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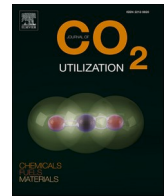
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Cashew nut shell biomass: A source for high-performance CO₂/CH₄ adsorption in activated carbon

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ABSTRACT

This study embarks on the synthesis of activated carbon (AC) from cashew nut shells using a potassium carbonate (K₂CO₃) activation process, with a specific focus on its practical application in high-pressure gas adsorption. Among the synthesized samples, MCAK85 emerged as the most efficient, demonstrating a specific surface area of 1693 m²/g and total and micropore volumes of 0.839 cm³/g and 0.641 cm³/g, respectively. Importantly, this bioorganic activated carbon exhibited high sorption capacities for CO₂ and CH₄, with uptake values of 11.0 mmol/g and 5.5 mmol/g at 10 bar at 25°C, and a CO₂/CH₄ selectivity range between 9.1 and 1.8. A comprehensive range of characterization techniques were employed to analyze the structural and chemical properties of the synthesized AC, providing valuable insights into the functional groups and molecular structure. The morphology of the AC was examined using SEM, while the point of zero charge was determined to understand the surface charge characteristics. Additionally, TGA was utilized to assess the thermal stability and composition of the AC. This study underscores the potential of utilizing agricultural waste, specifically cashew nut shells, in the creation of effective materials for gas storage and purification applications. The high-pressure adsorption capacity of the produced AC, coupled with its sustainable and eco-friendly nature, underscores its suitability for environmental and industrial applications, particularly in areas focusing on greenhouse gas capture and air purification, thereby inspiring further research and development in this field.

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 gasses like CO₂, CH₄, N₂O, and O₃. These gasses contribute significantly to atmospheric contamination and climate change. Especially the rapid surge in global CO₂/CH₄ emissions poses a significant and enduring threat to the

natural environment, standing out as the foremost contributor to adverse effects among greenhouse gases over several decades [1]. This persistent trend, a key driver of global warming and climate change, shows no signs of abatement. The substantial increase in atmospheric CH₄ and CO₂ levels, escalating at a rate of 0.17 % annually, can be primarily attributed to the Industrial Revolution. According to estimates by the National Oceanic and Atmospheric Administration [2], the atmosphere contained 421 parts per million (ppm) of CO₂ as of 2022. This

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represents a remarkable 50 % elevation compared to pre-industrial levels and an additional 13 % rise since the year 2000. Extensive research underscores that the upward trend in CO₂/CH₄ emission is predominantly a consequence of industrial activities, particularly the combustion of coal and petroleum [3–7]. Industries engaged in petroleum refining, cement production, steel and iron manufacturing, and power plant operations, operate intricate systems with complex processes and demands. These activities collectively exert a severe impact on the climate and temperature of the earth. Despite the challenges posed by CO₂ 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 the short term, one of the most feasible options to curtail CO₂ emissions is through capture and storage, a consensus supported by the Intergovernmental Panel on Climate Change (IPCC). The IPCC has set an ambitious goal of reducing CO₂ emissions by 50 % by 2050 [8,9].

In recent decades, there has been a concentrated effort to create novel solid materials with the objective of capturing deleterious gases. Among these materials are diverse forms of porous solids, chosen for their remarkable versatility and adaptability. Multiple technologies are available for capturing CO₂ emissions from combustion processes. These methods include absorption, cryogenics, carbonation-calcination cycles, the use of membranes, and adsorption. Notably, adsorption holds a distinct advantage over other techniques due to its superior selectivity and lower energy consumption, contribution to reduced associated production costs. The adsorbents utilized in this context must exhibit a porous structure and favorable surface chemistry. Given the acidic nature of CO₂, it is essential for the surface of the carbonaceous material to be appropriately tailored to enhance selectivity for this contaminant [10,11]. Currently various solids are under investigation for CO₂ adsorption, including activated carbons [12–15], zeolites [16,17], silica [18–20], metal-organic frameworks [21–23], and organic polymers [24].

Activated carbons, known for their porous nature and versatile adsorption capabilities, play a significant role in CO₂ 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 [25,26]. Globally, the annual production of activated carbon is estimated to reach approximately 100,000 tons [27, 28]. Predominant sources for commercial-scale activated carbon include wood, anthracite, bitumen charcoal, lignite, peat shell, and coconut. Additionally, alternative sources like olive and almond shells are increasingly being utilized. The carbon content of these materials varies from 40 % to 90 % (wt.), with a density ranging from 0.4 to 1.45 g/m³, 29, 30,. Efforts have been directed towards leveraging waste as raw materials for activated carbon production [29]. Agricultural residues, such as olive cores, biomass, rice husks, corn stalks, bagasse, fruit stones (cherry and apricot stones, grape seeds), hard shell (pistachio, almond, and pecan shells), fruit pulp, bones, and coffee beans, can also serve as sources [30–33]. The chosen raw material for activated carbon preparation should ideally be abundant, cost-effective, and safe [34,35]. Furthermore, minimizing mineral content and ensuring minimal biodegradability during initial storage are crucial considerations [36]. Cashew (*Anacardium occidentale*), originating from Brazil, is known for its resilience to pests, soil rejuvenation properties, and low maintenance during cultivation, making it an ideal crop with the potential for low production costs and income opportunities. Major global cashew producers include Vietnam, India, Nigeria, Ivory Coast, Brazil, and Indonesia, with Vietnam leading in exports. In Colombia, cashew cultivation is concentrated in various departments, offering a planting potential of 5,000 to 10,000 ha per year [37]. The cashew industry primarily focuses on processing cashew nuts, which make up 10 % of the fruit. The remaining 90 % is the edible pseudocarp, the cashew apple, widely used for juice production globally. Processing generates a substantial amount of shells, comprising 50–65 % of raw nuts. In Colombia, inadequate waste treatment for cashew shells poses environmental risks,

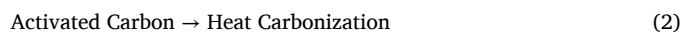
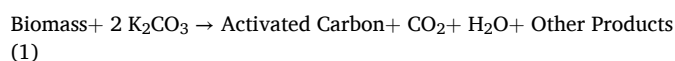
with direct deposition in open fields and potential contamination of water reservoirs. The Vichada region, a significant player in the Colombian cashew market, faces challenges in managing agricultural by-products, as evidenced by the processing of 5.2 tons of raw nuts in 2021, yielding only 1.4 tons of the desired commercial product [38]. This issue highlights the need for effective waste management practices in the cashew industry.

In this work, we convert an important biomass waste of post-industrial production into activated carbon using chemical activation with K₂CO₃. Its physicochemical properties were tested via different characterization techniques (N₂/CO₂ isotherm, FT-IR/Raman spectroscopy, SEM, TGA, and PZC), and it was used as a potential sorbent for CO₂ and CH₄ high-pressure adsorption, as well as its selectivity. This research not only contributes to the field of waste management by providing a novel method to repurpose industrial biomass waste but also offers insights into developing effective solutions for gas adsorption, crucial for addressing environmental challenges.

