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Influence of Activated Carbon Granulometry on H₂ Purification in Glycerol Reforming Syngas: Adsorption and Kinetic Analysis

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Abstract: This study investigates the adsorption performance of granular activated carbon (GAC) and pelletized activated carbon (PAC) for the purification of syngas produced from glycerol reforming, focusing on the removal of CO₂, CO, and CH₄. The adsorption process was studied at two different flow rates (0.5 L/min and 1 L/min) to assess the impact of particle size and gas flow rate on adsorption capacity. The results indicate that GAC exhibits superior multi-gas adsorption, particularly at lower flow rates, effectively capturing CO₂, CO, and CH₄, while PAC exhibits lower adsorption performance. Kinetic analysis revealed that the pseudo-second-order and Avrami models fit well with both adsorbents, though GAC aligns more closely with the Avrami model, reflecting its multi-step adsorption mechanism and greater pore diffusion efficiency. These findings highlight the importance of adsorbent size and flow rate in optimizing hydrogen purification processes, with GAC emerging as a highly efficient adsorbent for industrial-scale syngas treatment.

Keywords: hydrogen purification; granular activated carbon; pelletized activated carbon; breakthrough time analysis; CO₂ adsorption kinetics; intraparticle diffusion model



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1. Introduction

Hydrogen, as a promising clean energy carrier, offers high energy density and the potential to significantly reduce greenhouse gas emissions when used in fuel cells and combustion processes [1,2]. As the global demand for sustainable energy increases, renewable sources such as biomass, water, and waste glycerol have gained attention for hydrogen production [3,4]. However, the purity of hydrogen is a vital factor for ensuring the efficiency and safety of hydrogen-based systems [5]. Impurities such as carbon monoxide (CO), carbon dioxide (CO₂), methane (CH₄), and sulfur compounds can significantly reduce the performance of fuel cells and poison catalysts used in hydrogen-based processes, highlighting the importance of purification in the hydrogen production chain [6]. Therefore, effective methods to remove these impurities [4] are essential to satisfy the stringent purity requirements for hydrogen in various applications [7].

Several purification techniques have been developed to enhance hydrogen quality, including pressure swing adsorption (PSA) [8], membrane separation [9], cryogenic distillation [10], and chemical absorption [5]. Each technique has its advantages and limitations. PSA, for instance, is widely used for hydrogen purification due to its high efficiency and ability to selectively adsorb impurities under high pressure, but it is energy-intensive and may require expensive materials [8]. Membrane technologies, though promising for their low energy consumption and continuous operation, face challenges in terms of membrane selectivity and durability under harsh conditions [9]. Chemical absorption is effective for certain impurities, but the process can be slow and requires substantial chemical regeneration, which increases operating costs [5]. Adsorption-based purification [11], on the other hand, stands out for its versatility, cost-effectiveness, and the availability of a wide range of adsorbents that can be tailored for specific applications.

Among adsorbents, activated carbon (AC) is one of the most extensively studied materials due to its high surface area, porosity, and chemical stability [12]. It has been successfully used to remove contaminants such as CO₂, CO, and sulfur compounds from hydrogen-rich streams, and its effectiveness has been demonstrated in various studies [13,14], making it a promising candidate for hydrogen purification processes. For example, Lee et al. [15] reported that activated carbon derived from biomass, such as walnut shells, exhibited a CO₂ adsorption capacity of 9.2 mmol/g at 25 °C and 1 bar, showcasing its effectiveness at low temperatures. Similarly, research conducted by Zubbri et al. [16] investigated the effects of different activation parameters to identify the optimal conditions for maximum CO₂ capture. The highest CO₂ adsorption capacity achieved was 122.37 mg g^{−1} at 30 °C and 1 atm, demonstrating that modified activated carbons could significantly improve hydrogen purity by removing CO₂ from syngas. Moreover, these researchers [15,16] proposed a kinetic study that suggested the CO₂ adsorption mechanism on the adsorbent is governed by physisorption. Additionally, studies [17–19] on the kinetics of CO₂ adsorption on activated carbon have shown that the adsorption process is influenced by factors such as temperature, pressure, and the presence of other gases in the mixture. Other studies [20,21] have observed that under certain conditions, particularly at higher temperatures and pressures or lower flow rates, the adsorption mechanism can shift towards chemisorption, where stronger chemical bonds, such as bicarbonate formation on the adsorbent surface, play a role in the CO₂ capture process. These findings indicate that the adsorption process may involve a combination of physical and chemical interactions, depending on the operational parameters. Thus, understanding the adsorption behavior of CO₂ on activated carbon under different conditions is essential for optimizing the process and improving hydrogen recovery rates.

This study investigates the influence of activated carbon granulometry on the adsorption performance and purification of syngas derived from glycerol reforming. The primary objective is to evaluate and compare the adsorption kinetics and mechanisms of granular activated carbon (GAC) and pelletized activated carbon (PAC) in the removal of CO₂, CO, and CH₄ under various flow rates. By assessing the impact of particle size on adsorption efficiency, the study aims to optimize conditions for enhanced multi-gas removal, ultimately improving hydrogen purity and recovery for cleaner energy production. The research focuses on identifying the key kinetic and diffusion mechanisms involved in the adsorption process, highlighting the importance of granulometry in determining the effectiveness of activated carbon for industrial hydrogen purification applications.

2. Materials and Methods

2.1. Adsorbents Used and Methods Used for Their Characterization

For this study, a similar activated carbon was used in two different particle sizes: granular (1–4 mm) and pelletized (8 mm diameter and 25–35 mm length). This commercial carbon comes from thermally activated coconut shells, i.e., subjected to a physical activation process. Before the adsorption process, both adsorbents were dried in an oven at 105 °C for 24 h to ensure complete dryness. Their specifications are collected in Table 1.

Table 1. Specifications of used adsorbents.

Specification	GAC	PAC
Bulk density (kg/m ³)	454	520
Water content (%)	2.1	5.0
Iodine number (mg/g)	998	1000
Mechanical strength (%)	95.9	97.0

To effectively compare the two adsorbents and identify differences in their surface area and pore structure, the following properties were measured:

- Textural properties and compositional analysis using scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) using a JEOL JSM-6700F (Akishima, Tokyo, Japan) field emission SEM, equipped with an EDS probe using secondary (SE) and back scattered electron (BSE) detectors. The sample powders were fixed on a carbon adhesive tape and coated with a thin layer of gold of approximately 15 nm. Furthermore, the specific surface area, pore size, and pore volume of the samples were characterized by a Micromeritics ASAP 2020 analyzer (Quantachrome, Norcross, GA, USA) using nitrogen physisorption and applying the Brunauer–Emmett–Teller (BET) theory. The pore size distribution was calculated from the desorption branch of the isotherm using the BJM model. The micropore volume was calculated by the t-plot method. Approximately 0.05 g of material was initially degassed at 90 °C under vacuum for 60 min. Then, the temperature was raised to 150 °C and held for 240 min.
- Mineral phase characterization was investigated by X-ray diffraction (XRD) using a Siemens D-5000 diffractometer (Karlsruhe, Germany) with CuK α -radiation in the 2 θ range from 10 to 70°.

2.2. Adsorption Experiments

Adsorption experiments using activated carbon were performed in a cylindrical PVC fixed-bed reactor with dimensions of 34 cm in height and 6.35 cm in diameter. The reactor was loaded with either 0.129 ± 0.021 kg of GAC or 0.228 ± 0.014 kg of PAC and fed with synthetic syngas. The syngas composition consisted of 50% hydrogen, 15% carbon dioxide, 20% carbon monoxide, and 15% methane. This gas composition was selected based on findings from a previous investigation conducted by the authors, which analyzed the typical syngas produced during the glycerol reforming process [22].

Experiments were conducted at a pressure of 1 bar with two different gas flow rates: 0.5 L/min and 1 L/min. Flow rates of 0.5 L/min and 1 L/min were selected to investigate the performance of the adsorbents under conditions representing extended interaction (low flow rate) and typical industrial throughput (high flow rate). The outlet gas composition was continuously monitored using a maMoS Madur gas analyzer (Vienna, Austria), with measurements taken every second to ensure high accuracy. A schematic diagram of the experimental setup is presented in Figure 1. Breakthrough curves, adsorption capacity, and kinetic models under various operating conditions were derived from the collected data.

