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ADSORPTION OF 2,4- DICHLOROPHENOXYACETIC ACID (2,4-D) HERBICIDE ON ACTIVATED CARBON OF BRAZIL NUT SHELL

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ABSTRACT

Activated carbon is a material with a high fixed carbon content and large surface area, whose capacity for adsorbing organic compounds depends on the precursor material and the process it undergoes. 2,4-D is a molecule associated with numerous health hazards and is widely used in Brazil for weed control. In rural areas, its use can lead to contamination of surface and groundwater. This study aimed to evaluate the adsorption potential of 2,4-dichlorophenoxyacetic acid (2,4-D) using carbon derived from Brazil nut shell activated at 800 °C, comparing activation atmospheres of water steam and CO_2. Activated carbons, both with water steam and CO_2, were characterized in terms of pore diameter distribution using the Brunauer–Emmett–Teller (BET) theory, morphology by scanning electron microscopy (SEM), and thermal stability by thermogravimetric analysis (TGA). The activated carbons with steam and CO_2 presented high surface areas (397 ± 8 m²/g and 325 ± 7 m²/g, respectively). The micrographs showed high porosity in the activated carbons, and the loss of only 20% of their mass in the thermogravimetric test confirmed the material's thermal stability. The adsorption kinetics assay was performed by High-Performance Liquid Chromatography (HPLC) over time ranging from 0 to 120 minutes. The equilibrium time was 45 minutes for water steam-activated carbon, achieving 92.51% removal, and 120 minutes for CO_2-activated carbon with 84.81% of 2,4-D removed. The pseudo-second-order kinetic model best fit the data.

Keywords: Adsorption, Herbicide, Potability

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ADSORÇÃO DO HERBICIDA 2,4-D ÁCIDO 2,4-DICLOROFENOXIACÉTICO EM CARVÃO ATIVADO DA CASCA DA CASTANHA-DO-BRASIL

RESUMO – Carvão ativado é um material com elevado teor de carbono fixo e alta área superficial, cuja capacidade de adsorção de compostos orgânicos é dependente do material precursor e do processo a que é submetido. O 2,4-D é uma molécula que está associada à inúmeros danos à saúde humana e é amplamente utilizado no Brasil para o controle de plantas daninhas. Em áreas rurais seu uso pode levar a contaminação de águas superficiais e subterrâneas. Neste trabalho teve-se por objetivo avaliar o potencial de adsorção do ácido 2,4-diclorofenoxiacético (2,4-D) pelo carvão da casca da amêndoa da castanha-do-brasil ativado à 800ºC comparando-se as atmosferas de ativação por vapor d'água e CO_2. Os carvões ativados tanto com vapor quanto com CO_2 foram caracterizados quanto à distribuição de diâmetros de poros pela Teoria de Adsorção Multimolecular (BET), morfologia através de microscopia eletrônica de varredura (MEV) e estabilidade térmica por análise termogravimétrica (TGA). Os carvões ativados com vapor e CO_2 apresentaram elevadas áreas superficiais (397 ± 8 m^2/g e 325 ± 7 m^2/g, respectivamente). As micrografias demonstraram alta porosidade dos carvões ativados e a perda de apenas 20% de sua massa no teste de termogravimetria comprovou a estabilidade térmica do material. O ensaio de cinética de adsorção foi realizado por Cromatografia de Alta Eficiência (CLAE) nos tempos de 0 a 120 minutos. O tempo de equilíbrio foi de 45 minutos para o carvão ativado com vapor d'água, alcançando 92,51% de remoção e 120 minutos para o carvão ativado com CO_2 com 84,81% de 2,4-D removido. O modelo de cinética de pseudo-segunda ordem apresentou o melhor ajuste dos dados.

Palavras-Chave: Adsorção, Herbicida, Potabilidade

1. INTRODUCTION

The intensive use of agrochemicals in Brazil has raised concerns among professionals across various fields due to the potential risks these substances pose to both the environment and human health. Contaminated water used for human consumption represents a significant route of exposure (Fernandes Neto and Sarcinelli, 2009).

Given the essential role of water in biological systems, its quality, especially regarding the absence of contaminants is critical, with agrochemicals among the most impactful pollutants. Despite these risks, the indiscriminate use of pesticides remains the primary strategy for pest control and prevention in agriculture (Graymore et al., 2001). The herbicide 2,4-dichlorophenoxyacetic acid (2,4-D) is widely used to control weeds in crops, noted for its rapid action and low cost, which are key advantages (Kashyap et al., 2005). However, pesticides are harmful to humans, and studies have shown that their presence in drinking water can lead to adverse effects on the central and peripheral nervous systems, have immunosuppressive effects, or even be carcinogenic (Chiu et al., 2004; Kato et al., 2004; Merhi et al., 2007).

The 2,4-D is a selective, systemic, post-emergent herbicide belonging to the phenoxyacetic class. It can persist in the environment for several months, exhibiting residual activity in soil and water due to low rates of microbial degradation (Amarante Junior et al., 2002).