2. Methodology

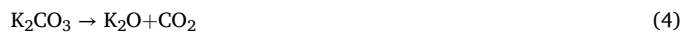
2.1. Preparation of activated carbons

The cashew nut shells (CNS) were obtained from Puerto Carreño (Vichada) province of Colombia. The CNS were stored at −4 °C before undergoing grinding. The frozen CNS were grounded using a blade mill with a 4 mm mesh. Then, a 50 % w/w solution of K₂CO₃ was used to impregnate the CNS. The impregnation ratio is 1:1 (activated carbon: activating agent), and the impregnation was conducted at a temperature of 85 °C while stirring for 3 hours. After this period, the temperature was raised to 150 °C, and the material was dried. The impregnated and dried materials underwent thermal treatment in a tubular furnace under an inert nitrogen atmosphere (150 mL/min), where potential reactions could occur according to Eqs. 1–3. The activation process was carried out at three different temperatures: 800 °C, 850 °C, and 900 °C (MCAK80, MCAK85 and MCAK90). The activation temperature is maintained for three hours, and the heating ramp is set at 5 °C/min. The activated carbons obtained undergoes multiple washing cycles until the pH of the washing water remains constant. Finally, the activated carbons were dried for 24 hours in a convection oven, as shown in Fig. 1.

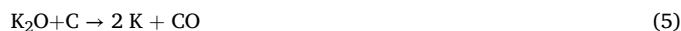


Additionally, the above reaction can be explored in more details as below:

Decomposition of potassium carbonate:



This initial step involves the thermal decomposition of potassium carbonate (K₂CO₃) at elevated temperatures. The decomposition yields potassium oxide (K₂O) and carbon dioxide (CO₂) as products. Further, interaction with carbonaceous precursor occurs:



This reaction is crucial for the activation process as it initiates the development of porosity in the carbon structure. Ultimately, the formation of active sites and pore development take place:

Potassium oxide reacts with carbon, resulting in the formation of carbon dioxide and the regeneration of potassium carbonate:



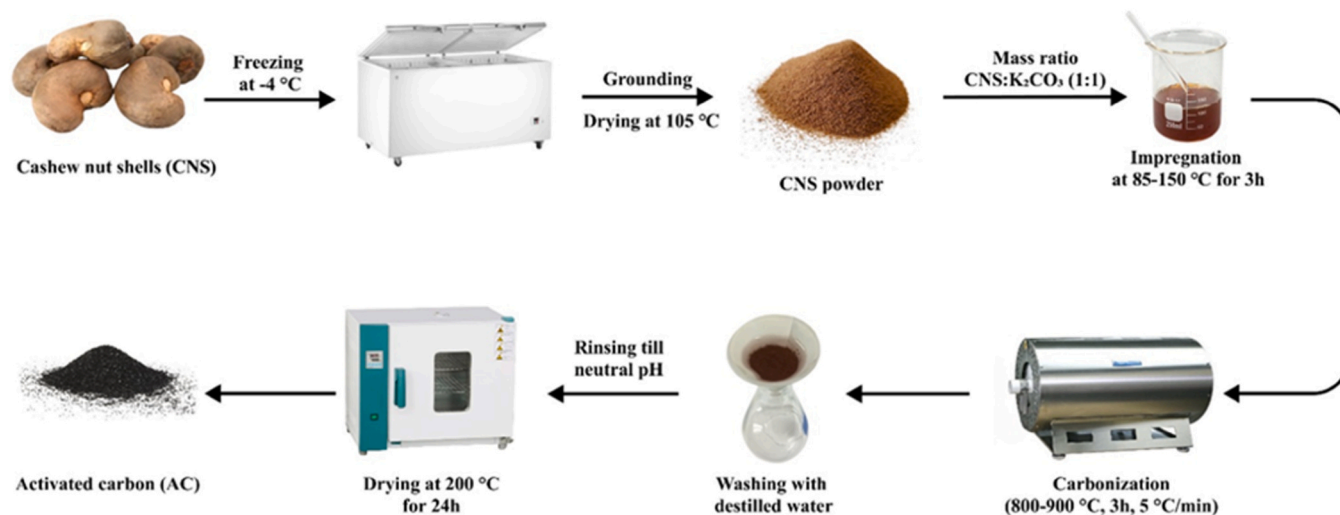


Fig. 1. Schematic preparation of activated carbon derived from cashew nut shells.



This sequence of reactions drives the conversion of potassium carbonate (K_2CO_3) and carbon (C) into various products under neutral conditions, promoting the formation of porous carbon structures with high surface activity [39].

2.2. Characterization of carbon-based materials

The thermogravimetric analysis technique is employed to assess the weight loss and thermal effects experienced by the CNS during pyrolysis under an inert atmosphere. Approximately 10–20 mg of the sample is taken and subjected to heating at a rate of 10 °C/min until reaching a temperature of 900 °C. The heating process is conducted with a nitrogen flow of 100 mL/min using an STA 7200 Hitachi High-Tech instrument equipped with the TAT 81 7200 standard analysis software. The structure of activated carbon is examined using the scanning electron microscopy (SEM) technique with the JSM 6490-LV JEOL microscope. Fourier transform infrared spectroscopy (FT-IR) is employed to identify functional groups in the activated carbon. The Thermo Scientific Nicolet 6700 equipment is utilized, scanning in the range of 400–4000 cm^{-1} . The sample is prepared with KBr, forming a tablet with a solid-KBr ratio of 0.1 %. Raman spectroscopy is performed using the Xplora model dispersive Raman spectrometer from Horiba Scientific. The instrument is equipped with a confocal microscope and three laser excitation lines at wavelengths of 514 nm, 632 nm, and 785 nm. The resulting Raman spectra are detected by a CCD detector. The point of zero charge values of each activated carbon were measured by preparing solutions adjusted to a range of 3–11 pH units by adding appropriate amounts of 0.1 M HCl and 0.1 M NaOH. Then, 0.5 g of the adsorbent sample is added to 50 mL of each solution. After 72 hours of stirring at room temperature, the final pH value is measured.

To determine the textural properties of the solids investigated in this study, nitrogen adsorption-desorption isotherms are conducted at a temperature of $-196^\circ C$. Approximately 0.1 g of carbonaceous samples are subjected to degassing at 250 °C for several hours using a Micromeritics ASAP 2020 equipment. The BET method is employed to calculate the specific surface area. The volume of micropores is assessed using the Dubinin-Astakhov method. The pore size distribution is calculated based on the NLDFT model. In addition, volumes of micropores (<1.4 nm) and narrow micropores (<0.7 nm) were calculated with CO_2 (99.99 % pure) adsorption at 0 °C.

High pressure adsorption isotherms were carried out in the ASAP

2050 sorption analyzer from Micromeritics. This equipment is designed to reach high pressures (greater than 15 bar). The hydrogen adsorption was carried out up to 10 bars at a temperature of 77 K. The high-pressure adsorption isotherms of CO_2 and CH_4 were measured up to 10 bars at a temperature of 298 K.