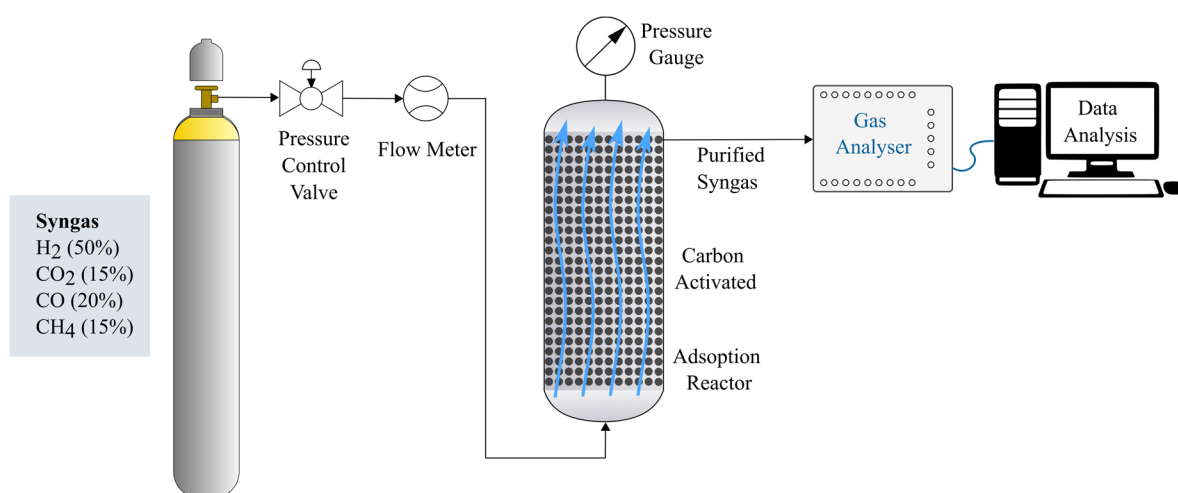


Figure 1. Scheme of experimental adsorption experiments.

The tests were considered complete when the ratio between the CO₂ volumetric concentration in the outlet gas composition with respect to the CO₂ volumetric concentration in the inlet gas composition reached the value of 0.97, considered the saturation value of

the adsorbent. Each experiment was repeated three times under the same pressure and flow rate; the adsorbent was replaced after each test.

3. Theory and Models

3.1. Kinetic Models

Kinetic models are fundamental tools for understanding adsorption processes, as they provide insight into both the rate and mechanisms by which adsorbates interact with adsorbents. These models are broadly categorized into two types: adsorption kinetic models and diffusion kinetic models. Adsorption kinetic models focus on the rate at which adsorbate molecules adhere to a solid surface over time, capturing the global kinetics of the process. Diffusion kinetic models, on the other hand, describe the movement of adsorbate molecules through a medium, whether via bulk diffusion or within the pores of the adsorbent material. The kinetic models selected for this study were chosen to reflect the specific characteristics of the CO₂ adsorption process and to provide a comprehensive understanding of the mechanisms involved.

3.1.1. Adsorption Kinetic Models

For carbon dioxide (CO₂) adsorption, several kinetic models are commonly used to predict the behavior of adsorbents [23–25]. Each model addresses a specific aspect of the adsorption mechanism, making their combined use essential for a holistic understanding. The pseudo-first-order (PFO) and pseudo-second-order (PSO) models provide insights into the global adsorption kinetics, focusing on physisorption and chemisorption processes, respectively. The Elovich model, commonly used for heterogeneous surfaces, was included to account for potential surface complexity and chemical interactions. The Avrami model was selected to describe systems where multipath adsorption or mixed adsorption mechanisms are expected, capturing the dynamic behavior of porous adsorbents like activated carbon.

The first-order kinetic model (PFO), also known as the Lagergren model, assumes that the rate of adsorption is proportional to the number of unoccupied adsorption sites. It is typically applied in cases where the adsorption process follows a physical adsorption mechanism, which is common in gas adsorption on porous materials [26].

The second-order kinetic model (PSO) suggests that the rate of adsorption is dependent on the square of the number of available adsorption sites [27]. This model is often used for systems where chemical adsorption, or chemisorption, plays a significant role, as it implies stronger interactions between the adsorbate and the adsorbent.

The Elovich model describes systems with heterogeneous surfaces and is often applied to chemisorption processes. It assumes that the adsorption energy decreases with an increase in the number of adsorbed molecules, making it suitable for complex adsorption systems, especially where surface heterogeneity and energy variations are present [26].

Finally, the Avrami model is used to describe the kinetics of phase transitions, and it can be adapted to analyze adsorption processes. This model is particularly helpful for understanding adsorption mechanisms that involve a combination of diffusion, surface reactions, and pore filling [28].

The above-mentioned adsorption kinetic models were linearized and applied to adsorption kinetic studies of carbon dioxide on hydrogen purification processes, as shown in Equations (1)–(4):

$$\text{PFO} : \ln(q_e - q_t) = \ln(q_e) - k_1 \cdot t \quad (1)$$

$$\text{PSO} : \frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{t}{q_e} \quad (2)$$

$$\text{Elovich} : q_t = \frac{1}{\beta} \cdot \ln(\alpha \cdot \beta) + \frac{1}{\beta} \cdot \ln t \quad (3)$$

$$\text{Avrami} : \ln\left(-\ln\left(1 - \frac{q_t}{q_e}\right)\right) = n_A \ln(k_A) + n_A \ln t \quad (4)$$

where q_e and q_t are the amount of adsorbate adsorbed at time t and at equilibrium (mg/kg), k_1 is the rate constant of the first-order adsorption (s^{-1}), k_2 is the rate constant of the second-order adsorption (kg/mg·s), α represents the initial adsorption rate (mg/kg·s), and β relates the covered surface to the activation energy for chemical adsorption (kg/mg), k_A is the rate constant of the Avrami model (L/mg·s), and n_A is the Avrami exponent.

3.1.2. Diffusion Kinetic Models

Three diffusion models were employed to investigate mass transfer processes. The Boyd model was applied to assess whether film diffusion controls the adsorption rate, while the inter-particle diffusion model examines molecular transport between neighboring adsorbent particles. Finally, the Weber–Morris intra-particle diffusion model provides insight into the movement of adsorbate molecules within the pores of the adsorbent.

The Boyd film diffusion model is widely employed in adsorption studies to determine whether the adsorption process is controlled by film diffusion, which refers to the mass transfer of adsorbate molecules through a thin boundary layer surrounding the adsorbent [29,30]. In this model, the external mass transfer of molecules from the bulk gas or liquid phase to the surface of the adsorbent is analyzed to assess if it plays a significant role in limiting the adsorption rate [31]. This model is expressed by the following equations:

$$B_t = -\ln \frac{\pi^2}{6} - \ln(1 - F) \text{ for } F > 0.85 \quad (5)$$

$$B_t = \left(\sqrt{\pi} - \sqrt{\left(\pi - \frac{\pi^2 F}{3} \right)} \right)^2 \text{ for } F < 0.85 \quad (6)$$

where F represents the fractional attainment of equilibrium, which indicates how much of the equilibrium adsorption capacity has been reached at a given time and it is calculated as q_t/q_e .

If the Boyd plot (B_t versus t) shows a linear relationship passing through the origin, it indicates that film diffusion is the controlling step, meaning that the resistance to mass transfer occurs primarily at the boundary layer between the adsorbent and the surrounding phase [26]. The model is useful for identifying the kinetics of gas–solid interactions, especially in cases where adsorption occurs rapidly on the external surface of the adsorbent, followed by slower internal diffusion.

The interparticle diffusion model examines the role of diffusion between adsorbent particles as a potential rate-limiting step in the adsorption process, assessing the transfer of molecules between neighboring adsorbent particles. This model is particularly relevant in systems where adsorbent particles are densely packed, as the diffusion of adsorbate through the void spaces between particles can significantly impact the overall adsorption rate. According to the interparticle diffusion model, a linear relationship is expected when plotting $\ln(1 - q_t/q_e)$ against time, where the intercept corresponds to the value of $\ln(6/\pi^2)$. This linearity suggests that the diffusion of adsorbate molecules between particles plays a significant role in the adsorption process, particularly during the early stages of adsorption, when concentration gradients are steep and diffusion rates are highest [30,32].