Among the various available treatment methods, such as slow filtration and membrane separation processes, activated carbon adsorption stands out. This technology is regarded as one of the most effective and reliable water treatment systems for the removal of micro-contaminants and is favored for its operational efficacy (Ren et al., 2011).

Activated carbon is widely used in water treatment due to its high adsorptive capacity (Saka, 2012). This material is commonly applied globally in wastewater treatment, potable water processing, gas purification, and as a support in catalysis (Olivares-Marin et al., 2009).

In Brazil, Brazil nuts are an economically significant non-timber forest product. These seeds are collected and processed in regional agroindustries. Approximately 33,000 tons of Brazil nut seeds are harvested annually, with about half considered waste (IBGE, 2021). One potential use for this byproduct is in water purification.

Activated carbon derived from Brazil nut shells, pyrolyzed at 600, 700 and 800 °C and activated by steam and CO_2, was developed and characterized in terms of its physicochemical properties, achieving yields above 84% (w/w), basic pH, a density of 0.23±0.03 g/cm³, and a large surface area. The best results were obtained for activated carbon produced at 800 °C in both activation atmospheres, making these the selected samples for evaluating the adsorption of 2,4-D.

The objective of this study was to assess the adsorption potential of activated carbon from Brazil nut shells for the removal of 2,4-dichlorophenoxyacetic acid, a herbicide widely used in agriculture and known for its potential to contaminate water sources.

2. MATERIAL AND METHODS

The carbon was produced from Brazil nut shells (*Bertholletia excelsa*). The raw material's particle size was heterogeneous, ranging from 4 to 65 mm, as the shells were used in their natural state. Samples of 300 ± 5 g of shell were placed in a metal crucible measuring 340 mm in length and 68 mm in internal diameter (Fortelab model T-1200/H–1z) and heated at a rate of 10 °C/min to reach target temperatures of 600 °C, 700 °C, and 800 °C. After reaching these temperatures, the material was held at the set temperature for an additional 30 minutes to complete pyrolysis. Two atmospheres were used to activate the carbon: a) steam, generated in a vertical boiler (EIT) at 1 Kgf/cm², and b) commercial CO_2 at a pressure of 0.58 Kgf/cm², for 40 minutes (Castro et al., 2023).

The specific surface areas of the activated carbon were determined using the Brunauer, Emmett, and Teller (BET) method, while micropore size distribution was analyzed through Density Functional Theory (DFT). The samples were preheated at 120 °C under vacuum for 12 hours, and nitrogen adsorption isotherms were obtained at nitrogen's boiling point using the Micromeritics Tristar II Kr 3020 instrument.

Thermogravimetric analysis (TA Instruments SDT Q600) and Scanning Electron Microscopy (SEM, Jeol JSM 6060) were conducted on samples produced at 800 °C for each activation method, as these samples demonstrated the best results in terms of proximate analysis, pH, density, infrared spectra, and surface area in the BET test (Castro et al., 2023).

For the adsorption study, 0.01 g of activated carbon was added to 20 mL of water containing herbicide at concentrations of 2.5, 5.0, and 10.0 µg/mL in 50 mL Erlenmeyer flasks. These were placed on a mixer (SP Labor) at 150 rpm and maintained at 25 °C for 24 hours. After mixing, the samples were filtered, and the herbicide's adsorption capacity at each concentration was determined by high-performance liquid chromatography (HPLC). Tests proceeded with the 5.0 µg/mL concentration, as it showed the highest adsorption retention. The amount of carbon used for this test was determined according to ASTM D3860-98 (ASTM International, 2004).

The adsorption kinetics and equilibration time study for 2,4-D was conducted using 50 mL containers, with 20 mL of 2,4-D solution at 5 µg/mL added to each. The samples were agitated, with intervals of two minutes between each sample until a total stirring time of 30 minutes was reached. From this point, the residence time intervals were increased to five minutes up to a total of 60 minutes, after which intervals of 30 minutes were added, with the final two samples agitated for 90 and 120 minutes, respectively. After the designated time periods, the samples were filtered and analyzed using a Perkin Elmer Series 200 chromatograph set to 230 nm. The system included a stainless steel Phenomenex Luna C18 column (5 µm, 250 x 4 mm) with a Phenomenex Luna C18 (5 µm) stationary phase pre-column. The mobile phase consisted of acidified acetonitrile and water (pH 3.0) in a 90:10 v/v ratio, with a flow rate of 1.0 mL/min. The concentrations of 2,4-D were calculated using a standard calibration curve.

3. RESULTS

The specific surface area for shell was 0.35±0.05 m^2g^{-1}, for carbon at 600, 700 and 800 °C were 15±1, 61±3 and 72±3 m^2g^{-1}, respectively. The specific surface area for samples activated by CO_2 at 600, 700 and 800 °C were 90±3, 199±5 and 325±7 m^2g^{-1}, respectively. From steam activation the results were 141±4, 338±7 and 397±8 m^2g^{-1}, for samples activated at 600, 700 and 800 °C, respectively (Figure 1).