3. Results and discussion

3.1. Textural properties

Fig. 2 shows the N_2 adsorption isotherms depicted in the dataset exhibit a distinctive Type I profile, indicative of the microporous nature of the material under investigation. This type of isotherm is characterized by a rapid and steep initial nitrogen uptake at low relative pressures, signifying the efficient filling of micropores. Such behavior aligns with materials possessing well-defined microporous structures, where the majority of adsorption occurs within the micropore volume [40]. Moreover, observation is the presence of a very small H4-type hysteresis loop in the isotherm. The H4 hysteresis loop is associated with slit-shaped pores, reflecting a narrow range of pore sizes. Although relatively rare, the occurrence of H4 hysteresis indicates a specific type of mesoporosity, namely, slit-like mesopores [41]. The steep ascent in

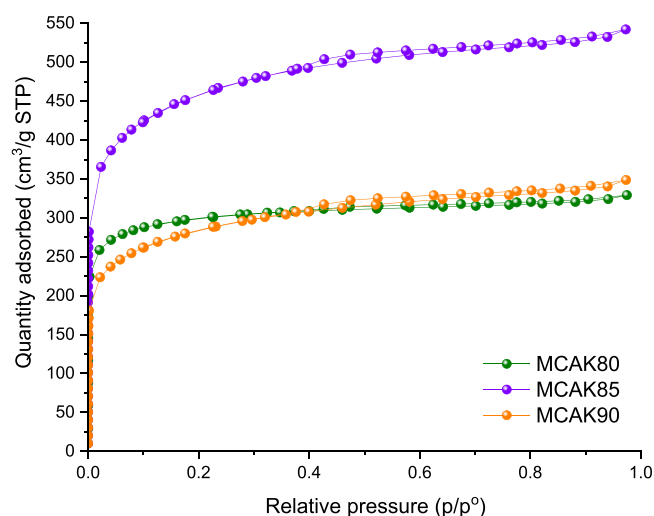


Fig. 2. Nitrogen isotherms for carbon samples activated at 800 °C, 850 °C and 900 °C.

adsorption at low relative pressures, in conjunction with the Type I isotherm, underscores the material's efficient and swift nitrogen adsorption within the microporous structure. This characteristic is particularly desirable for applications requiring high microporosity, such as in gas storage or separation processes. The very small H4-type hysteresis loop suggests the presence of a limited range of slit-like mesopores, contributing to the overall adsorption capacity in a controlled manner. The coexistence of the Type I isotherm and the very small H4-type hysteresis loop signifies a dual porosity characteristic. The material primarily exhibits microporosity, characterized by efficient adsorption within micropores, while also featuring a limited range of slit-like mesopores. This combination positions the material as a compelling candidate for applications demanding precise control over CO₂ and CH₄ gas adsorption, including gas storage and selective gas separation processes [42,43].

Table 1 shows the textural properties of carbon samples subjected to diverse activation temperatures (800°C, 850°C, and 900°C), providing profound insights into their suitability for gas sorption applications, particularly emphasizing the adsorption of CO₂ and CH₄. The activation temperature plays a pivotal role in shaping the porosity of the carbon material, influencing its gas sorption capabilities. The specific surface area (S_{BET}), a fundamental metric indicating available surface for gas adsorption, underscores a significant divergence among the samples. Notably, the material activated at 850°C exhibits a substantial increase in S_{BET} (1693 m²/g) compared to its counterparts activated at 800°C (1164 m²/g) and 900°C (1038 m²/g). In this study, a non-local density functional theory (NLDFT) model was utilized, employing the N₂ and CO₂ adsorption-desorption isotherm at -196 °C and 0 °C, respectively, to ascertain the pore size distributions. Total pore volume (V_{total}), a holistic indicator of space available for gas storage, further substantiates the impact of the activation temperature on pore development. The sample activated at 850°C outperforms others with a V_{total} of 0.839 cm³/g, highlighting superior gas storage potential compared to those activated at 800°C (0.510 cm³/g) and 900°C (0.539 cm³/g). The calcination process at 850°C fosters the creation of a larger pore volume, providing ample space for gas storage. While the average pore size remains consistent across samples, maintaining an average of 1.63 nm, the nuanced impact of activation temperature on microporous volume (V_{micro}) is crucial. Micropores, characterized by their dimensions below 2 nm, play a critical role in high-capacity gas sorption. The 850°C-activated sample has a notably higher V_{micro} (0.641 cm³/g) compared to counterparts activated at 800°C (0.494 cm³/g) and 900°C (0.397 cm³/g).

The variation in pore size among the samples activated at different temperatures. It appears that the smaller pore size observed in the sample activated at 900°C compared to those activated at 800°C and 850°C may be attributed to the intensified carbon gasification process at higher temperatures. At elevated temperatures, such as 900°C, the activation process tends to be more vigorous, leading to increased carbon removal through gasification reactions. This enhanced gasification may have resulted in the closure or collapse of larger pores, thereby yielding a material with a smaller average pore size compared to samples activated at lower temperatures. This explanation aligns with the well-established understanding of carbon activation kinetics, where higher temperatures promote more rapid gasification reactions and subsequent pore development. Therefore, it is plausible that the heightened gasification kinetics at 900°C led to the observed reduction in pore size.

Table 1
Textural parameters of the bioorganic prepared activated carbons.

AC sample	$S_{BET}, m^2/g$	$V_{TOT}, cm^3/g$	Pore size, nm	$V_{micro}, cm^3/g$
MCAK80	1164	0.51	1.82	0.494
MCAK85	1693	0.839	1.63	0.641
MCAK90	1038	0.973	1.63	0.397

As can be observed in Fig. 3(a,b), which presents the pore distribution of the volume of micropore diameters the highest peaks are seen around 0.35 nm (narrow micropores <0.7 nm), a part of that is mostly focused between 1 and 1.35 nm, related to the two highest peaks at 1.1 and 1.2 nm for MCAK-850 and one the highest peak at 1.3 nm for MCAK-900; the mesopore diameters are largely centred in the range 2–4 nm. Micropores, owing to their size, offer an ideal environment for efficient adsorption, with CO₂ and CH₄ molecules readily accommodated within these confined spaces. The observed decrease in textural properties for the sample MCAK-900 activated at 900°C may be attributed to intensified carbon gasification processes. At higher temperatures, excessive activation can lead to the over-gasification of the carbon matrix, resulting in a reduction of surface area and pore volume. This phenomenon may be associated with the increased severity of reactions during activation at 900°C, causing a loss of structural integrity and a decrease in porosity. The PSD of ACs below 1 nm arising from kinetic restrictions of N₂ molecules at 77 K was examined with CO₂ adsorption at 273 K [44].

3.2. Fourier-transform infrared spectroscopy (FT-IR)

Fig. 4 shows the comprehensive Fourier-transform infrared (FTIR) analysis conducted on a diverse spectrum of activated carbon matrices has details regarding their chemical composition, particularly in relation to distinct functional groups. This rigorous examination, reliant on the identification of indicative frequencies, has afforded a nuanced understanding of the molecular architecture of the activated carbon samples.