The Weber–Morris intraparticle diffusion model is used to examine the diffusion of adsorbate molecules into the pores of the adsorbent. It assumes that adsorption occurs in multiple stages, with intraparticle diffusion being the rate-limiting step [33]. According to this model, adsorption occurs in multiple phases: first, external mass transfer (or surface diffusion) of the adsorbate molecules to the surface of the adsorbent, followed by intraparticle diffusion into the pores. The model is particularly useful for porous materials, as it distinguishes between the external and internal resistance to mass transfer. To explore the rate-controlling steps in CO₂ adsorption, kinetic data were analyzed using the Weber–Morris intraparticle diffusion model.

$$q_t = k_{WM} \cdot t^{\frac{1}{2}} + C \quad (7)$$

where k_{WM} represents the intraparticle rate constant ($\text{mg}/\text{kg}\cdot\text{s}^{0.5}$), and C is a constant that allows for determining the thickness of the fluid film surrounding the adsorbent surface (mg/kg). When plotting the adsorbed amount versus the square root of time, a linear relationship in the Weber–Morris plot suggests intraparticle diffusion control.

4. Results and Discussion

4.1. Adsorbents Characterization

The images obtained by scanning electron microscopy, see Figure 2, show the different morphology of the two types of activated carbon used as adsorbents. In both cases, the presence of crystals with different structure and size associated with the crystallization of different compounds, whose chemical composition comes from the materials used during the manufacture and activation of the carbon, can be seen, as occurs in previous studies [34–36]. EDS analyses performed in different areas of both carbon samples confirm the presence of different chemical elements other than carbon (see Table 2).

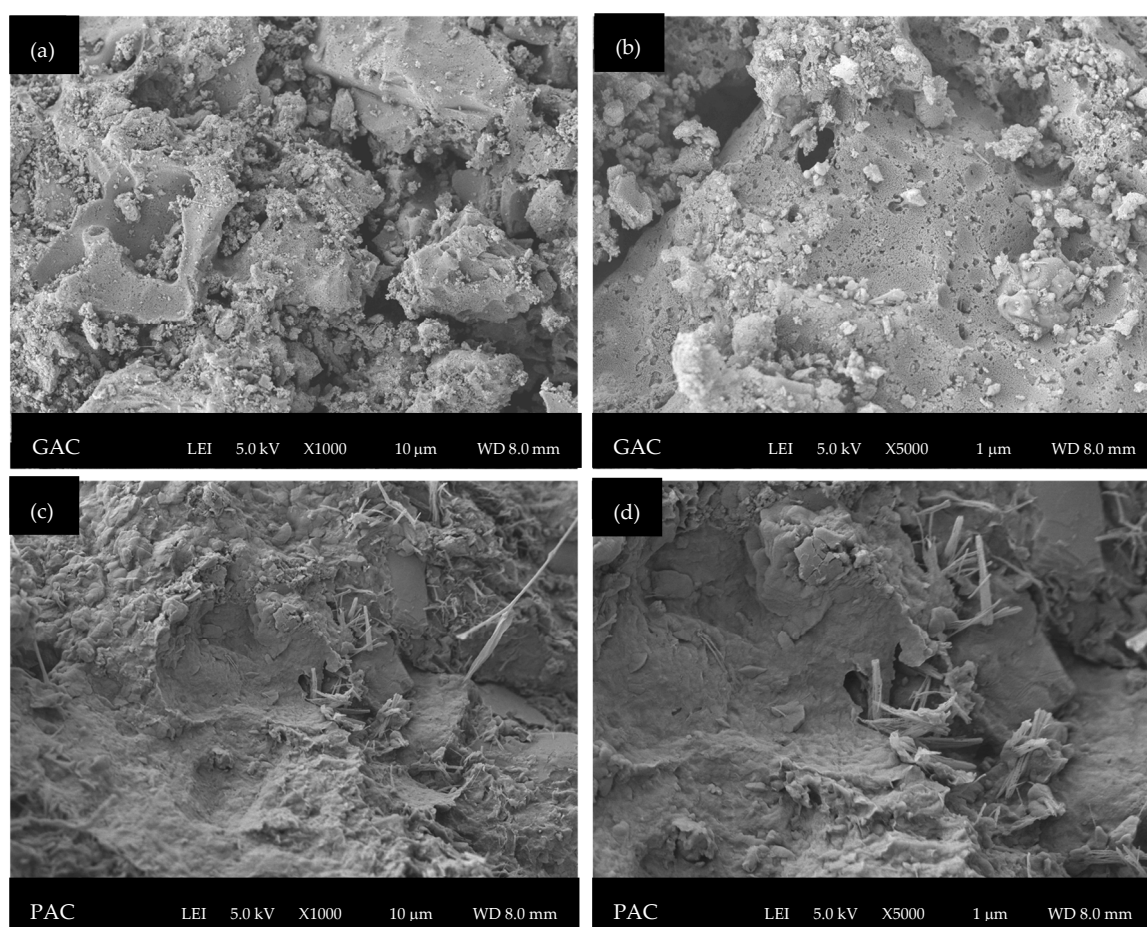


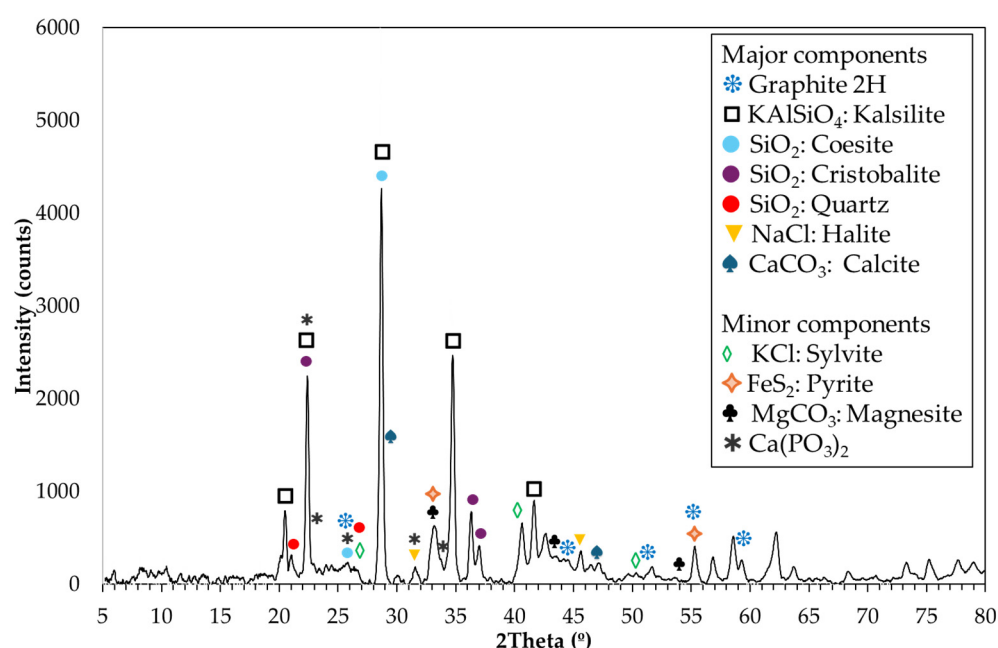
Figure 2. SEM micrographs of the activated carbon used with different granulometries: GAC (a,b) and PAC (c,d). Figures (b,d) correspond to micrographs at higher magnification.

The main difference can be seen in terms of the size distribution of pores. In GAC, see Figure 2a,b, both pores between particles and micropores within the coal grains are visible, with an important pore volume within the nanorange (i.e., below $1\ \mu\text{m}$). The presence of this wide range of pore sizes accessible to fluids favors a higher specific surface area in the carbon. In the case of PAC, the surface is smoother than in GAC. In this carbon, no surface cracking caused by evaporation of the activation reagents is visible. This fact reduces the porosity of the carbon and causes the presence of nanometric pores, which is not evident.

Table 2. Chemical composition of the activated carbons used. The concentration is expressed in weight percentage.

Chemical Element	%wt
Si	14.09
Ca	12.19
Al	3.81
Fe	2.05
Mg	0.89
Na	0.83
K	0.73
S	0.54

The presence of these chemical elements is also detected in the composition of the crystalline minerals that appear in the diffractograms obtained (see Figure 3). As reported in previous studies [34], the carbons activated thermally from coconut shells have some crystalline compounds in their composition from both the raw materials used in the manufacturing process and the crystalline compounds formed as a result of the activation process. In this way, it is normal to detect calcium carbonates, calcium phosphates, and silicon oxides in the composition of commercial activated carbons [34].

**Figure 3.** XRD pattern showing the main minerals that appear in the composition of the activated carbon.

Among the crystalline compounds present, the presence of silicon and graphite oxides that form at high temperatures is detected, as is the case of cristobalite and coesite. This fact is indicative that the carbon used has been activated at high temperatures, probably higher than 1200 °C, for the different phases detected to form, as shown in the diagram modeled by Ford et al. [37].