The N2 sorption/desorption isotherms of

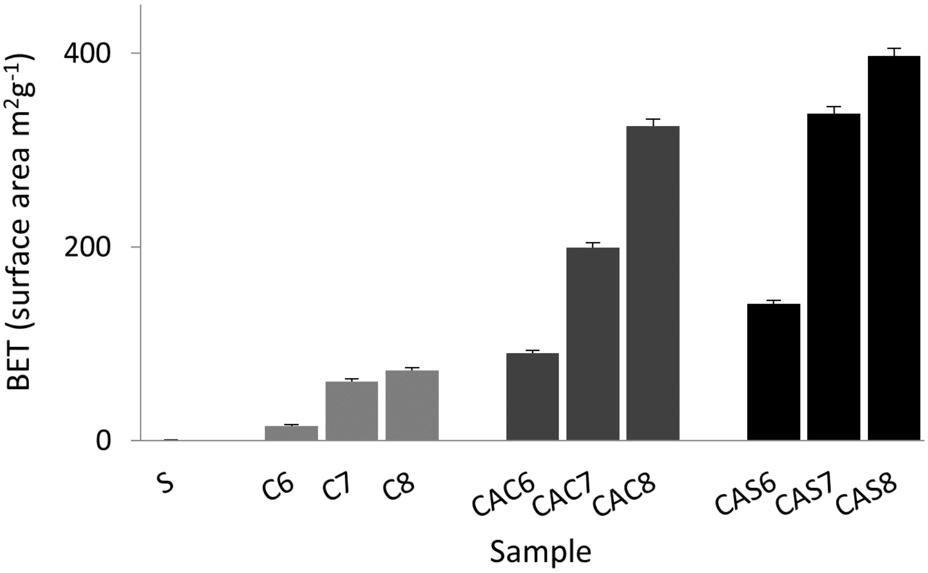


Figure 1. Surface area of the carbon produced at 600, 700 and 800 °C and activated with CO_2 or steam. S= Shell, C6= Carbon at 600 °C, C7= Carbon at 700 °C, C8= Carbon at 800 °C, CAC6= Carbon activated by CO_2 at 600 °C, CAC7= Carbon activated by CO_2 at 700 °C, CAC8= Carbon activated by CO_2 at 800 °C, CAS6= Carbon activated by steam at 600 °C, CAS7= Carbon activated by steam at 700 °C, CAS8= Carbon activated by steam at 800 °C

Figura 1. Área superficial do carvão produzido a 600, 700 e 800 °C e ativados com CO_2 ou vapor. S= Casca, C6= Carvão a 600 °C, C7= Carvão a 700 °C, C8= Carvão at 800 °C, CAC6= Carvão ativado com CO_2 a 600 °C, CAC7= Carvão ativado com CO_2 a 700 °C, CAC8= Carvão ativado com CO_2 a 800 °C, CAS6= Carvão ativado com vapor a 600 °C, CAS7= Carvão ativado com vapor a 700 °C, CAS8= Carvão ativado com vapor a 800 °C

the carbon activated by CO_2 (Figure 2A) and by steam (Figure 2B) are type I, characteristic of microporous materials, according to IUPAC classification. The isotherms for carbon activated by both atmospheres showed high adsorption of N2 under low pressures and higher intensity of porous. The intensity of porous were 1.18, 1.17 and 1.24 nm, for carbon activated by CO_2 at temperatures of 600, 700 and 800 °C, respectively. For the samples activated by steam at 600 and 700 °C, the porous of 1.18 nm and 1.00 nm for sample activated at 800 °C for the same atmosphere.

The thermogravimetric analysis demonstrates the thermal stability of the materials through the loss of mass that occurs with the increase in temperature. This loss was approximately 10% from 20 to 250 °C. The highest loss was 47% and occurred from 250 to 370 °C, at 400 and 600 °C was observed loss of 10%, and from 800 to 1000 °C there was not significant loss of mass (Figure 3).

The thermogravimetric analysis of the carbon produced at 800 °C and activated by steam showed only 20% of loss from its initial mass. Since, 60% was lost at up to 100 °C and 25% to the temperature of 750 °C and then stabilization was observed (Figure 4 A). Otherwise, in carbon produced at 800 °C and activated by CO_2 about 40% of loss occurs up to 90 °C and up to 800 °C occurs the loss of another 20% (Figure 4 B).

Surface of activated carbons showed that the cracks and the pores of samples activated by CO_2 (Figure 5.1 A, B and C) were smaller than those activated by steam (Figure 5.2 A, B and C). The last also presents the curvilinear surface with deeper pores.