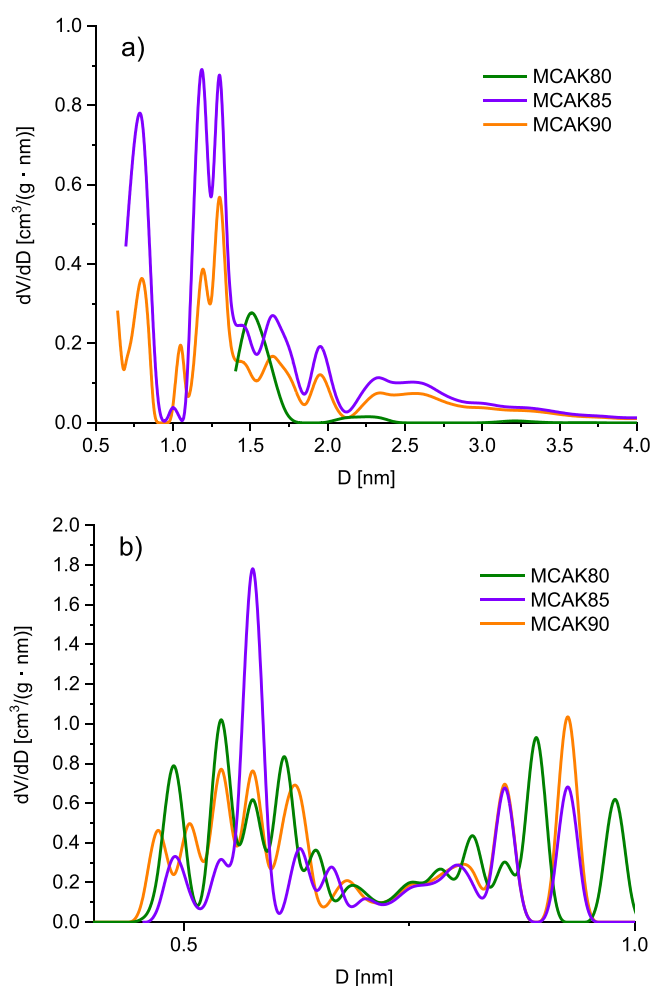


Fig. 3. Pore size distribution determined with the DFT method based on N₂ adsorption isotherm (a) and CO₂ adsorption isotherm (b).

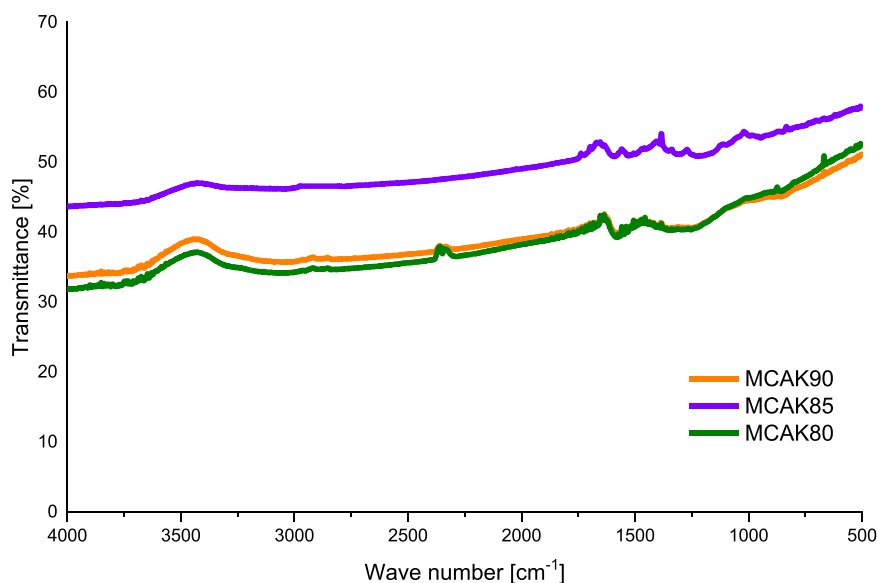


Fig. 4. FTIR spectra for the sample activated at 800°C, 850°C and 900°C.

Within the high-frequency region of 3700–3584 cm^{-1} , the FTIR spectra exhibited a medium peak intensity with sharp characteristics, indicative of the O-H stretching vibration associated with alcohol functional groups [45]. This observation implies the presence of hydroxyl moieties, possibly arising from the thermal treatment during activation or residual oxygen-containing precursors within the biomass source. Transitioning to the mid-frequency range of 1700–1600 cm^{-1} , a medium peak intensity manifested, denoting the C=C bending vibration characteristic of alkene functionalities [46]. This observation suggests the incorporation of unsaturated carbon-carbon bonds, which may have originated from the precursor biomass or undergone transformation during the high-temperature activation process. Further analysis of the spectral data within the range of 1350–1000 cm^{-1} revealed a distinctive stretching vibration corresponding to C-N bonds, indicative of amine functional groups [47].

The presence of amines implies the existence of nitrogen-containing compounds, potentially derived from the original biomass feedstock or introduced during the activation process (Table 2). Upon correlating the indicative frequencies with their corresponding functional groups, a significant revelation emerged. Activated carbon samples subjected to higher activation temperatures, specifically at 800°C and 900°C, exhibited discernible signals associated with alkene and amine compounds. This insight underscores the influence of elevated activation temperatures on the preservation or formation of these functional groups within the activated carbon structure. Remarkably, the sample MCAK-850 processed at 850°C presented a distinct compositional profile characterized predominantly by aromatic compounds. This deduction was made based on the absence of characteristic peaks associated with alkene and amine functionalities. The nuanced variations observed in the activated carbon’s molecular architecture at different temperatures underscore the complexity of the activation process and its impact

Table 2
Functional groups of activated carbons from CNS.

Absorption (cm^{-1})	Appearance	Group	Compound Class
3700–3584	Medium peak intensity, sharp	O-H Stretching vibration	Alcohol
1700–1600	Medium peak intensity	C=C Bending vibration	Alkene
1350–1000	-	C-N Stretching vibration	Amine

on functional group evolution.

3.3. Raman spectroscopy

Fig. 5 shows the Raman spectra provide a sophisticated spectroscopic fingerprint, allowing for the detailed characterization of carbon bonding configurations within the activated carbon. The D peak, associated with disordered regions, and the G peak, associated with ordered graphitic structures, collectively unveil the intricate interplay of molecular arrangements that define the heterogeneous nature of the material’s microstructure. The presented data affords an insight into the microstructural characteristics of the activated carbon samples, elucidated through the discernment of well-defined D and G peaks in their Raman spectra. These distinctive peaks serve as indicative markers of the material’s heterogeneous microstructure, where the D peak arises from the vibration of carbon-carbon sp^2 bonds, indicative of disorder or structural irregularities. In contrast, the G peaks result from the vibration of sp^2 carbon bonds within an ordered structure reminiscent of graphite [48]. The degree of graphitization was calculated using the ratio of intensities of the D peak and G peaks where:

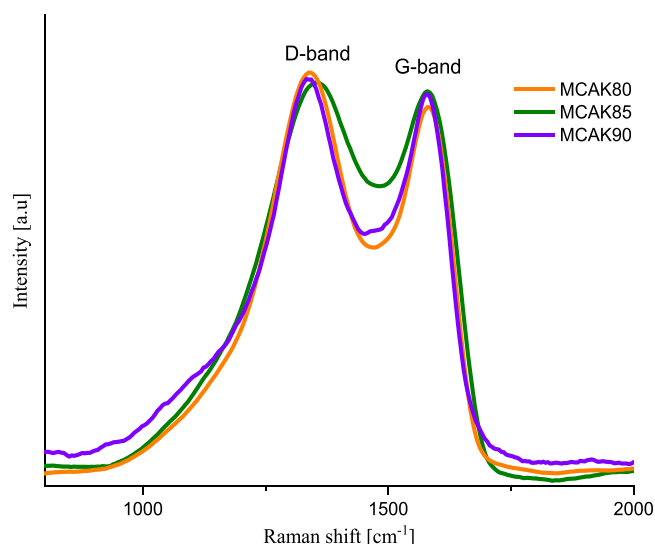


Fig. 5. Raman spectra for the samples activated at 800°C, 850°C and 900°C.

$$R = \frac{I_D}{I_G} \tag{9}$$

R – is the degree of graphitization of carbon materials;
 I_D – is the intensity of the D peak;
 I_G – is the intensity of the G peak.