The presence of potassium and phosphorus in activated carbons derived from coconut shells is often linked to the use of activating agents, such as KOH and H₃PO₄, which remain in the carbon structure [38]. These elements contribute to modifying the surface characteristics of the carbon, enhancing its porosity and adsorption capacity [39].

Chloride comes from the HCl used in the activated carbon washing process to adjust the pH value [40]. The anion chloride subsequently crystallizes with sodium to form halite and with potassium to form sylvite [34].

The presence of Ca and Mg in activated carbons is attributed to the composition of the coconut shells, which naturally contain traces of calcium and magnesium in their composition [41]. These elements, when subjected to activation processes at high temperatures and in the presence of CO₂, are transformed into carbonates. In addition to these compounds, another element very present in the composition of the coconut shell is iron [41]. The presence of iron oxides is indicative that the thermal process has taken place in an atmosphere containing oxygen.

Finally, the diffractogram shows the presence of KAlSiO₄. This complex silicate compound can come from the reaction between the KOH, used in the activation process of carbon, with aluminum and silica present in the raw biomass.

The data obtained by BET and shown in Table 3 show that the specific surface area of GAC carbon is much higher than that of PAC (about 25 times higher); this is due to the particle size and the smaller pore size.

Table 3. BET surface area, total pore volume, and average pore diameter of the studied activated carbon.

	GAC	PAC
BET surface area (m ² ·g ^{−1})	1121	44
Average pore diameter (nm)	3.4	22.5
Total pore volume (cm ³ ·g ^{−1})	0.27	0.15
Total micropore volume (cm ³ ·g ^{−1})	0.22	0.01

In addition, it can be seen that the volume of pores, within the measuring range of the equipment, is lower in PAC and that there is hardly any volume corresponding to the range of micropores whose access size is below 2 nm, which is consistent with SEM analyses. While in GAC, 80% of the pore volume detected corresponds to micropores, the rest falling in the mesopore range.

From the pore size distribution, which shows the distribution ranged from 2 nm to 119 nm, i.e., the mesoporous range and part of the macroporous range (Figure 4), the mesopore content with respect to the macropore content for PAC is in the order of 8% and 92%, respectively. On the contrary, in GAC, the percentage of mesopores represents 86% (appreciating an important access size diameter at 3.9 nm) compared to 14% of macropores. Therefore, the importance of the mesoporous in this activated carbon is greater than in PAC. Furthermore, in GAC there is a marked peak at the beginning of the graph indicating that there is an important volume below 2 nm, a range from which the contribution of micropores begins.

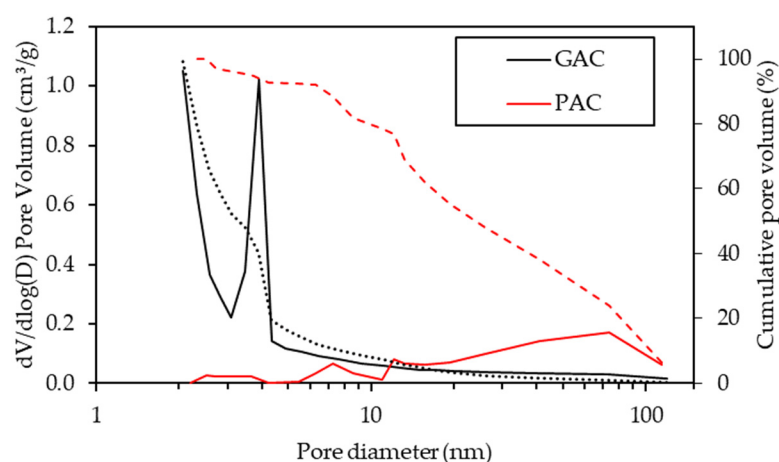


Figure 4. Pore size distribution of GAC in black and PAC in red. The incremental pore volume is shown with solid lines, while the cumulative volume is shown with dashed lines.

This different pore size distribution has an influence on the adsorption capacity of activated carbon since it depends on the relationship between the size-shape of the molecule to be retained and the pore size distribution of the carbon. As shown in previous studies [42], if the molecules to be adsorbed have a size much smaller than the pore diameter, the molecules are adsorbed with little strength, and the process is not very efficient; if they are larger than the pore size, no adsorption occurs, and if the pore diameter is adapted to the size of the molecules to be adsorbed, the process will be more efficient, producing a stronger adsorption.

With respect to the nitrogen adsorption–desorption isotherms (see Figure 5), GAC can adsorb a greater amount of N_2 than PAC. The adsorption curve of GAC carbon corresponds to the type IV isotherm characteristic of mesoporous solids since it presents a hysteresis cycle, which is associated with the capillary condensation characteristic of adsorption/desorption in mesopores. Its hysteresis cycle is H4, which corresponds to limited amounts of mesopores bounded by micropores [43]. This fact could be seen in the SEM images.

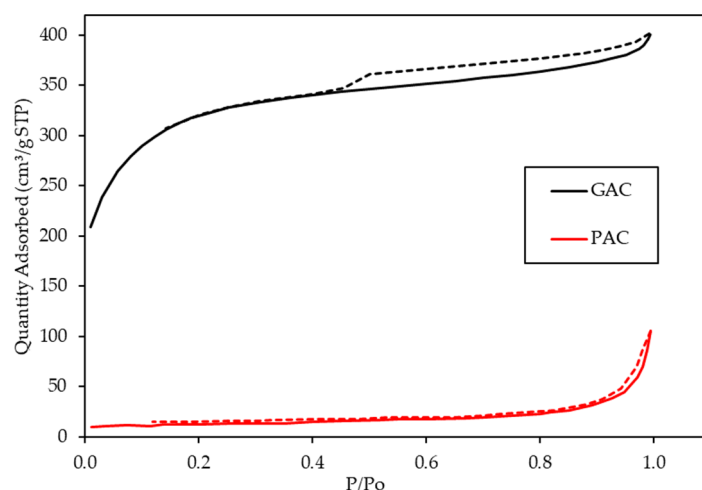


Figure 5. N_2 adsorption–desorption isotherms for the activated carbon used with different granulometries: granular (GAC in black) and pelletized (PAC in red): (solid lines) adsorption, (dashed lines) desorption.

In the case of PAC coal, its adsorption isotherm corresponds to a type III characteristic of non-porous or macro-porous materials (which is the case of this carbon), where the interactions between adsorbate and adsorbent are low and the adsorbed molecules are clustered around the most favorable sites on the surface [44,45].

4.2. Breakthrough Response Curves

Figure 6 illustrates the breakthrough response curves for granular activated carbon (GAC) at two gas flow rates of 0.5 L/min and 1 L/min. It was observed that the breakthrough time increased from 157 s (Figure 6b) to 463 s (Figure 6a) as the flow rate decreased from 1 L/min to 0.5 L/min, indicating that a lower flow rate allows for longer contact time between the gas and the adsorbent, improving the adsorption efficiency. This behavior aligns with findings from other studies [46], which show that higher flow rates reduce the residence time of gas molecules in the adsorbent bed, leading to earlier breakthrough points. This can be attributed to the fact that slower flow rates allow for more contact time between the gas and the adsorbent, as the gases remain in contact with the carbon bed for a longer time, leading to greater adsorption efficiency.

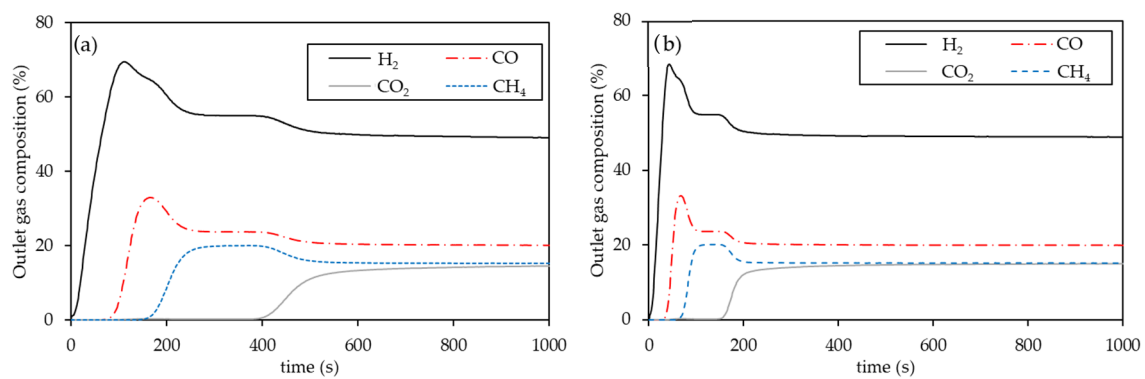


Figure 6. Breakthrough curves of GAC at different gas flow rates: (a) 0.5 L/min; (b) 1 L/min.

