Brasil nut mesocarp (*Bertholletia excels*) as a Biomass Source for Activated Carbon Production: Correlation Between Thermal Treatment and Adsorption Performance

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Abstract: The activated carbon investigated in this work was produced from the extractive residues of Brazil nut processing, more specifically from the mesocarp of the Amazonian fruit. The process was performed by muffle pyrolysis, with ZnCl₂ impregnation, at 400 and 500 °C. All samples were characterized by X-ray diffractometry, thermogravimetry, CHNS elemental analysis, scanning electron microscopy, and adsorption/desorption of N₂. The results were promissory, with 99% removal of methylene blue for the CA25 material, which has a surface area of 1236 m² g⁻¹, much higher than commercial coal (CAC, 618 m² g⁻¹). The adsorption kinetics best fit the pseudo-second-order model for all materials. The maximum adsorption capacity obtained was 195.3 mg g⁻¹. Therefore, the extractive residue of Brazil nut has excellent potential for the development of activated carbon, which can be used effectively to mediate environmental contamination in a given aqueous medium.

Keywords: Brazil nut; activated carbon; adsorption; methylene blue.

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1. Introduction

Nowadays, the ever-worsening pollution of aquatic environments can be attributed to steep population growth and the consequent increase in consumption. Due to the overpopulation, industries are pushed to new levels of production to attend to global needs, and consequently, the release of toxic industrial wastewaters into natural water sources is significantly increased [1,2]. Several effluent treatment techniques have been used and studied to solve this issue, including coagulation, chemical degradation, biological degradation, ion exchange, adsorption, and advanced oxidation techniques, such as photodegradation [3–8].

In the context of adsorption processes, activated carbons can be highlighted as one of the most promising adsorbent materials [9–11]. An elevated surface area and porosity characterize these carbonaceous materials, which possess a variety of superficial active sites that can be modified by the activation process [12–15]. However, the regeneration process of commercial activated carbon is considerably expensive and complex, which renders the application of this material economically unviable [16]. Therefore, to reduce the overall costs

of such adsorption processes, the use of low-cost agricultural wastes as precursors for activated carbons has emerged as a promising strategy [17,18].

Various extractive wastes have produced activated carbons in recent literature, ranging from barks, leaves, seeds, pulps, and roots [19-23]. Among the incredible diversity of promising materials, the extractive residue of Brazil nuts is an interesting object of research due to its significant carbonaceous content, allowing its shells (mesocarp) to be effectively used in the production of activated carbon [24]. It is reported that 1 ton of Brazil nuts generates close to 1.4 tons of mesocarp [25]. Thus, the application of the Brazil nut mesocarp as a raw material when preparing pyrolyzed activated carbon is highly relevant, as its potential has been scarcely investigated in recent literature.

Therefore, the main objective of the present work was the preparation and characterization of activated carbon produced from Brazil nut mesocarp. In addition, the investigation of their adsorption capacity was performed using methylene blue dye in an aqueous medium.

2. Materials and Methods

2.1. Materials.

Zinc chloride (ZnCl₂, purity > 98%), chloride acid (HCl, purity > 37%), sodium chloride (NaCl, purity >99%), sodium hydroxide (NaOH, purity > 98%) activated carbon (100 mesh particle size) and Methylene Blue (C₁₆H₁₈ClN₃S.xH₂O) were purchase from Sigma-Aldrich.

2.2. Activated carbon preparation.

Firstly, samples of Brazil nut mesocarp were washed in running water to remove impurities. The mesocarp was fragmented into small pieces, washed with distilled water, predried at room temperature for 48 h to remove excess water. They were then transferred to an oven at 110 °C for 24 h. The resulting mesocarp fragments were ground in a knife mill, LABOF model, obtaining a sample with 30 mesh granulometry (IN-30).

The activated carbons were prepared following two methodologies.

Method 1 - 40g of IN-30 was added to a porcelain crucible and thermally treated using a muffle furnace, model GDG 3P-S 18000, following the methodology: 1 h at 150, 200, 250, 300, 350, and 400 °C (heating rate of 10 ° C min⁻¹ between the temperature ramps). The pyrolyzed material and ZnCl₂ (1:1 mass ratio) were added to 50mL of distilled water. This mixture remained under magnetic stirring for 3 h, to achieve homogenization, followed by oven drying at 105 °C (24 h) for impregnation. The impregnated material was calcined in a muffle furnace, under a natural atmosphere, at 400 °C for 1 h. After cooling, the material was washed with 1.0 mol L⁻¹ HCl solution and distilled water until neutral pH was achieved. Finally, the material was dried in an oven at 105 °C for 24 h. This material was named CA14 [26].