The adsorption equilibrium of the herbicide solution in contact with steam-activated carbon was reached at 45 minutes, with an adsorption capacity of 8.48 mg/g (Figure 6). At equilibrium, 92.51% of 2,4-D was removed. In contrast, for the solution in contact with CO_2-activated carbon, equilibrium was reached at 120 minutes, with an adsorption capacity of 5.40 mg/g (Figure 7) and a removal rate of 84.81%. Thus, steam-activated carbon

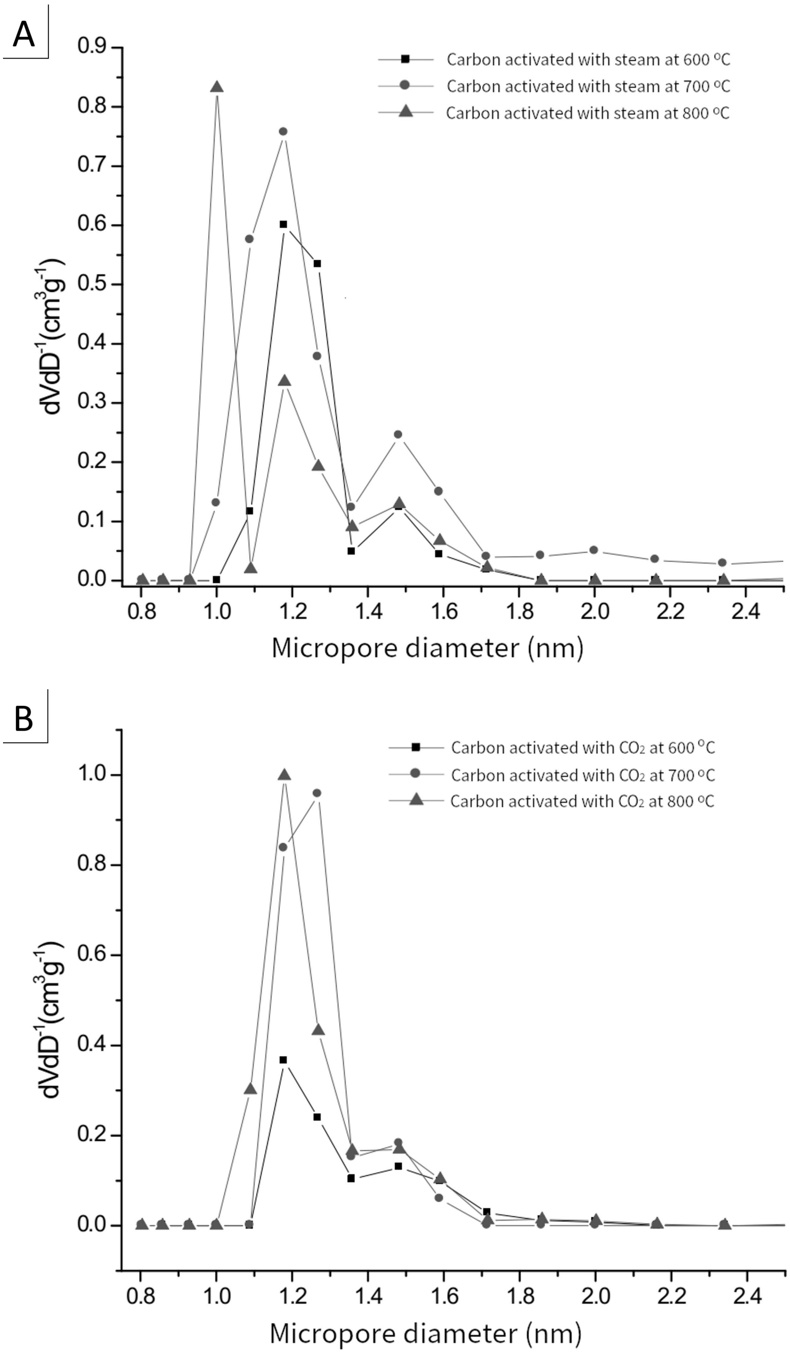


Figure 2. Polydispersion of micropore diameter for CO$_2$-activated carbon (A) and steam-activated carbon (B) at temperatures of 600, 700 and 800 °C

Figura 2. Polidispersão de diâmetro de microporos para carvão ativado por CO$_2$ (A) e por vapor (B) em temperaturas de 600, 700 e 800 °C

achieved equilibrium more quickly, with a higher adsorption capacity and a greater percentage of 2,4-D removal compared to CO$_2$-activated carbon.

The data fitted to pseudo-first-order and pseudo-second-order kinetic models for both CO$_2$- and steam-activated carbons (Figures 6 and 7) showed that the pseudo-second-order model provided the best fit. The values of K, qe, and R2 (Table 1) confirm that this model is the most appropriate to describe the adsorption kinetics of 2,4-D onto Brazil nut shell-activated carbon.