This is more clearly seen in Figure 7, which shows in detail the hydrogen breakthrough curve at different flow rates. At low flow rates, granular carbon can adsorb each gas for a longer time, showing a much less steep slope of the curve and a longer saturation phase for each of the gases present in the mixture. To give an example, phase 2, during which CH_4 is still adsorbed, is more durable at low flow rates than at high flow rates, allowing one to obtain a purer mixture in hydrogen for a longer time. The same happens with the other phases identified in the graph.

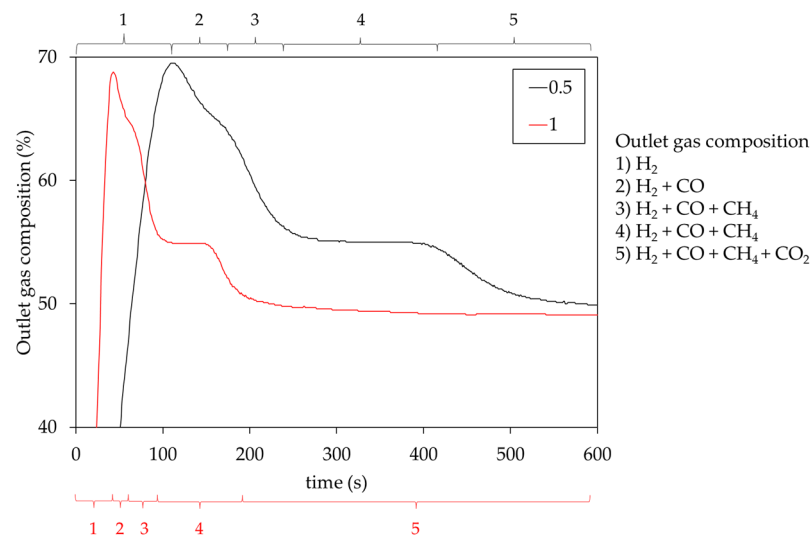


Figure 7. Breakthrough curves of H_2 using GAC at different gas flow rates: 0.5 L/min and 1 L/min. The different phases during which the gases shown on the left are released are indicated vertically.

On the other hand, the time to achieve 97% bed saturation decreased from 2329 s at 0.5 L/min to 1272 s at 1 L/min, highlighting that higher flow rates accelerate the saturation of the adsorbent bed. Other studies [47,48] confirm that lower flow rates enhance the effective adsorption capacity of activated carbon by improving the diffusion and mass transfer of gas molecules to the active sites within the carbon's pores. As a result, more CO_2 is captured before the bed saturates, leading to longer breakthrough and saturation times. This finding aligns with research [49,50] indicating that reduced flow rates allow for increased time for diffusion and adsorption within the pores of the adsorbent. For example, a study on CO_2 and CH_4 adsorption on coconut-shell-based activated carbon found that higher adsorption capacities were achieved at lower flow rates, improving the separation of gas mixtures like CO_2 and CH_4 [51]. This study found that the breakthrough time for CO_2 was approximately 18 min, while for CH_4 it was around 6 min, and as the flow rate increases, these breakthrough times tend to decrease. Additionally, adsorption studies [48,52] with other gases have demonstrated that the lower flow rate extends break-

through times, which can enhance adsorption efficiency and bed saturation. The observed differences in breakthrough times are influenced by the molecular characteristics of the gases and the adsorption environment. CO₂ exhibits the longest breakthrough times due to its high quadrupole moment and stronger interaction with the adsorbent surface, particularly in micropores [53]. In contrast, CH₄, being non-polar, has weaker adsorption interactions, resulting in shorter breakthrough times [54]. These trends are further modulated by the structural properties of the adsorbents [55]; GAC's larger surface area and mesoporous distribution prolong breakthrough times compared to PAC's more compact structure.

For pelletized activated carbon (PAC) (Figure 8), the breakthrough time was nearly constant, with 22 s at 0.5 L/min (Figure 8a) and 15 s at 1 L/min (Figure 8b), suggesting that the pelletized form may have a reduced capacity to adsorb gases effectively under different flow conditions, possibly due to its lower surface area and pore accessibility. For example, Nguyen et al. [56] found that pelletized activated carbon-based materials may exhibit reduced gas adsorption capacity under varying flow conditions due to oxidation stability and resistance to aggregation. In the case of saturation times, a similar trend was observed, with breakthrough times of 776 s at 0.5 L/min and 573 s at 1 L/min, indicating that lower feed rates allow for more extended adsorption periods before saturation occurs.

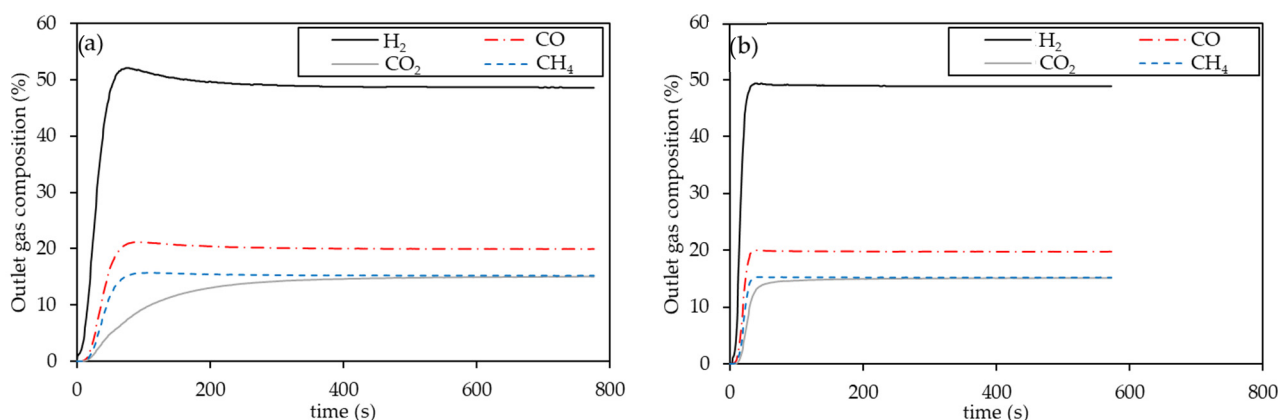


Figure 8. Breakthrough curves of PAC at different gas flow rates: (a) 0.5 L/min; (b) 1 L/min.

In contrast to the granular carbon, the different adsorption phases of the other gases, i.e., the selectivity in the adsorption process, were not so pronounced. In this case, PAC showed a similar behavior towards CO and CH₄. Additionally, adsorption of both CO and CH₄ was also observed for GAC (Figure 6) at both flow rates (0.5 L/min and 1 L/min), though the adsorption was more significant at the lower flow rate of 0.5 L/min. Specifically, the breakthrough time for CO was 90 s at 0.5 L/min and 40 s at 1 L/min. Methane exhibited a slightly higher breakthrough time compared to CO, with values of 164 s at 0.5 L/min and 68 s at 1 L/min. This highlights the versatility of GAC in adsorbing multiple gases simultaneously. The ability of GAC to adsorb both CO and methane further emphasizes its utility in multi-gas adsorption processes. This is in line with previous studies [57,58] that have demonstrated the efficiency of activated carbon materials in adsorbing various impurities, such as CO₂, CO, and CH₄, in syngas or hydrogen purification processes. Baamran et al. [59] found that activated carbons can achieve high purity levels of hydrogen (99.6%) while selectively adsorbing CO₂, CO, and CH₄, with a selectivity order of CO₂ > CH₄ > CO. The difference observed in this research in breakthrough times between CO and CH₄ at the same flow rates can be attributed to their molecular size and adsorption affinity. Methane, being larger and less polar than CO, typically has a longer breakthrough time [60], which aligns with the findings from other authors [47], who have also noted that larger, non-polar molecules tend to adsorb more slowly compared to smaller, more polar molecules like CO. The findings of this research suggest that slower feed rates are preferable for maximizing the adsorption capacity, especially in processes where multiple impurities, such as CO and methane, need to be removed.

Summarizing, granular activated carbon (GAC) demonstrates superior adsorption capacity for multiple gases, such as CO and CH₄, compared to pelletized carbon (PAC). This can be due to the fact that GAC presents a higher surface area [51], favorable pore distribution [52,61] with pores of all sizes, both micro and mesopores, and superior mass transfer properties [51]. It is important to point out that the size of AC particles also plays an important role; smaller particles exhibited higher adsorption rates at lower flow rates, emphasizing the importance of both flow dynamics and particle characteristics in optimizing adsorption processes [49].