The measured frequencies of the D and G peaks, spanning 1330–1400 cm⁻¹ and 1580–1600 cm⁻¹, respectively, align closely with reported values in the literature for disordered carbon matrices. This agreement substantiates the credibility of our experimental findings and reinforces the notion of a heterogeneous microstructure prevalent in the activated carbon samples. A more intricate analysis involves the assessment of the degree of disorder within the carbon matrices, quantified through the intensity ratio of the D peak to the G peak (I_D/I_G). Across the spectrum of elaborated activated carbons, this ratio falls within the range of 0.846–0.857. Such a span is recognized by prior studies as characteristic for non-ordered carbon materials (Table 3). Importantly, higher values within this range suggest an augmented presence of aromatic rings and a diminished occurrence of carbon-containing structural defects. This tendency fosters the formation of functional groups on the material’s surface, often entailing oxygen atoms.

3.4. Scanning electron microscopy (SEM) analysis

Fig. 6 provides a comprehensive microstructural examination of activated carbon surfaces, using SEM micrographs to unveil intricate details crucial to understanding of the material’s adsorption characteristics, particularly in the context of CO₂ and CH₄ adsorption. The micrographs within Fig. 6 disclose discernible microporous networks embedded within the CA structures. Remarkably, these micropores exhibit an absence of clogging by extraneous particles, indicative of a well-defined and open microporous morphology. In the realm of gas adsorption, this observation holds paramount significance, as an unimpeded microporous structure is inherently favorable for facilitating efficient and selective adsorption of CO₂ and CH₄ molecules [49,50]. The lack of pore blockage ensures the uninhibited accessibility of micropore space, thus optimizing the material’s adsorption performance by allowing for unencumbered gas-surface interactions. Concurrently, the examination of macroporous surfaces across various AC samples reveals a striking uniformity, notwithstanding differences in activation temperatures during synthesis. This consistent microporous morphology assumes pivotal importance in the realm of gas adsorption applications. Macropores, serving as conduits for gas diffusion, contribute to the accessibility of the inner microporous structure. The observed uniformity implies that activation temperatures, while influencing microstructural features, do not substantially modify the broader macroporous architecture. This steadfast consistency ensures a reliable and reproducible gas adsorption behavior across diverse samples, emphasizing the material’s potential for application in gas separation and storage systems. Importantly, it should be emphasized that the considered type of material derived from nut biomass appears to be a worthy contender for the title of high-quality substrate rich in micropores, which has been confirmed in other studies [51–53].

Table 3
Raman D and G peak frequencies and intensities rates I_D/I_G for all activated carbon samples.

Temperature (°C)	D peak frequency (cm ⁻¹)	G peak frequency (cm ⁻¹)	I _D /I _G
900	1343.1	1580.4	0.849
850	1349.2	1573.9	0.857
800	1327.1	1568.1	0.846

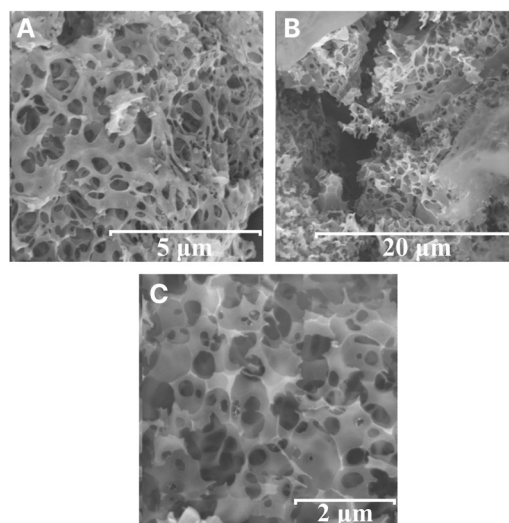


Fig. 6. SEM micrographs A) MCAK800 (5 μm), B) MCAK850 (20 μm), C) MCAK900 (2 μm).

3.5. Point of zero charge (PZC)

The point of zero charge (pHpzc) of an adsorbent is a critical parameter representing the pH at which the material’s surface attains a state of electrical neutrality. This concept is pivotal in understanding the electrochemical interactions governing adsorption phenomena. When the pH of the solution designated for adsorption surpasses the pH_{pzc}, the adsorbent’s functional groups undergo protonation due to an excess of H⁺ ions. Conversely, at pH values below the pH_{pzc}, deprotonation occurs as a result of the presence of OH⁻ ions. Furthermore, in situations where the pH of the solution exceeds the pH_{pzc}, yielding negative net charges, a predilection arises for the attraction of cations to the activated carbon matrix. In contrast, at pH values lower than the pH_{pzc}, a competitive environment ensues, driven by the prevalence of H⁺ ions within the positively charged matrix. This milieu favors the attraction and subsequent adsorption of anions. The specific points of zero charge values for the activated carbon samples (MCAK-800=7.2; MCAK-850=7.3; and MCAK-900=7.6) (Table 4) signify pH conditions at which the surface charge is nearly neutral. This near-neutral pH at the pH_{pzc} implies that the anticipated adsorption behavior of the prepared samples is not significantly influenced by charge-induced attraction effects. The proximity to neutrality at the pH_{pzc} underscores a balanced electrochemical state, indicating that the surface charge of the activated carbon samples plays a limited role in dictating their adsorption characteristics under these conditions [54]. The delineation of pH_{pzc} values offers a nuanced understanding of the electrochemical intricacies governing the adsorption behaviour of activated carbon. This level of detail is crucial for designing and optimizing adsorption processes in gas-phase adsorption, where pH-dependent interactions play a pivotal role in dictating adsorption efficacy [55]. Table 3. pH at the point of zero charge for samples activated at 800°C, 850°C and 900°C.

3.6. Thermogravimetric (TGA) analysis

The thermogravimetric analysis (TGA) of untreated cashew nut shell (CNS) has provided nuanced insights into the intricate thermal decomposition processes inherent to this biomaterial (Fig. 7 and Fig. 8). The

Table 4
Zero Charge values for the activated carbon samples.