The procedure was repeated at the calcination temperature of 500 °C, and the CA15 sample was obtained.

Method 2 - The IN-30 and ZnCl₂ were added in 50mL of distilled water (1:1 mass ratio). This mixture remained under magnetic stirring for 3 h, to reach homogenization, followed by oven drying at 105 °C (24 h) for impregnation. The impregnated material was pyrolyzed in a muffle furnace, model GDG 3P-S 18000, under natural atmosphere, following the methodology: 1 h at 200, 300, and 400 °C (heating rate of 10 ° C min⁻¹ between the https://biointerfaceresearch.com/

temperature ramps). The pyrolyzed material was washed with 1.0 mol L^{-1} HCl solution and water until neutral pH was achieved and oven-dried at 105 °C for 24 h. This material will be named CA24 [27].

The CA25 sample was obtained using the same procedure; however, an additional temperature plateau of 500 $^{\circ}$ C was added to the thermal treatment.

Commercial activated carbon (CAC) was used as reference material in all analyses performed.

2.3. Characterization.

The X-ray diffraction patterns (XRD) of all materials were obtained using a Shimadzu diffractometer, XRD-6000 model, using CuK α radiation ($\lambda = 0.154184$ nm), collecting the XRD data in the 2 θ interval between 10° and 60°; current, voltage and step size of were set to 30 mA, 45 kV, and 0.02°, respectively.

Fourier transform infrared spectroscopy (FTIR) of samples was performed using a Thermo Fisher Scientific spectrometer (NicoletTM ISTM 10) using pellets of the samples coupled with potassium bromide (10% *wt/wt*). The vibrational data were collected in the range between 400 and 4000 cm⁻¹ at 32 scans for each sample with a resolution of 2 cm⁻¹.

 N_2 adsorption/desorption isotherms were performed using a QuantaChrome Multistation surface analyzer, model Autosorb 3B. The isotherms were determined using 0.10 g of the samples at 77 K. The samples were previously degassed at 180 °C for 24 h. Total volume and pore size were determined by the BJH method.

The morphology of samples was studied using a Field Emission Gun Scanning Electron Microscopy (FEG-SEM) model Quanta FEG 250, operating at 20 kV and 60 pA.

The carbon (C), hydrogen (H), nitrogen (N), and sulfur (S) content of the samples was measured using a Perkin-Elmer CHNS/O elemental analyzer (2400 Series II model).

The TGA/DTG curves were obtained on a Perkin Elmer thermogravimetric analyzer model TGA7. Each sample (10mg) was heated continuously, in the temperature range of 25-900 °C (heating rate of 10 °C min⁻¹), in an N₂ atmosphere with a flow of 50 mL min⁻¹. Alumina (Al₂O₃) was the reference material.

For the point of zero charges (PZC) determination, approximately 50 mg of the adsorbent material was added to 50 mL of aqueous NaCl solution. Different solutions were prepared, each possessing a different value of pH, ranging from 2 to 12. The system remained under mechanical agitation for 24 h. The final pH of the system was measured with a Quimis pH meter (model Q400AS). The pH_{PZC} value was determined graphically from the plotted data of initial pH versus final pH [28].

2.4. Contact time effect.

To determine the time necessary to reach the adsorption equilibrium, the experiments were conducted at room temperature (25 °C) and pH ~ 6.5. Aliquots of the solution were collected at predefined time intervals. The methylene blue concentrations were measured on a Thermo Scientific UV-Vis spectrophotometer TM (GENESYS 10S model) at the wavelength of 665 nm. The activated carbon dosage was 0.5g L⁻¹ in 100 mL of 100 mg L⁻¹ methylene blue solution.

2.5. Adsorption isotherms.

About 10 mg of the activated carbon sample was mixed with 20 mL of methylene blue solution and stirred on a mechanical stirrer. The studies were performed varying the initial concentrations of methylene blue from 40 to 100 mg L⁻¹. After the adsorption equilibrium was reached, the residual dye concentration was determined using a Thermo Scientific TM UV-Vis spectrophotometer (GENESYS 10S model) at the wavelength of 665 nm.