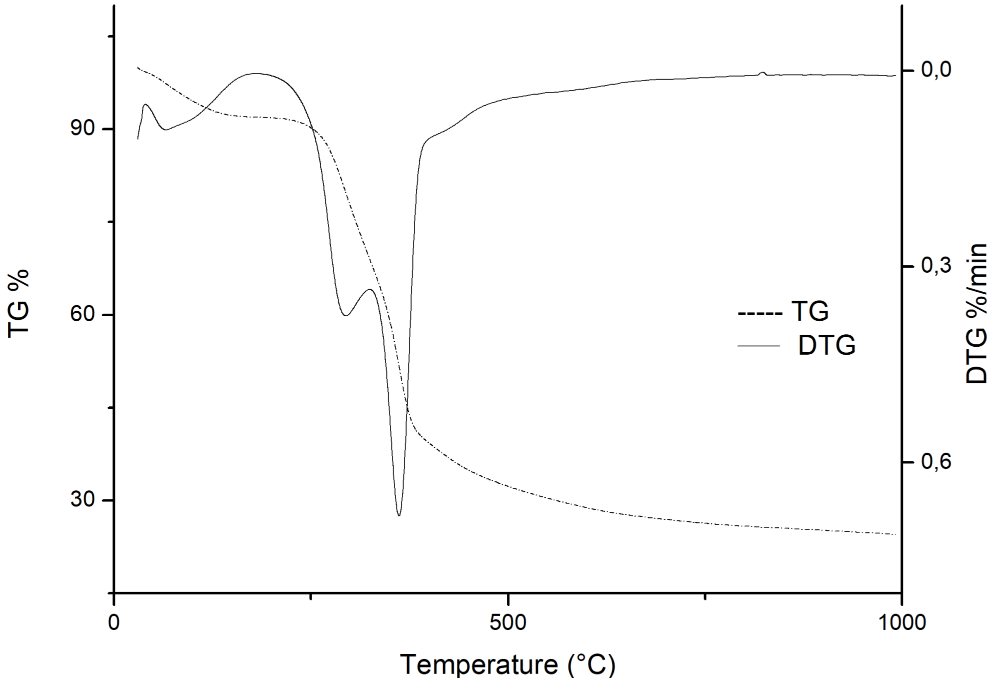
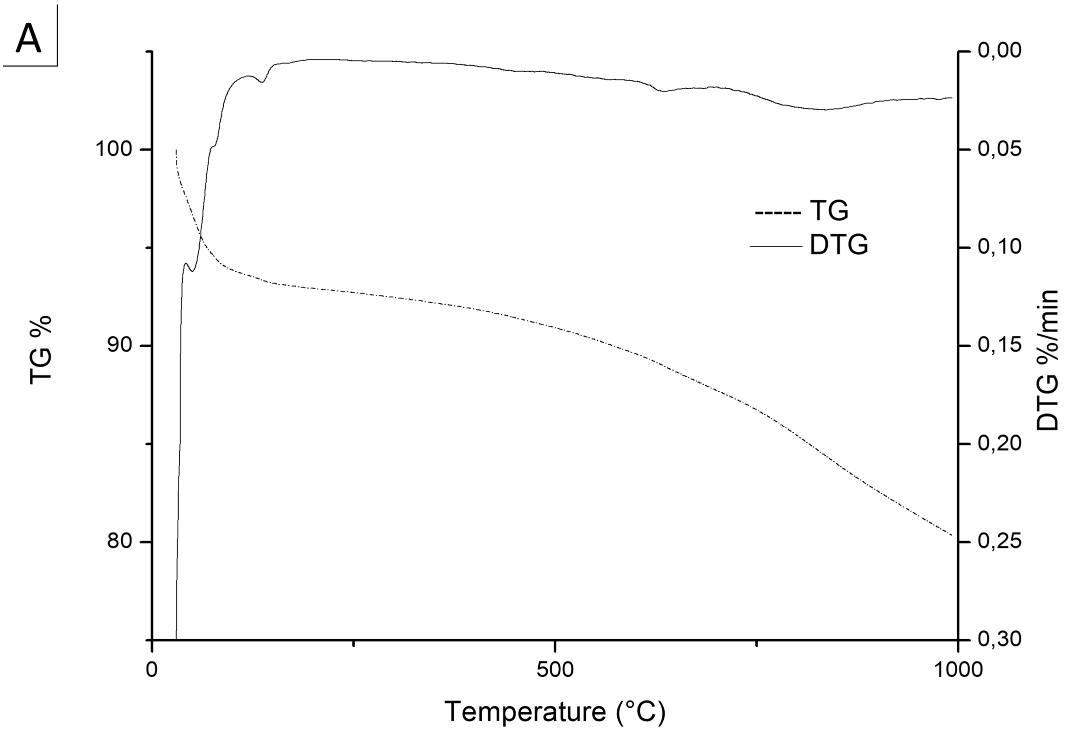


Figure 3. Brazil nut shell mass loss during the raising of the temperature from 20 to 1000 °C