Sample’s Activation Temperature [°C]	800°C	850°C	900°C
pH Point of Zero Charge	7.2	7.3	7.6

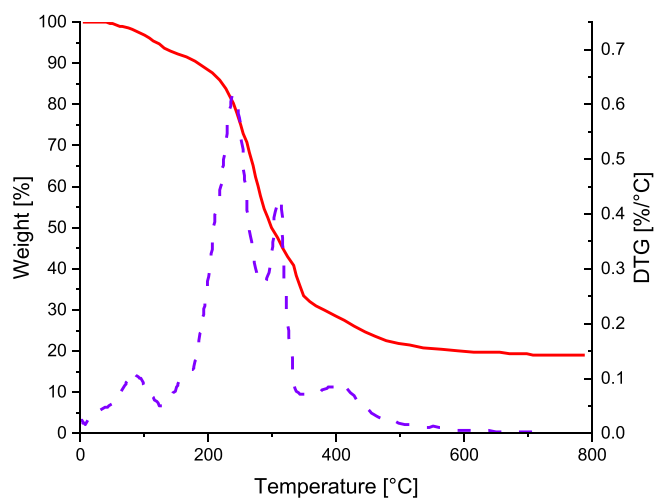


Fig. 7. TGA of raw CNS.

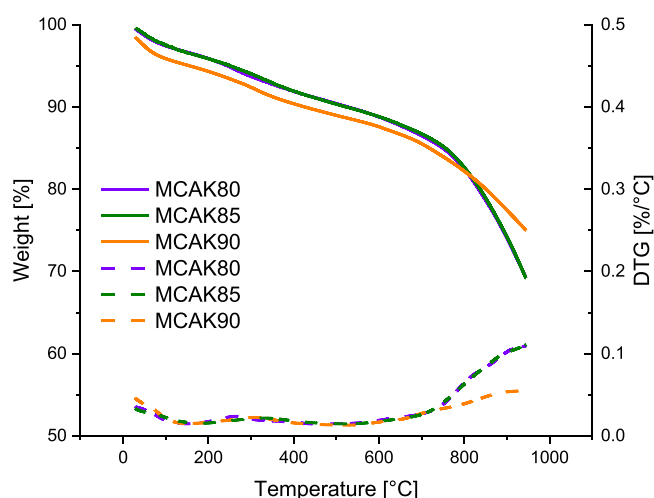


Fig. 8. TGA of activated carbons produced from CNS.

three distinct peaks observed at approximately 250°C, 320°C, and 400°C in the TGA curve signify complex thermal events related to the diverse chemical constituents within CNS. The first decomposition peak at 250°C is specifically associated with the decarboxylation of anacardic acid, a key component found in cashew nut shell liquid (CNSL). Anacardic acid undergoes thermal decomposition, leading to the formation of cardanol [56]. This process is essential to elucidate, as it sheds light on the transformation of a specific bioactive compound under thermal conditions, impacting the potential applications of CNS in various fields. The subsequent decomposition events, occurring in the temperature range of 300–400°C, are attributed to the thermal breakdown of other components present in CNSL, such as cardanol. The identification of these temperature ranges for decomposition is crucial for understanding the stability and behaviour of CNSL constituents under varying thermal conditions, providing fundamental knowledge for applications in pyrolysis or thermal processing. Furthermore, the observation that the solid fraction of CNS, comprising structural carbohydrates like starch and natural fibers, degrades within the same temperature range (300–400°C) underscores the complexity of the CNS matrix [57]. The simultaneous decomposition of these diverse components at similar temperatures necessitates a comprehensive understanding of the thermal dynamics governing each constituent, facilitating tailored approaches for the extraction or processing of specific compounds. The derivative thermogravimetry (DTG) curve reinforces these observations

by delineating three principal decomposition steps. The distinctive features of the DTG curve between 250°C and 400°C highlight the thermal events associated with CNSL constituents, providing a finer resolution of the decomposition process. This detailed characterization aids in identifying optimal temperature ranges for the controlled release or extraction of specific CNSL compounds with desired properties. The negligible weight loss observed at temperatures exceeding 500°C suggests that conducting CNS activations at higher temperatures is advisable. This recommendation is grounded in the desire to minimize residual CNSL remnants, which could be undesirable in certain applications. The scientific rationale behind this recommendation lies in the enhanced thermal stability of CNS matrix components at temperatures surpassing 500°C, reducing the likelihood of undesired byproducts and residues. Similar results and conclusions were obtained by Papadopoulos & Chrissafis [58].

3.7. CO₂ and CH₄ high-pressure adsorption

The CO₂ and CH₄ capture capacities of MCAK80, MCAK85, and MCAK90 were examined at 298 K and in the range 0–10 bar. Fig. 9 (a,b) shows a comparative analysis of the performance of activated carbon samples in terms of CO₂ and CH₄ adsorption isotherms. The experimental findings demonstrate that MCAK85 has the most significant CO₂ uptake, measuring 11.0 mmol/g at 10 bar, owing to its superior surface area (1693 m²/g) and micropore volume (0.641 cm³/g). This illustrates

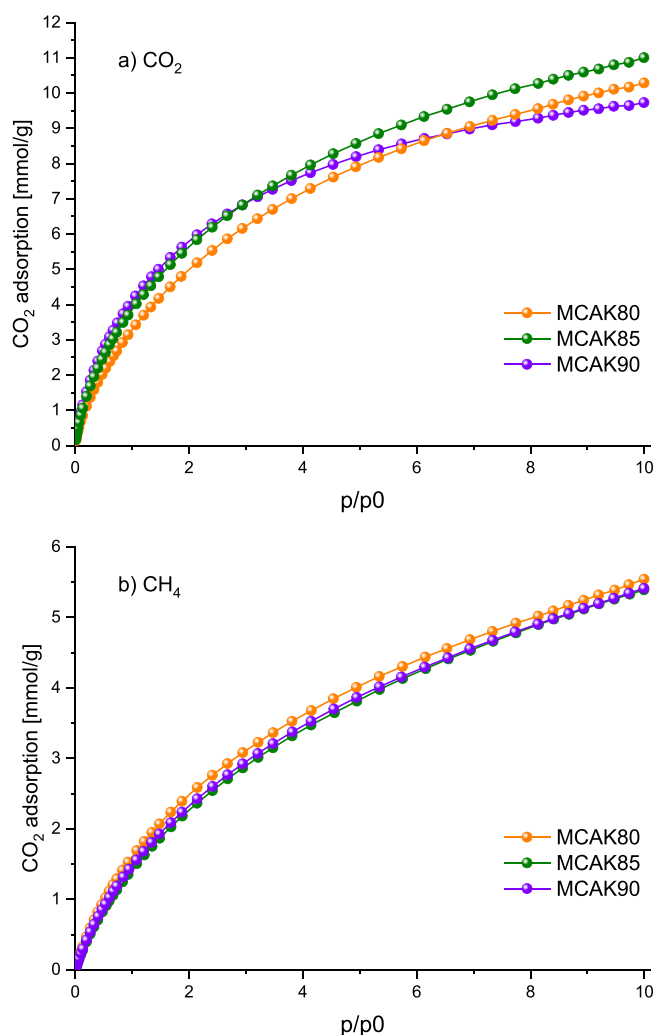


Fig. 9. CO₂ (a) and CH₄ (b) high-pressure isotherms of measured at 25°C in the range of 0–10 bar.

that the presence of microporosity greatly affects the adsorption of CO₂, whereas MCAK85 (0.494 cm³/g) and MCAK90 (0.397 cm³/g) exhibits lower CO₂ adsorption capacities, reaching 10.30 and 9.70 mmol/g, respectively. On the other hand, the CH₄ adsorption curves exhibit little divergence, with the only noticeable difference being the variance in CH₄ uptake (5.4–5.5 mmol/g).

