of climate change due to rising levels of greenhouse gases in the atmosphere have spurred the development of technologies to mitigate emissions of gases such as CO_2 and CH_4. In this study, three activated carbons derived from cashew nut shells were utilized to adsorb single-component gases. Equilibrium adsorption isotherms for CO_2 and CH_4 were measured at 25 °C over a pressure range of 0 to 10 bar. The adsorption equilibrium was modeled using Langmuir, Freundlich, Toth, and Sips isotherms. Model parameters were calculated using the Solver Add-in in Microsoft Excel through non-linear regression. The Sips isotherm model best described CO_2 adsorption, while the Toth isotherm model was most suitable for CH_4. The maximum adsorption capacities for CO_2 and CH_4 were 6.03 mmol/g and 3.98 mmol/g, respectively. The high-pressure adsorption capacity of these activated carbons, combined with their sustainable and eco-friendly nature, highlights their potential for greenhouse gas capture.

Keywords: biomass waste; chemical activation; activated carbon, CO_2 and CH_4 adsorption

1. Introduction

In recent years, the international community has seen a heightened awareness of climate change, promoting increased exploration of technologies aimed at mitigating emissions of greenhouse gases like CO_2 and CH_4. Despite the challenges posed by CO_2 emissions contributing to climate change and posing threats to human health, there is a pressing need for effective and acceptable solutions, even as green technology may seem ambitious.

In recent decades, there has been a concentrated effort to create novel solid materials with the objective of capturing harmful gases. Among these materials are diverse kinds of porous solids, chosen for their remarkable versatility and adaptability.

Activated carbons (AC), known for their porous nature and adsorption capabilities, play a significant role in CO_2 adsorption due to their textural characteristics, high surface area, tunable porosity, high degree of surface reactivity, good stability, and affordable low price for industrial applications [1,2]. Biomass residue or agricultural by-products represent potential sources of raw material for AC production [3].

The main goal of this study is to prepare microporous materials as potential sorbent for CO_2 and CH_4 high-pressure adsorption from the agricultural by-product cashew nut shell (CNS) using chemical activation with K_2CO_3. By examining the adsorption capabilities of AC under high-pressure conditions, this study contributes to the development of efficient and environmentally

friendly materials for gas separation and purification processes.

2. Methodology

2.1 Preparation of activated carbons

A lab-scale tubular reactor (Thermolyne 21100) was employed for the carbonization of CNS under inert conditions with a nitrogen (N_2) atmosphere and a heating rate of 5 °C/min until reaching a maximum temperature of 550 °C, maintained for three hours. This temperature was chosen based on prior experiments by Cruz-Reina *et al*. [4]. The resulting biochar was then impregnated with K_2CO_3 in a mass ratio of 1:1 (char: K_2CO_3). The dried impregnated biochar samples were subsequently heated at three different temperatures (800 °C, 850 °C, and 900 °C) for three hours under N_2 atmosphere (flow rate of 150 mL/min) using the previously described tubular reactor. The obtained ACs underwent multiple washing cycles until the pH of the washing water stabilized. Finally, the ACs were dried for 24 hours in a convection oven. The ACs are designated as MBKC80, MBKC85, and MBKC90, corresponding to their respective activation temperatures of 800 °C, 850 °C, and 900 °C.

2.2 Characterization

To determine the textural properties of the solids investigated in this study, N_2 adsorption-desorption isotherms were conducted at -196 °C. Approximately 0.1 grams of carbonaceous samples were subjected to degassing at 250 °C for several hours using a Micromeritics ASAP 2020 instrument. The Brunauer-Emmett-Teller (BET) method was employed to calculate the specific surface area. The volume of micropores was assessed using the Dubinin-Astakhov method, and the pore size distribution was calculated based on the Non-Local Density Functional Theory (NLDFT) model. Additionally, the pore size distribution (PSD) of micropores were obtained using carbon dioxide (CO_2, 99.99% pure) adsorption at 0 °C.

2.3 High-pressure adsorption isotherms

Single gas (CO_2 and CH_4) equilibrium adsorption isotherms were measured in a Magnetic Suspension Balance (MSB), by Rubotherm® (Bochum, Germany). The adsorbents were degassed in situ under vacuum (10^{-3} bar) at 300 °C, until no mass variation in the system was observed. After that, the measuring chamber was cooled down to the experiment temperature of 25 °C and the single gas pressure was increased stepwise until approximately 10 bar. Total mass uptake was measured and the application of equilibrium models allowed to calculate the uptake of each individual gas of the mixture.

3. Results

3.1 Textural properties

Fig. 1 presents the N_2 adsorption-desorption isotherms from the dataset, which display a distinctive Type I profile, indicative of the microporous nature of the investigated material. The textural properties are presented in Table 1.

Fig. 1. Nitrogen adsorption-desorption isotherms at -196 °C of activated carbons.