Figura 3. Perda de massa da casca da Castanha-do-brasil durante o aumento da temperatura de 20 para 1000 °C



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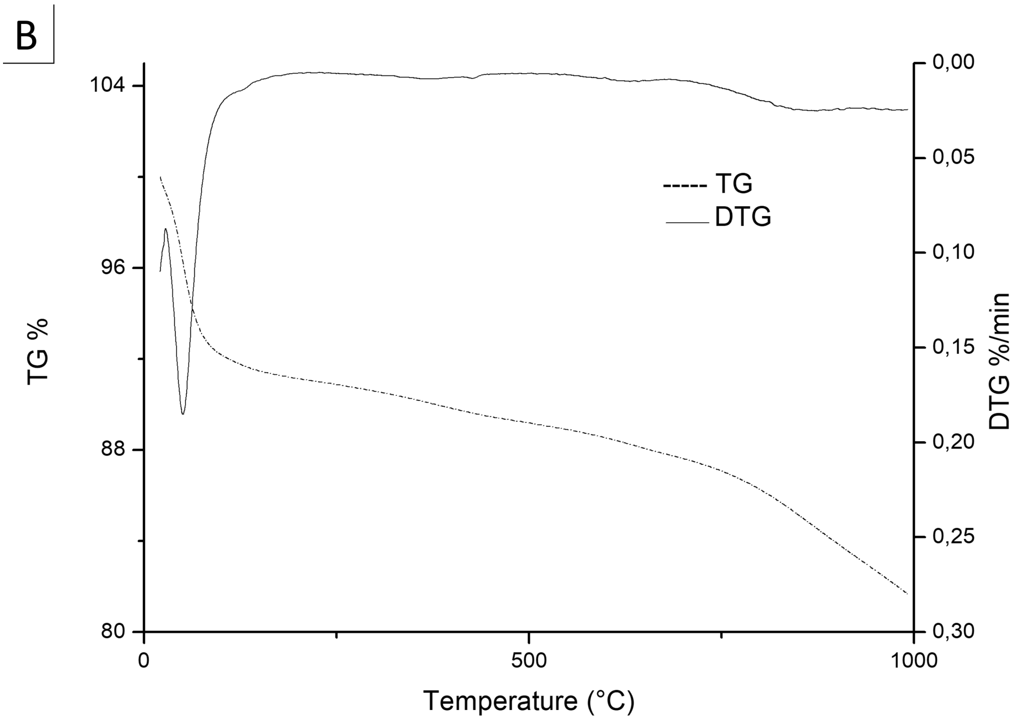

Figure 4. Mass loss of steam-activated carbon (A) and CO_2-activated carbon (B) during raising the temperature from 20 to 1000 °C

Figura 4. Perda de massa dos carvões ativados com vapor (A) e CO_2 (B) durante o aumento de temperatura de 20 para 1000 °C

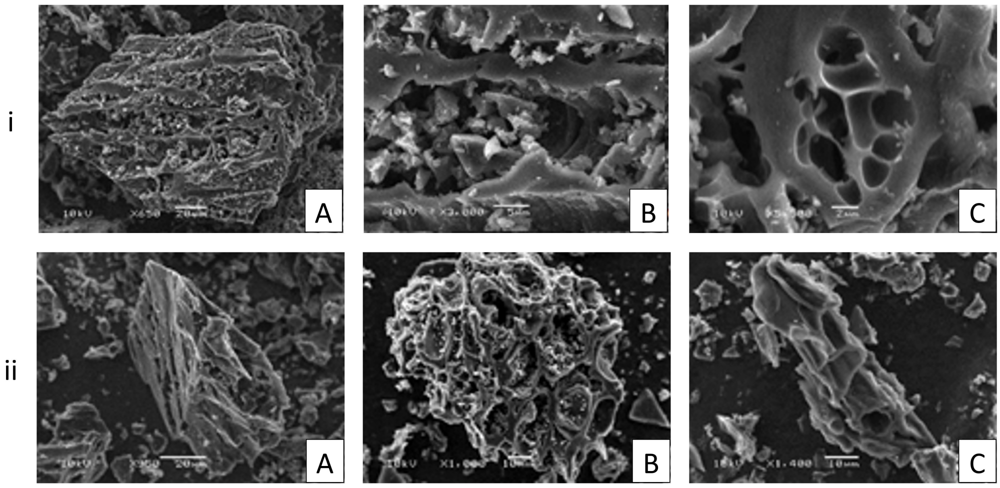

Figure 5. (i) Photomicrographs (SEM) of Brazil nut shell carbonized at 800 °C and activated by CO_2, using magnification of 650x (A), 3000x (B) and 5500x (C). (ii) Photomicrographs (SEM) of Brazil nut shell carbon, produced at 800 °C, activated by steam, using magnification of 950x (A), 1000x (B) and 1400x (C)