The adsorption mechanisms of CO₂ and CH₄ on ACs obtained from biomass can be intricately shaped by the micropore architecture, gas molecular dimensions, and prevailing physical adsorption processes. This intricate interplay is particularly notable under ambient conditions (25°C and pressures reaching up to 10 bar). The micropore configuration within biomass-derived activated carbon, featuring nanoscale dimensions, establishes a comprehensive network of minuscule adsorption sites. Operating at 25°C, the moderate temperature strikes a balance between kinetic factors and thermodynamics. When combined with pressures up to 10 bar, these conditions create a favorable environment for the efficient diffusion of gases into the micropores. The molecular dimensions of CO₂ and CH₄ are pivotal in this adsorption process. CO₂, possessing a smaller molecular diameter of approximately 0.33 nm, readily infiltrates the micropores, participating in physical adsorption driven by van der Waals forces. Similarly, CH₄, with a slightly larger molecular diameter of about 0.38 nm, experiences physical adsorption within the micropores, utilizing van der Waals interactions with the carbon surface [59]. Within the realm of surface functional groups, the activation procedure introduces diverse oxygen-containing moieties, such as hydroxyl (-OH), carbonyl (C=O), and carboxyl (-COOH) groups. Additionally, the inclusion of carbon-carbon double bonds (C=C) and carbon-nitrogen (C-N) groups adds complexity to the adsorption dynamics. C=C groups, renowned for their π-electron cloud, contribute to heightened adsorption, particularly for CO₂, through π-π interactions. Conversely, C-N groups introduce polar characteristics, fostering interactions with both CO₂ and CH₄, thereby influencing the overall adsorption capacity [60,61].

The data presented in this work have been comprehensively compared with findings reported in the relevant literature in Tables 5 and 6.

3.8. Relation of CO₂/CH₄ adsorption with textural properties

The relationship between CO₂/CH₄ adsorption and various textural properties was examined, as given in Fig. 10. This study reveals a notable variation in the correlation between CO₂/CH₄ adsorption

Table 5
CO₂ adsorption capacities for carbon materials presented within the literature.

Precursors	CO ₂ adsorption capacity (mmol/g)	Temperature (°C)	Pressure (bar)	References
Cashew nutshell	4.0	25	1	This work
Cashew nutshell	11.0	25	10	
Cashew nutshell	6.2	0	1	[62]
Arundo donax (Stem)	4.1	0	1	[63]
Arundo donax (Stem)	21.2	0	30	
Black locust	5.9	0	1	[64]
Black locust	3.8	25	1	
Coffee grounds	7.2	0	1	[65]
Coffee grounds	4.2	25	1	
Coffee grounds	16.4	0	10	
Coffee grounds	12.7	25	10	
Coconut shell	5.6	0	1	[66]
Coconut shell	3.9	25	1	
Lignin waste	4.6	25	1	[67]
Lignin waste	17.3	25	20	
Jujun grass & Camellia japonica	5.0	25	1	[68]
Jujun grass & Camellia japonica	21.1	25	20	
Mesquite wood	6.5	5	3	[69]
Mesquite wood	26.0	25	30	

Table 6
CH₄ adsorption capacities for carbon materials presented within the literature.

Precursors	CH ₄ adsorption capacity (mmol/g)	Temperature (°C)	Pressure (bar)	References
Cashew nutshell	1.7	25	1	This work
Cashew nutshell	5.5	25	10	
African palm shell	7.6	25	45	[70]
Coconut shell	7.7	25	40	[71]
Corncob	16.8	25	34.5	[72]
Cornelian cherry stones	2.5	25	1.2	[73]
Damson plum stones	1.4	25	1.2	
Olive stones	13.3	5	35	[74]

capacity and different textural properties of the materials and prove aforementioned assumptions of mechanism. The most significant observation is the strong correlation between adsorption capacity and microporosity, as indicated by the high R² values ranging from 0.991 to 0.994. This suggests that microporosity is a critical factor in the adsorption process for these gases. In stark contrast, the correlation with total pore volume is minimal, with an R² value of only 0.056, implying that total pore volume might not be a significant determinant in the adsorption efficiency of CO₂ and CH₄ under the conditions tested. The Brunauer-Emmett-Teller (BET) surface area exhibits a moderate correlation, with R₂ values between 0.914 and 0.967, indicating its relevance but not as pronounced as microporosity. These findings contribute to a deeper understanding of the adsorptive behavior of ACs for CO₂/CH₄ capture and storage.

3.9. CO₂/CH₄ selectivity studies

The preference of an adsorbent material in selecting CO₂ over CH₄ is crucial for a range of environmental, industrial, and economic considerations in certain industrial uses. Based on the adsorption patterns of CO₂ and CH₄ at 25 °C, an in-depth analysis of the selectivity between CO₂ and CH₄ was carried out. This research involved calculating the gas selectivity of CO₂/CH₄ using the ideal adsorption solution theory (IAST) to precisely estimate the effectiveness of the separation process.

The IAST approach, developed by Myers and Prausnitz, is extensively employed for determining the adsorption selectivity of gas mixtures in porous substances [75]. This integration follows a specific equation of state to provide an accurate assessment.

$$S_{IAST} = \frac{q_{CO_2(p)} \cdot p_{CH_4}}{q_{N_2(p)} \cdot p_{CO_2}} \quad (10)$$

where: S_{IAST} is the selectivity coefficient, q_{CO2(p)} and q_{CH4(p)} refer to the uptake of specific gas [mmol/g], p_{CH4} and p_{CO2} are the partial pressure in the mixture.

As a result, our focus was on investigating the selectivity for a CO₂/CH₄ (0.5/0.5) binary mixture. In this context, Eq. (1) is modified and expressed in the following specific form:

$$S_{IAST(EQ)} = \frac{q_{CO_2(p)}}{q_{CH_4(p)}} \quad (11)$$

Fig. 11 displays the selectivity data derived from IAST for both equimolar and flue gas CO₂/CH₄ mixtures at 25 °C. It's notable that there's a marked decline in the CO₂/CH₄ selectivity ratio for both gas compositions up to a pressure of 0.2 bar. Specifically, the selectivity coefficient of CO₂ relative to CH₄ varied significantly, ranging from 9.1 to 1.8 correlating with a pressure increase from 0.01 to 10 bar.