4.3. Adsorption Kinetics Analysis

Figures 9 and 10 show the experimental data fitting to all kinetics models for both adsorbents, PAC (pelletized activated carbon) and GAC (granular activated carbon). The kinetic parameters and correlation coefficients for each model are summarized in Tables 4 and 5. The evaluation of model applicability was conducted through the correlation coefficient (R^2) and the agreement between experimental and theoretical values of equilibrium adsorption capacity (q_e) through statistical measures such as the sum of squared errors (SSE) and the chi-square (χ^2) test.

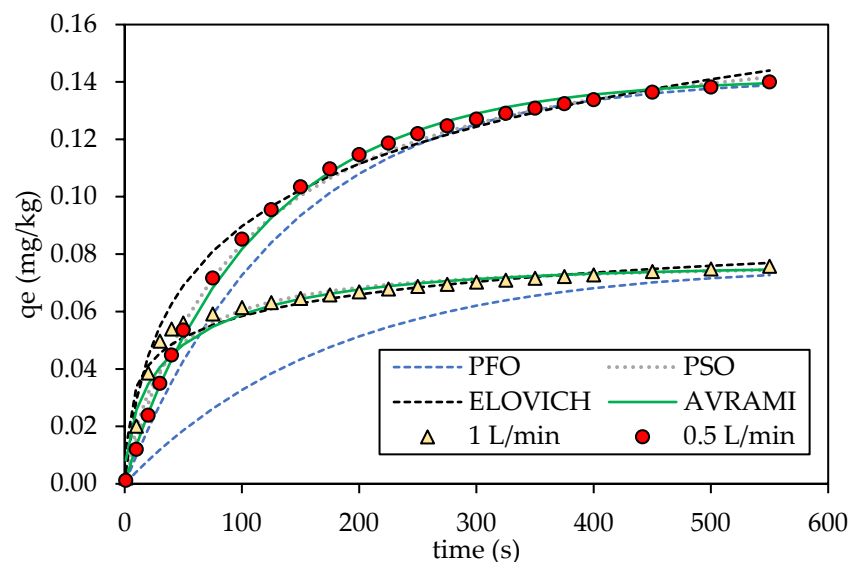


Figure 9. Fitting results for experimental data of PAC at different gas flow rates.

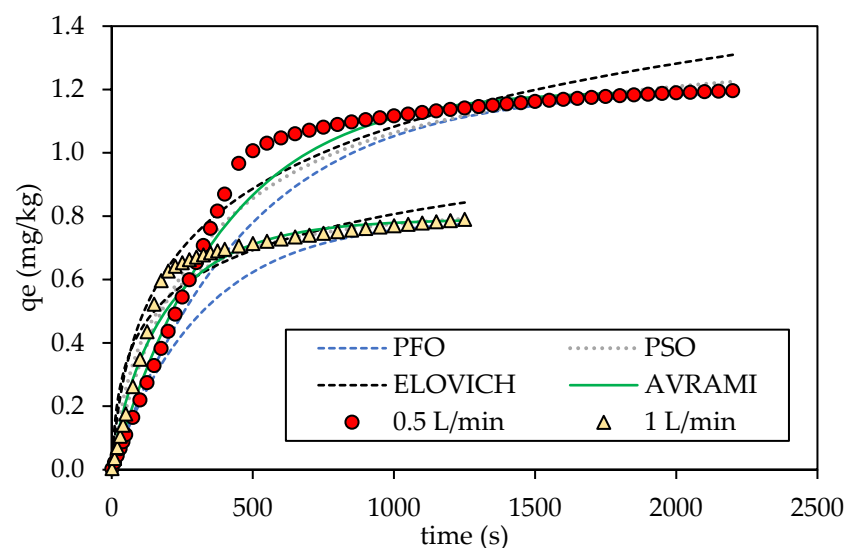


Figure 10. Fitting results for experimental data of GAC at different gas flow rates.

Table 4. Comparison of kinetic model constants for PAC.

Kinetic Model	Parameters	Flow Rate	
		0.5 L/min	1 L/min
Experimental	q_e (mg/kg)	0.1415	0.0763
Pseudo-First Order	q_e (mg/kg)	0.1221	0.0304
	k_1 (s ⁻¹)	0.0725	0.056
	R^2	0.9929	0.9585
	SSE	0.2294	1.2002
	χ^2	38.7799	7879.7
Pseudo-Second Order	q_e (mg/kg)	0.1675	0.0785
	k_2 (kg/mg·s)	0.0594	0.4280
	R^2	0.9974	0.9989
	SSE	0.0024	0.0037
	χ^2	1.2449	2.1715
Elovich	q_e (mg/kg)	0.1469	0.0774
	α (mg/kg·s)	0.0047	0.0431
	β (kg/mg)	30.395	91.743
	R^2	0.9683	0.9346
	SSE	0.0204	0.0046
Avrami	χ^2	168,740	4.7607
	q_e (mg/kg)	0.1402	0.0747
	k_A (L/mg·s)	0.0080	0.0071
	n	0.9401	0.5571
	R^2	0.9959	0.9290
	SSE	0.0019	0.0043
	χ^2	0.5465	4.0798

Table 5. Comparison of kinetic model constants for GAC.

Kinetic Model	Parameters	Flow Rate	
		0.5 L/min	1 L/min
Experimental	q_e (mg/kg)	1.2000	0.7916
Pseudo-First Order	q_e (mg/kg)	0.8163	0.4149
	k_1 (s ⁻¹)	0.0021	0.0031
	R^2	0.9603	0.9455
	SSE	330.63	175.14
	χ^2	788.59	2446.2
Pseudo-Second Order	q_e (mg/kg)	1.4021	0.8687
	k_2 (kg/mg·s)	0.0022	0.0095
	R^2	0.9823	0.9941
	SSE	10.606	1.4214
	χ^2	36.486	14.099
Elovich	q_e (mg/kg)	1.3259	0.8462
	α (mg/kg·s)	0.0116	0.0215
	β (kg/mg)	3.4211	6.0423
	R^2	0.9028	0.9065
	SSE	21.547	3.4444
Avrami	χ^2	623.97	47.113
	q_e (mg/kg)	1.1974	0.7867
	k_A (L/mg·s)	0.0026	0.0044
	n	1.0189	0.8594
	R^2	0.9731	0.9519
	SSE	5.2638	1.8741
	χ^2	12.369	12.666

It can be observed that the pseudo-first order and Elovich kinetic models exhibit poor fits for PAC and GAC, suggesting that the adsorption mechanism involves more complex interactions between the adsorbate (CO_2) and the adsorbents than these models can capture [62]. This aligns with previous research [63], which shows that first-order kinetics often fail to describe the behavior of chemisorption-dominated processes.

The experimental results are more consistent with pseudo-second order (PSO) and Avrami kinetic models. The PSO model, in particular, suggests that the adsorption process is governed by surface reactions and chemisorption at the gas–solid interface [64]. This model assumes that adsorption rates are controlled by the availability of active sites on the adsorbent and that chemical interaction rather than simple physical adsorption is the rate-limiting step. The Avrami kinetic model indicates that carbon dioxide adsorption is a complex, multi-path adsorption process [27].

In the case of PAC (Figure 6), the pseudo-second-order kinetic model not only provided higher R^2 values but also demonstrated better agreement between experimental and calculated values through lower SSE and χ^2 values. This suggests that the adsorption of CO_2 on PAC is strongly influenced by chemisorption mechanisms, possibly involving the formation of bicarbonate ions on the surface due to the interaction between CO_2 and the adsorbent surface. This aligns with other studies [59,62,63] that have shown that CO_2 adsorption on porous materials like activated carbon often involves chemical modifications on the surface.

For GAC, however, the Avrami kinetic model provided a better fit (Figure 10), with improved agreement between the theoretical and experimental q_e values (Table 5). The Avrami model suggests that the adsorption process for GAC involves multiple pathways, including surface diffusion, intra-particle diffusion, and chemisorption [65]. This more complex, multi-path adsorption process was also observed by Serna-Guerrero et al. [66], who applied the Avrami kinetic model to describe the CO_2 adsorption on amine-functionalized mesoporous silica gel. Wei et al. [17] proposed the Avrami kinetic model for activated carbon.

Additionally, the comparison between the pseudo-second-order model for PAC and the Avrami model for GAC highlights the differences in adsorption mechanisms between these two adsorbents. While PAC appears to rely more heavily on chemical interactions (as suggested by the pseudo-second-order model), GAC involves a combination of both physical and chemical processes, which is captured more effectively by the Avrami model. This difference may be attributed to the varying surface characteristics and pore structures of the adsorbents, which influence their respective adsorption capacities and mechanisms. This finding confirmed that the particle size range plays an essential role in the adsorption process. Similar results were found by Ha et al. [49].