Figura 5. Fotomicrografias (SEM) da castanha-do-brasil carbonizada a 800 °C e ativada por CO_2, usando aumentos de 650x (A), 3000x (B) e 5500x (C). (ii) Fotomicrografias (SEM) da castanha-do-brasil carbonizada a 800 °C, ativada por vapor, usando aumentos de 950x (A), 1000x (B) e 1400x (C)

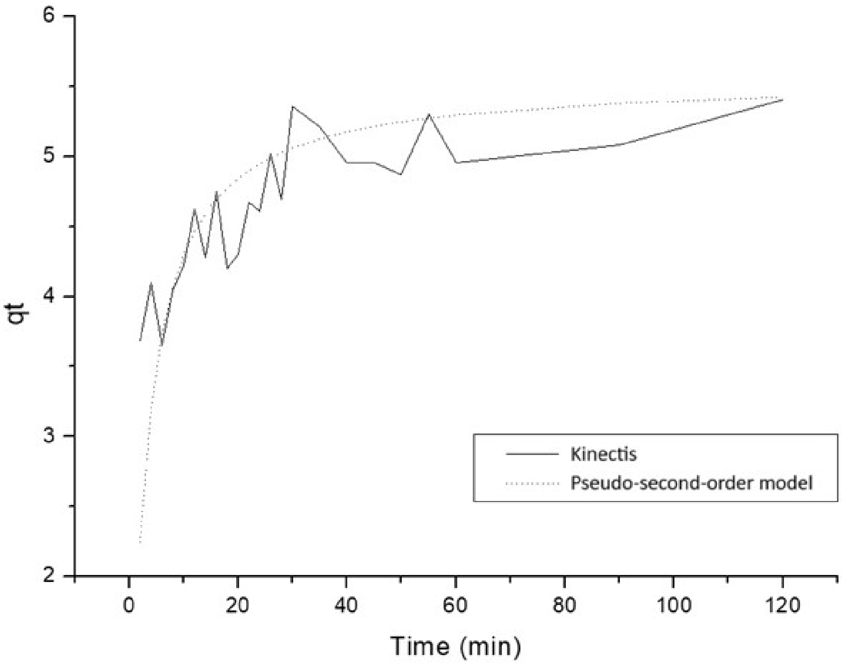

Figure 6. Adsorption kinetics and adjustments of the pseudo second order model of the activated carbon produced at 800 °C and activated CO_2

Figura 6. Cinética de adsorção e os ajustes do modelo pseudo-segunda ordem do carvão ativado produzido a 800 °C e ativado com CO_2

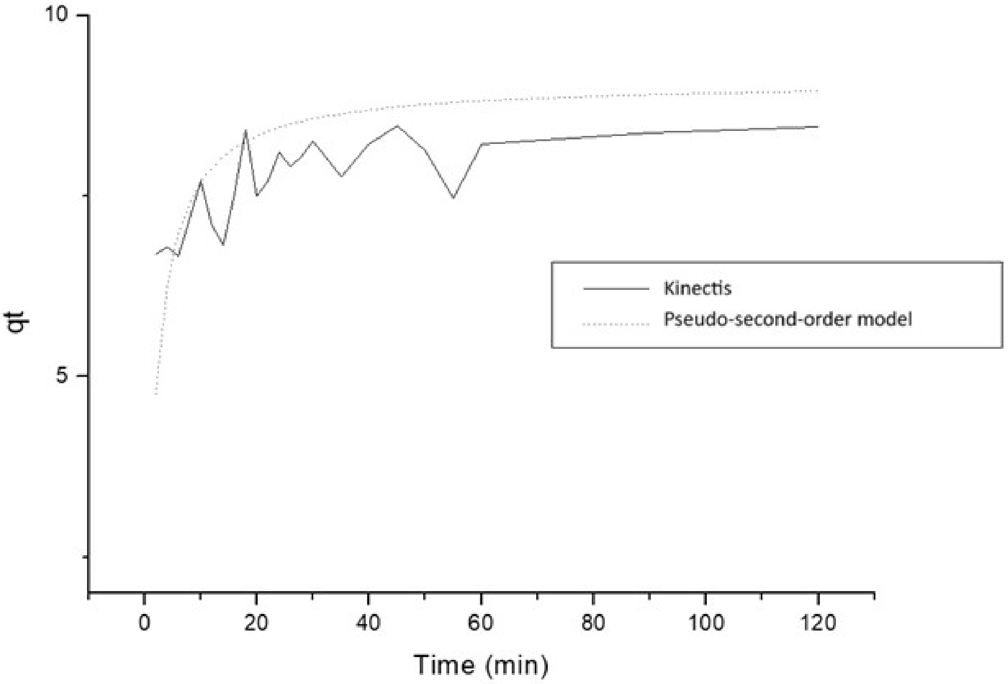

Figure 7. Adsorption kinetics and the adjustment of the pseudo-second-order model of the activated carbon produced at 800 °C and activated with steam