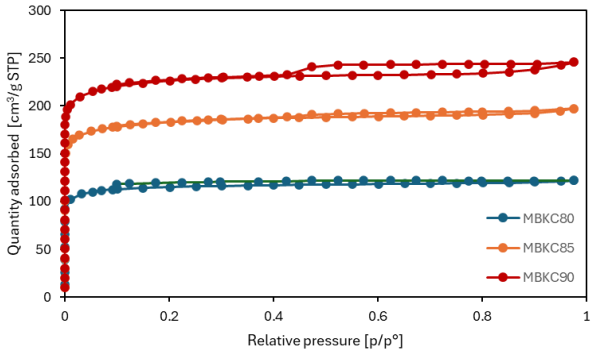
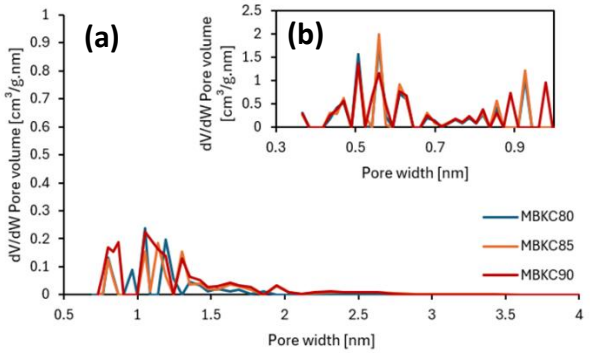


Table 1. Textural properties of the bioorganic prepared activated carbons.

Material	S_{BET} (m^2/g)	V_{total} (cm^3/g)	Pore size (nm)	V_{micro} (cm^3/g)
MBKC80	457	0.189	1.53	0.177
MBKC85	720	0.305	1.42	0.283
MBKC90	891	0.380	1.44	0.347

Fig. 2 illustrates the pore size distribution curves derived from Density Functional Theory (DFT) analysis for ACs obtained from CNS.

Fig. 2. Pore size distribution determined with the DFT method based on N_2 adsorption isotherm (a) and CO_2 adsorption isotherm (b).



3.2 High-pressure adsorption

Fig. 3-5 show a comparative analysis of the performance of activated carbon samples in terms of CO_2 adsorption isotherms.

Fig. 3. High pressure (0-10 bar) CO_2 isotherm at 25 °C for MBKC80.

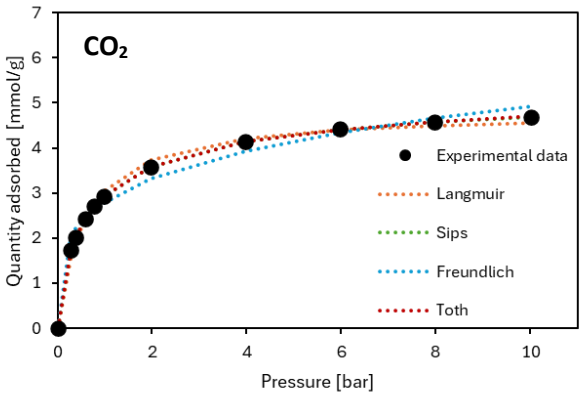


Fig. 4. High pressure (0-10 bar) CO_2 isotherm at 25 °C for MBKC85.

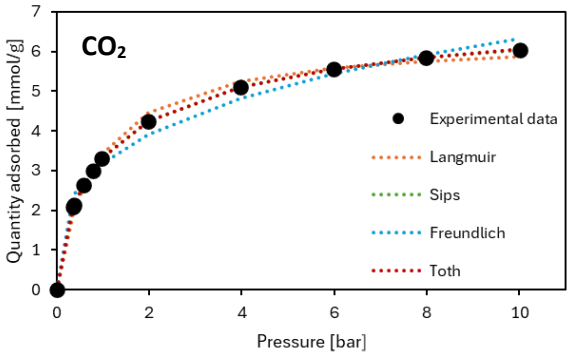


Fig. 5. High pressure (0-10 bar) CO_2 isotherm at 25 °C for MBKC90.

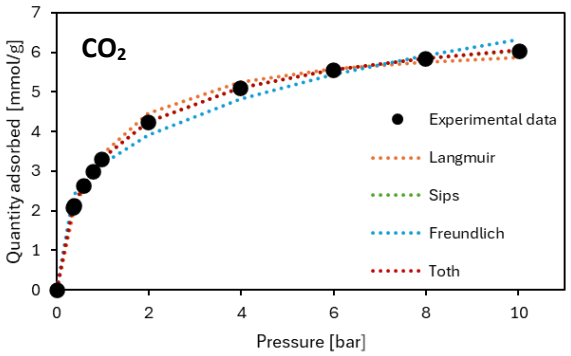


Fig. 6-8 show a comparative analysis of the performance of activated carbon samples in terms of CH_4 adsorption isotherms.

Fig. 6. High pressure (0-10 bar) CH_4 isotherm at 25 °C for MBKC80.