4.4. Diffusion Analysis

The Boyd diffusion model, inter-particle diffusion model, and Weber–Morris intra-particle diffusion model were employed to better understand the mechanism involved in the CO_2 adsorption process, particularly in identifying potential rate-controlling steps.

The plot of B_t versus time for both GAC and PAC adsorbents at varying gas flow rates, as shown in Figure 11, illustrates different adsorption behaviors. At a gas flow rate of 1 L/min, the plots show significant deviations from linearity, indicating non-ideal behavior. However, at lower flow rates (0.5 L/min), the adsorption process exhibits a more linear trend, although the plot does not pass through the origin (Table 6). This suggests that at lower flow rates, the adsorption process is closer to ideal conditions, potentially due to the increased contact time between the gas and adsorbent, allowing for more complete diffusion. Despite the linearity observed at lower flow rates, the fact that the plots do not pass through the origin implies that intraparticle diffusion is not the sole rate-controlling step, consistent with the Boyd diffusion model's conclusion that film diffusion is not the dominant mechanism [29]. The findings are in agreement with Rashidi et al. [67], who evaluated the mechanism of CO_2 adsorption on activated carbon and found non-linear fittings, concluding that more than one process affected the CO_2 adsorption.

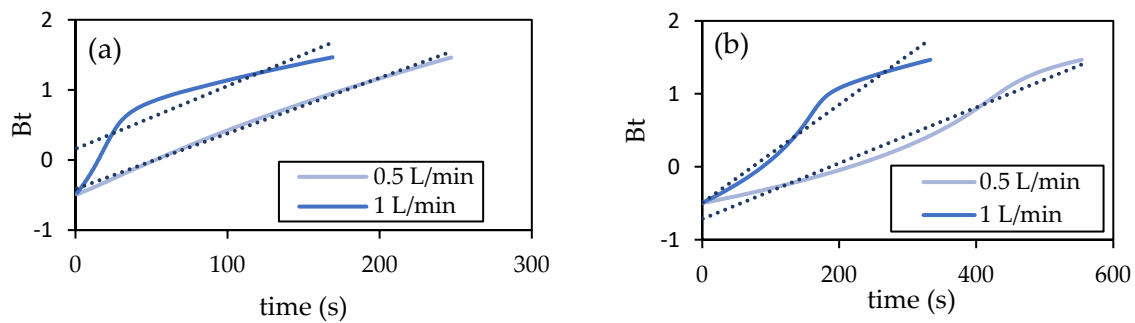


Figure 11. Boy diffusion model plots at different gas flow rates and linear regression (dotted line): (a) PAC; (b) GAC.

Table 6. Fitting parameters for Boyd film diffusion model for both adsorbents.

Adsorbent	Parameters	Flow Rate	
		0.5 L/min	1 L/min
PAC	slope	0.0090	0.0079
	intercept	0.1586	−0.4149
	R^2	0.8242	0.9947
GAC	slope	0.0038	0.0067
	intercept	−0.7163	−0.4958
	R^2	0.9695	0.9597

The findings of this research suggest that diffusion within the pores plays a more significant role in the adsorption process, especially at higher velocities where film diffusion limitations are minimal. Similar studies have reported comparable findings, where lower flow rates tend to promote linear behavior due to the extended time for gas-adsorbent interactions, allowing diffusion processes to proceed more efficiently [68,69]. For example, Tobarammekul et al. [70] found that the diffusion time of CO₂ with a flow rate of 1 L/h was longer than at 5 L/h, which led to an enhanced CO₂ adsorption capacity, suggesting that a slower flow rate allows more time for CO₂ to diffuse and interact with the adsorbent's surface and pores. This prolonged interaction time improves the adsorption efficiency because the gas molecules have more opportunity to enter and diffuse within the pores of the adsorbent, leading to a higher adsorption capacity.

The application of the interparticle diffusion model to CO₂ adsorption on activated carbon is shown in Figure 12.

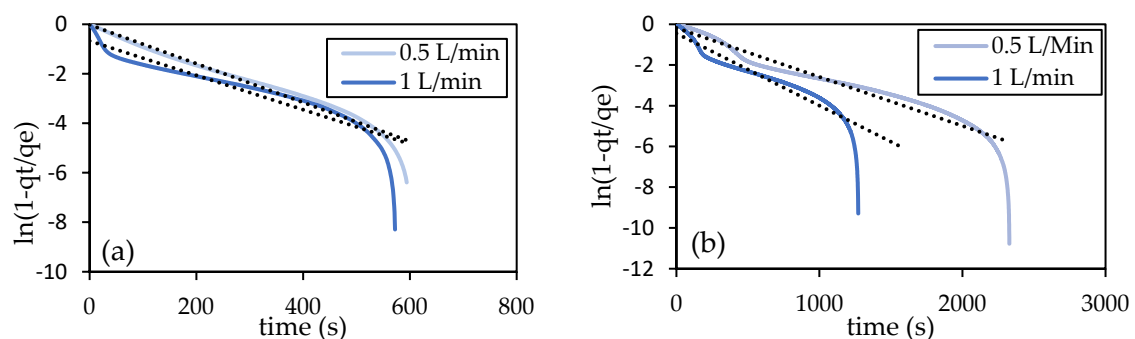


Figure 12. Interparticle diffusion model plots at different gas flow rates and linear regression (dotted line): (a) PAC; (b) GAC.

The results indicate that the plots do not exhibit linearity, and the intercept values deviate from the expected $\ln(6/\pi^2)$, suggesting that interparticle diffusion is not the rate-limiting step for CO₂ capture in both GAC and PAC. Instead, other mechanisms, such

as surface adsorption or intraparticle diffusion, are likely to govern the rate-limiting step in this process. Similar conclusions have been reached in other studies [66], where non-linearity in the plots also indicated that inter-particle diffusion was not dominant in CO₂ adsorption on porous materials, pointing instead to multi-step adsorption mechanisms or the significance of pore structure on adsorption behavior. Choi et al. [71] explored the efficiency of GAC in capturing multiple gases, focusing on pore distribution and surface area. They found that both surface adsorption and pore diffusion contribute to the overall kinetics of CO₂ capture on activated carbon, and intraparticle diffusion plays a significant role in the adsorption process, but it is not the sole rate-limiting step.

According to Weber–Morris intraparticle diffusion, adsorption typically involves two key stages: (1) the transport of adsorbate molecules from the bulk gas phase to the surface of the adsorbent and (2) the subsequent diffusion of the molecules into the internal pores of the adsorbent. The model assumes that if intraparticle diffusion is the only rate-limiting step, the plot of adsorption capacity (q_t) versus the square root of the time ($t^{1/2}$) should yield a straight line passing through the origin. However, in most cases, the lines deviate from the origin. This deviation suggests that the intra-particle diffusion was not the sole rate-limiting mechanism.

In this study, the linear plots generated from the experimental data (Figures 13 and 14) obtained correlation coefficient (R^2) varies from 0.846 to 0.967 and showed deviations from the origin with intercept values ranging from -0.0027 to 0.2396 mg/kg (Table 7), suggesting that the adsorption process is controlled by more than one step; other factors like external mass transfer, boundary layer resistance, and surface adsorption also contribute to the overall process. This finding is consistent with other studies [66], which also highlight the involvement of surface adsorption and boundary layer diffusion in addition to intra-particle diffusion.

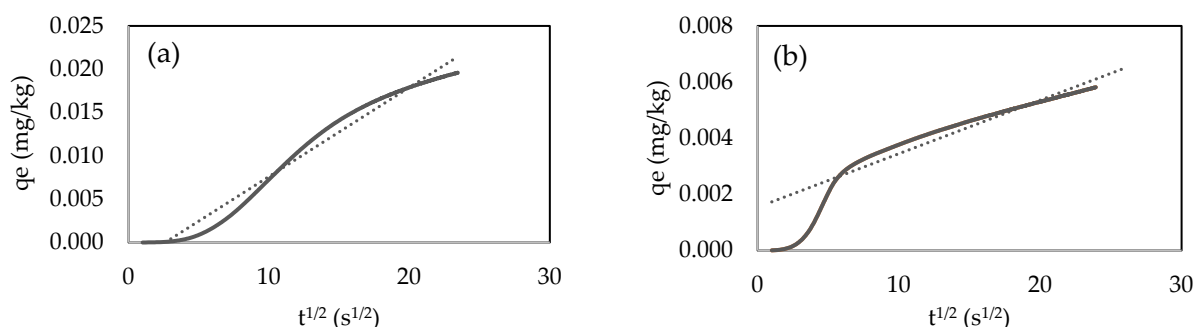


Figure 13. Weber–Morris model plots for PAC at different gas flow rates and linear regression (dotted line): (a) 0.5 L/min; (b) 1 L/min.