Figura 7. Cinética de adsorção e os ajustes do modelo pseudo-segunda ordem do carvão ativado produzido a 800 °C e ativado com vapor

Table 1. Adsorption rate constants of the pseudo-second-order model and calculated and experimental values obtained for the two types of activated carbon tested

Tabela 1. Constantes de taxa de adsorção do modelo de pseudo-segunda ordem, e valores q_e calculado e experimental obtidos para os dois tipos de carvão ativado testados

Activation atmosphere	$q_{e\ experim}$ (mg/g)	Pseudo-second order		
		K_2	q e calc (mg/g)	R^2
Steam	8.48	0.06	9.09	0.99
CO_2	5.40	0.06	5.55	0.99

4. DISCUSSION

In both activation atmospheres tested, increasing the temperature led to an increase in surface area. This can be attributed to the greater degradation of organic compounds at higher temperatures during the production and activation of the activated carbon, which results in the removal of volatile materials and consequently a larger surface area. The higher surface areas observed in activated carbon are due to the partial combustion of carbon during the activation process (Yang and Lua, 2003; Castro et al., 2023). This aligns with the results of this study, where steam and CO_2 were used as activating agents across three temperatures, with steam proving particularly effective. Steam promotes the detachment of condensable and non-condensable gases, thereby increasing the surface area of the activated carbon compared to CO_2.

All samples exhibited a microporous profile, independent of the activation atmosphere. This profile is confirmed by the higher adsorption volume of N_2 under low pressure and the small pore diameter (less than 2.0 nm) (Rimolli et al., 2023). The scanning electron microscopy (SEM) images show that CO_2-activated carbon has a surface with cracks and fissures (Figure 5i) and shallower pores, while the water steam-activated charcoal displays a curved surface with deeper pores (Figure 5ii). Both types of activated carbon exhibited well-developed porosity.

The pore size observed corresponds with the activated carbon morphology shown in the SEM images. CO_2-activated samples displayed small transitional and transverse pores, similar to pistachio shell-activated carbon produced at 800 °C and activated with CO_2. As most organic volatiles are expelled, the activated carbon surface becomes fractured, porous, coarse, and rough characteristics essential for effective adsorption, thus yielding a greater surface area (Kwiatkowski and Broniek, 2017).

In the thermogravimetric analysis of the Brazil nut shell, the first stage corresponds to the loss of water and some volatile components. The second stage, which shows the highest percentage of weight loss, is attributed to the decomposition of hemicellulose and cellulose, with the release of condensable gases such as methanol, wood tar, and acetic acid, along with non-condensable gases like H_2O, CO, CH_4, CO_2, and H_2. Lignin begins to decompose around 370 °C. Between 500 and 600 °C, further degradation of cellulose and hemicellulose occurs, resulting in an initially porous surface that facilitates the diffusion of the activating gas through the particles, allowing further reactions with the internal structure to develop more porosity. At 600 °C, the mass loss stabilizes, indicating the minimum temperature required for effective charcoal production from this material (Bouchelta et al., 2008; Shoaib and Al-Swaidan, 2015).

Comparing the thermogravimetric analysis results for raw Brazil nut shell and its activated carbon confirms that the pyrolysis process was effective. This suggests that the carbon is stable at high temperatures, as volatile organic components were expelled, leaving stable fixed carbon behind.

The amount of 2,4-D adsorbed at equilibrium reflects the maximum adsorption capacity of the activated carbon under the tested conditions. This result arises because the adsorption rate depends on available adsorption sites (Hameed et al., 2009). The surface area of water steam-activated carbon is higher than that of CO_2-activated carbon, explaining the higher adsorption rate of the herbicide by the former. The decrease in adsorption rate over time can be attributed to the occupation of active sites by adsorbate molecules, resulting in fewer available sites as equilibrium is approached (Njoku and Hameed, 2011).

5. CONCLUSION

The activated carbons demonstrated a large surface area and were highly efficient in removing 2,4-D, regardless of the activation atmosphere. Steam-activated carbon showed a higher adsorption rate of 2,4-D in the initial minutes. The pseudo-second-order model provided the best fit for the experimental kinetic data in both activation atmospheres. These results indicate that low-cost activated carbons have a high adsorption capacity for the 2,4-D herbicide.

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AUTHOR CONTRIBUTIONS

P.M.C.: Conceptualisation (lead), writing—original draft (lead), methodology (equal), investigation (lead), visualisation (lead), formal analysis (lead). S.R.F.: supervisor of technical analysis, writing—original draft (support), visualisation (support). M.R.S investigation (support), formal analysis (support). A.A.M. electron microscope investigation, image interpretation. R.M.N.: supervision (support), writing—original draft (support), methodology (equal), formal analysis (support). E.M.P.: supervision (lead), writing—original draft (support), methodology (equal), formal analysis (support), statistical analysis development. All authors have read and agreed to the published version of the manuscript.

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