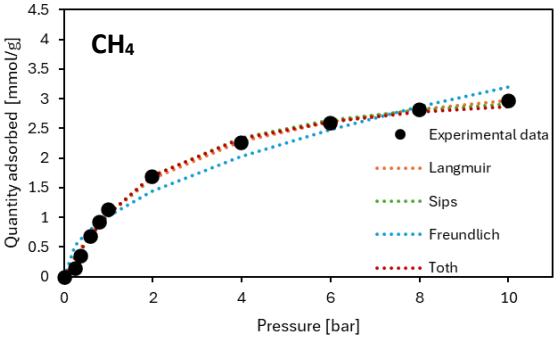


Fig. 7. High pressure (0-10 bar) CH_4 isotherm at 25 °C for MBKC85.

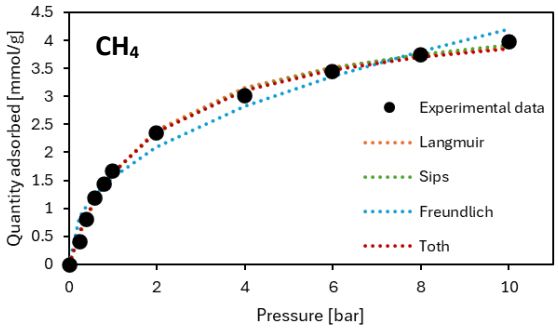
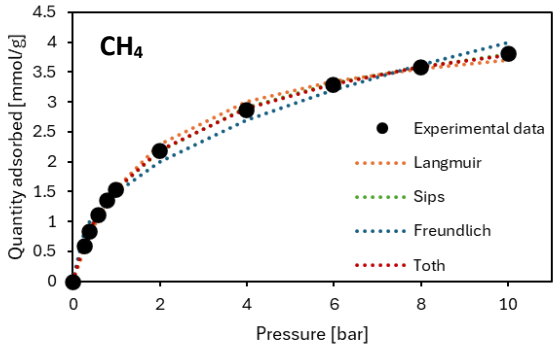


Fig. 8. High pressure (0-10 bar) CH_4 isotherm at 25 °C for MBKC90.



The materials exhibit a pronounced affinity for CO_2 adsorption. Specifically, MBKC85 and MBKC90 demonstrate higher CO_2 adsorption capacities at low and moderate pressures compared to MBKC80, attributable to their higher specific surface area. CO_2 adsorption in this pressure range is predominantly influenced by specific surface area and total available pore volume. Regarding CH_4, at low pressures, all materials under study adsorb comparable amounts; however, above 2 bar, MBKC85 and MBKC90 exhibit significantly enhanced CH_4 adsorption. This observation suggests that microporosity and surface chemistry are less critical factors, with total pore volume being the primary determinant of CH_4 adsorption.

4. Conclusions

In this study, the development and characterization of activated carbon derived from cashew nut shells using a K_2CO_3 two-step activation process is presented. Among the various samples obtained, the most efficient one, labeled as MBKC90, demonstrated qualities in terms of surface area and pore volume. Specifically, it exhibited a specific surface area of 891 m^2/g, along with total and micropore volumes of 0.380 cm^3/g and 0.347 cm^3/g respectively. Notably, ACs showcased a sorption capacity, particularly for CO_2. The CO_2 and CH_4 uptake were at 6.0 mmol/g and 4.0 mmol/g for the MBKC85, respectively, under a pressure of 10 bar at a temperature of 25 °C. The successful utilization of cashew nut shells, a widely available agricultural waste product, in producing ACs, is a significant step towards sustainable and eco-friendly material science. This approach not only adds value to what is typically considered waste but also offers a solution for gas sorption applications. The performance of the MBKC85 sample in terms of gas uptake and selectivity indicates its potential for practical applications in areas like gas storage.

Acknowledgements

This research was supported by Apoyo Financiero para Doctorados de la Universidad de Los Andes. Autours also thank to INCT CAPICUA (process n° 406710/2022-8, CNPq) and CAPES.

References

[1] J. Serafin, B. Dziejarski, J. Sreńscek-Nazzal, An innovative and environmentally friendly bioorganic synthesis of activated carbon based on olive stones and its potential application for CO_2 capture, Sustainable Materials and Technologies, 38 (2023) e00717.

[2] G. Singh, K.S. Lakhi, S. Sil, S.V. Bhosale, I. Kim, K. Albahily, A. Vinu, Biomass derived porous carbon for CO_2 capture, Carbon, 148 (2019) 164-186.

[3] A. Samsuri, F. Sadegh-Zadeh, B. Seh-Bardan, Characterization of biochars produced from oil palm and rice husks and their adsorption capacities for heavy metals, International Journal of environmental science and technology, 11 (2014) 967-976.

[4] L. J. Cruz-Reina, J. S. Flórez-Rojas, G. D. López, I. Herrera-Orozco, C. Carazzone, R. Sierra, Obtention of fatty acids and phenolic compounds from Colombian cashew (Anacardium occidentale) nut shells using pyrolysis: towards a sustainable biodiesel production, Heliyon, 9.8 (2023).