Table 7 shows the selectivity values for various carbon-based materials as found in existing literature, measured at 10 bar and with an

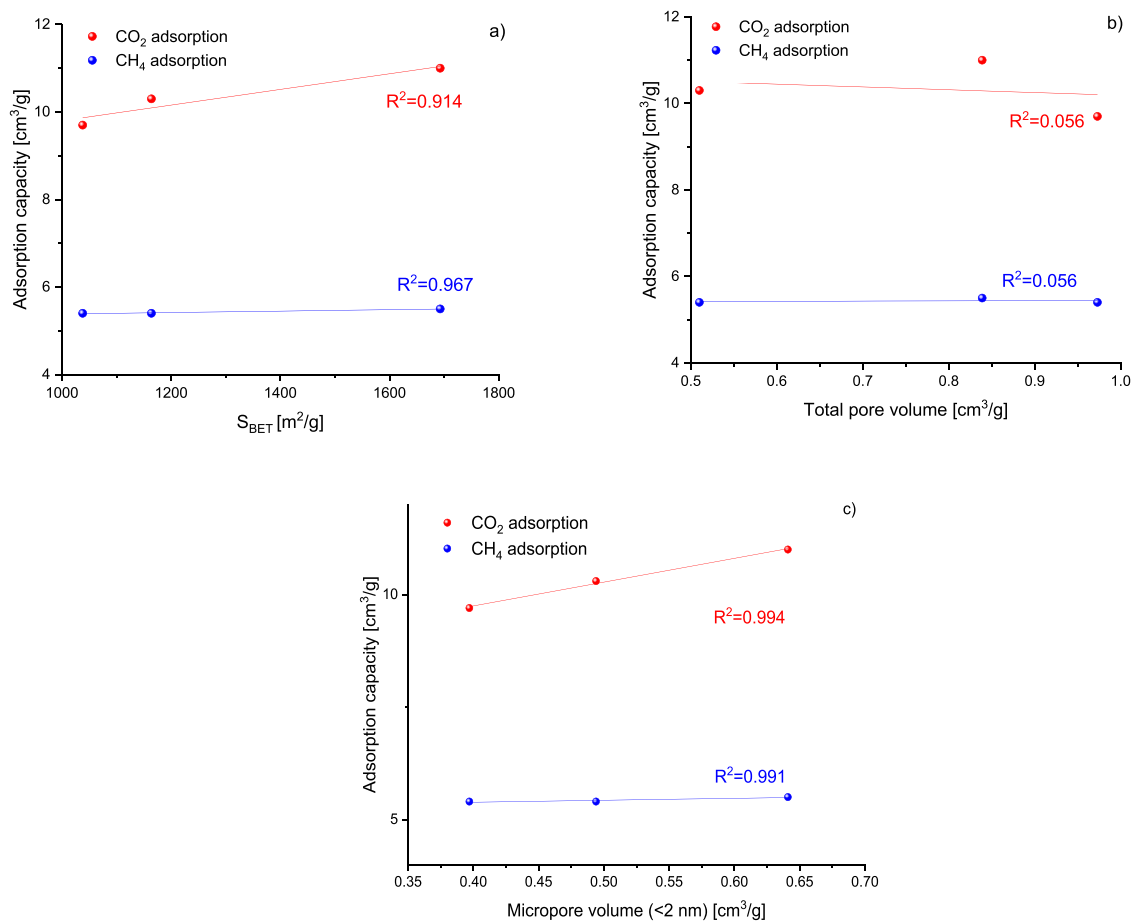


Fig. 10. CO₂/CH₄ adsorption uptake at 25 °C up to 10 bar as a function of (a) BET surface area (b) total pore volume, and (c) micropore volume <2 nm.

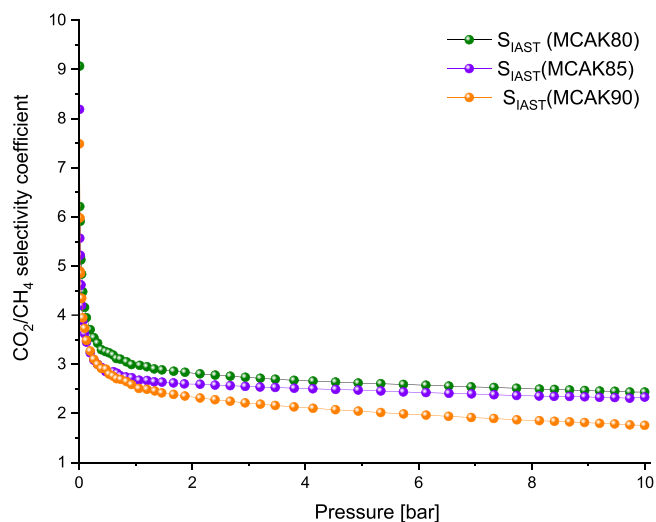


Fig. 11. CO₂/CH₄ selectivity of MCAK samples versus pressure at 25 °C.

initial CO₂ molar concentration approximately around 50 %. The selectivity values achieved in this study are similar to those reported for carbonaceous materials under comparable conditions.

4. Conclusions

In this study, the development and characterization of activated

Table 7

Comparison of CH₄/CO₂ selectivity of carbonaceous materials at 10 bar.

Material	Selectivity	Temperature (°C)	References
MCAK80	2.4	25	This work
MCAK85	2.3	25	This work
MCAK90	1.8	25	This work
WV1050	5.2	30	[76]
Norit R1	2.7	25	[77]
Honeycomb monoliths	2.0	26	[78]
A35/4	3.4	20	[79]
Ordered mesoporous carbon	3.0	25	[80]
Desorex K43-Na	2.1	25	[81]
GAC 1240	2.7	30	[82]

carbon derived from cashew nut shells using a K₂CO₃ activation process is presented. Among the various samples synthesized, the most efficient one, labeled as MCAK85, demonstrated impressive qualities in terms of surface area and pore volume. Specifically, it exhibited a specific surface area of 1693 m²/g, along with total and micropore volumes of 0.839 cm³/g and 0.641 cm³/g respectively. Notably, ACs showcased a remarkable sorption capacity, particularly for CO₂ and CH₄. The CO₂ and CH₄ uptake were at 11.0 mmol/g and 5.5 mmol/g for the MCAK85, respectively, under a pressure of 10 bar at a temperature of 25°C. Furthermore, the material displayed selective adsorption capabilities, with a CO₂/CH₄ selectivity range of 9.1–1.8. The successful utilization of cashew nut shells, a widely available agricultural waste product, in producing high-quality activated carbon, 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 an

efficient solution for gas sorption applications. The high performance of the MCAK85 sample in terms of gas uptake and selectivity indicates its potential for practical applications in areas like gas storage, air purification, and perhaps even in tackling environmental challenges such as greenhouse gas capture.

CRedit authorship contribution statement

Óscar Fonseca-Bermúdez: Writing – original draft, Methodology, Investigation, Formal analysis, Data curation. **Marta Gil Bonillo:** Data curation, Writing – original draft. **Juan Moreno-Piraján:** Writing – original draft, Supervision, Methodology, Conceptualization. **Jarosław Serafin:** Writing – review & editing, Writing – original draft, Visualization, Validation, Project administration, Formal analysis, Data curation. **Rocío Sierra-Ramírez:** Supervision, Data curation, Conceptualization. **Ghualm Farid:** Writing – original draft. **Bartosz Dziejarski:** Writing – review & editing, Writing – original draft, Visualization, Validation, Formal analysis, Data curation. **Liliana Giraldo:** Writing – original draft, Supervision, Methodology, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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