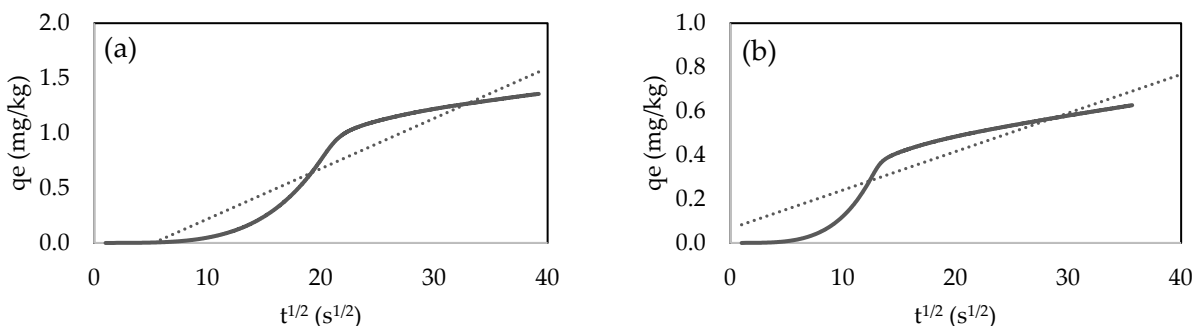


Figure 14. Weber–Morris model plots for GAC at different gas flow rates and linear regression (dotted line): (a) 0.5 L/min; (b) 1 L/min.

Table 7. Summary of Weber–Morris diffusion model for both adsorbents.

Adsorbent	Parameters	Flow Rate	
		0.5 L/min	1 L/min
PAC	k_{WM} (mg/kg·s ^{0.5})	0.0010	0.0002
	C (mg/kg)	−0.0027	0.0015
	R^2	0.9671	0.8956
	SSE	2.2696	6.4600
	χ^2	108,747	74,417
GAC	k_{WM} (mg/kg·s ^{0.5})	0.0458	0.0175
	C (mg/kg)	−0.2396	0.0654
	R^2	0.8964	0.8458
	SSE	332.17	56.959
	χ^2	2365.8	351.50

On the other hand, it can be observed that the presence of different linear regions in the plots of Figures 13 and 14 indicated that more than one mechanism was contributing to the adsorption process, which occurs in three steps where each region corresponds to a different adsorption mechanism. This behavior is consistent with findings from other studies, which also observed multi-step adsorption processes [49,72]. In general, the first region reflects the external surface adsorption or boundary layer diffusion, where the adsorbate rapidly adheres to the external surface of the adsorbent. The second region usually represents intra-particle diffusion within the mesopores, where diffusion slows down as the adsorbate penetrates deeper into the adsorbent's structure. The third region indicates the final equilibrium stage, where the adsorption rate becomes very slow as the active sites on the adsorbent are nearly saturated. This final stage is controlled primarily by diffusion within the micropores, where the adsorbate finds fewer available sites and must diffuse more slowly into the fine pore structures [73,74]. To analyze the adsorption mechanism of both adsorbents, the values for each stage of the linear plot are presented in Tables 8 and 9, detailing the slope, intercept, and correlation coefficient (R^2) for every adsorption stage.

The granular activated carbon (GAC) exhibited significantly higher slope values for the second stage (0.0590 and 0.0591 for both flow rates), while pelletized activated carbon (PAC) showed much lower values (0.0097 and 0.0114). The higher slope in the second region for GAC indicates a much more rapid adsorption process during this phase, suggesting that the rate-limiting step during this middle stage of adsorption may involve faster diffusion into mesopores. In contrast, PAC shows slower mesopore diffusion, likely due to its more compact structure. This finding is in accordance with the results of Egrani et al. [75].

Table 8. Intraparticle diffusion parameters for CO₂ adsorption at different stages for PAC.

Adsorption Stages	Parameters	Flow Rate	
		0.5 L/min	1 L/min
1st	$k_{WM,1}$ (mg/kg·s ^{0.5})	0.0042	0.0074
	C (mg/kg)	−0.0033	−0.0061
	R^2	0.9847	0.9827
2nd	$k_{WM,2}$ (mg/kg·s ^{0.5})	0.0097	0.0114
	C (mg/kg)	−0.0157	−0.0138
	R^2	0.9902	0.9746
3rd	$k_{WM,3}$ (mg/kg·s ^{0.5})	0.0026	0.0011
	C (mg/kg)	0.0811	0.0503
	R^2	0.974	0.9826

Table 9. Intraparticle diffusion parameters for CO₂ adsorption at different stages for GAC.

Adsorption Stages	Parameters	Flow Rate	
		0.5 L/min	1 L/min
1st	$k_{WM,1}$ (mg/kg·s ^{0.5})	0.0085	0.0136
	C (mg/kg)	−0.0074	−0.0118
	R^2	0.9811	0.9811
2nd	$k_{WM,2}$ (mg/kg·s ^{0.5})	0.0590	0.0591
	C (mg/kg)	−0.3433	−0.2228
	R^2	0.9801	0.9776
3rd	$k_{WM,3}$ (mg/kg·s ^{0.5})	0.0077	0.00071
	C (mg/kg)	0.8671	0.5473
	R^2	0.9845	0.9698

For both adsorbents, the third region, which represents the final phase of adsorption as equilibrium is approached, has the lowest slope values. This phase represents the gradual filling of the micropores and a shift towards equilibrium. The low slope in the final region for both adsorbents suggests that intra-particle diffusion is becoming less influential, with other mechanisms (e.g., equilibrium adsorption on the surface or pore filling) being dominant. This behavior has been documented in other studies of CO₂ adsorption on different carbon-based materials [76].

Table 8 shows that PAC exhibits a steeper decline in slope at higher flow rates, indicating that it reaches the equilibrium phase quicker but with lower overall adsorption capacity. On the other hand, GAC (Table 9) maintains a higher adsorption rate into the second phase, demonstrating its superior capacity for handling multi-gas adsorption. The superior performance of GAC can be attributed to its larger surface area and better pore distribution, allowing for more efficient adsorption over a wider range of conditions [77].

5. Conclusions

This study demonstrates the superior adsorption capacities for CO₂, CO, and CH₄ of granular activated carbon (GAC) over pelletized activated carbon (PAC) for syngas purification derived from glycerol reforming. The larger surface area, mesoporous distribution, and optimized pore structure of GAC resulted in a CO₂ adsorption capacity of 156.3 mg/g at a flow rate of 0.5 L/min, significantly higher than the 92.4 mg/g achieved by PAC under the same conditions. Furthermore, breakthrough times for CO₂ were 462 s for GAC and 157 s for PAC at a flow rate of 1 L/min, highlighting GAC's ability to extend gas retention and improve adsorption efficiency in multi-gas systems.

Kinetic analysis revealed distinct adsorption behaviors for the two adsorbents. The pseudo-second-order model best described PAC, indicating chemisorption as the dominant mechanism. In contrast, GAC followed the Avrami kinetic model, reflecting a more complex, multi-path adsorption process that incorporates surface adsorption and intraparticle diffusion. Diffusion studies using the Boyd, interparticle diffusion, and Weber–Morris confirmed that adsorption in both adsorbents involves multiple mechanisms, with intraparticle diffusion playing a significant but not exclusive role in limiting the adsorption rate.

The results of this research confirm GAC's suitability for industrial hydrogen purification processes requiring efficient multi-gas removal and prolonged breakthrough times. The study underscores the importance of particle size, surface area, and pore structure in optimizing adsorption efficiency for cleaner energy production.

6. Future Perspectives

This study provides valuable insights into the adsorption performance of GAC and PAC for hydrogen purification. However, future research should extend these findings by exploring a broader range of operational conditions, such as higher pressures, diverse flow rates, and syngas compositions, to evaluate performance under industrial scenarios.

Additionally, incorporating adsorbents with varying surface chemistries or functionalizations could provide deeper insights into the selectivity and efficiency of multi-gas removal processes. For example, hybrid systems combining GAC with complementary technologies, such as pressure swing adsorption or membrane separation, could be tested to optimize hydrogen purity and throughput simultaneously.

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