3. Results and Discussion

3.1. Characterization.

 $\label{eq:stability} The \ N_2 \ adsorption-desorption \ isotherms \ of \ activated \ carbon \ samples \ are \ shown \ in Figure 1.$



Figure 1. N₂ adsorption-desorption isotherms for the activated carbon samples.

The activated carbon samples CA14, CA15, CA24 and, CA25 have a similar graphical pattern, typical of type I isotherm of microporous solids (pore size less than 2 nm)[29]. The CAC isotherm presents a smaller hysteresis region than that of the activated carbons, suggesting that the amount of mesopores in this structure is larger. The CAC isotherm also exhibits a diagonal growth, typical of the presence of macropores [30].

Table 1 presents the specific surface area (SSA) and pore volume (Vp) values for all the samples. The CAC SSA and Vp values were used for comparison purposes.

Sample	$SSA (m^2g^{-1})$	$Vp \ (cm^3 g^{-1})$
CAC	618	0.291
CA24	796	0.291
CA25	1236	0.578
CA14	539	0.271
CA15	678	0.345

Table 1. Specific surface area and pore volume for the activated carbon samples.

As Table 1 shows, the SSA values of samples CA25, CA15, and CA24 were higher than that of the CAC, especially for CA25, which has practically double the surface area of the commercial activated carbon, with a value of $1236 \text{ m}^2 \text{ g}^{-1}$. The values of Vp followed the same

trend observed for the *SSA* in the samples, the highest obtained by the CA25 ($0.578 \text{ cm}^3\text{g}^{-1}$). Therefore, it is clear that the textural properties of the CA25 sample were superior to the ones of the CAC, which is promising for adsorption applications [31].

Figure 2 shows the SEM micrographs of the commercial and prepared activated carbon samples (CAC, CA14, CA15, CA24, and CA25, respectively).



Figure 2. SEM images of the activated carbon samples (CAC, CA14, CA15, CA24, and CA25).

In the micrograph of CAC, shell-like pores (Region B) are observed, characteristic of mesoporous materials. In region A, stacked layers can be observed, which may be formed by graphitic material.

The SEM analysis of activated carbons produced through Method 1 shows that the increase in the pyrolysis temperature to 500 °C favored the unclogging and formation of pores, as the micrograph of the CA15 shows a more developed porous network [32]. Therefore, the temperature of 400 °C was probably not enough to favor pore formation, as the CA14 presents a lesser porous structure and reduced specific surface area (Table 1).

The CA15 and CA25 presented the existence of transport pores, as evidenced by the presence of channels on the surface of the particles (Regions C and D) [33]. These structures can significantly increase the adsorption capacity of the activated carbon due to their action as

displacement channels for fluids, easily bringing fluids to the innermost pores of the material [34].

The TGA and DTG curves of the activated carbon samples and the IN-30 are shown in Figure 3.



Figure 3. TGA and DTG curves for IN-30, CAC, CA14, CA15, CA24, and CA25.

For the IN-30 sample, the first event led to 8.2% of moisture loss (H₂O) at temperatures lower than 85 °C. In the second event, the 74.0% mass loss was attributed to the thermal degradation of hemicellulose, cellulose, and lignin in the temperature range of 170 to 690 °C. This event is related to the decomposition of organic matter and the consequent generation of carbonized material [35]. The third event occurred at a temperature above 690 °C and can be attributed to the residues.

The TGA and DTG curves of the activated carbons show that the first event is represented by a slope close to 90 °C, related to the mass loss of H₂O adsorbed on the surface of these materials. The second event occurs in the temperature range between 350 and 850 °C, corresponding to the loss of volatile substances, such as CO, CO₂, H₂, and CH₄, due to the thermal decomposition of the activated carbon [36]. The last event, above 850 °C, refers to residual materials, such as fixed carbon (C), ash (inorganic), and ZnCl₂.

Sample	С	Н	Ν	S	C/H
IN-30	46.82	5.59	0.39	0.45	8.73
CAC	75.82	2.44	0.21	0.18	31.07
CA14	61.66	3.58	1.40	0.23	17.22
CA15	61.83	3.97	1.46	0.28	15.57
CA24	55.84	2.44	1.02	0.24	22.88
CA25	59.76	3.10	1.38	0.26	19.27

Table 2. C, H, N, and S contents (% m m⁻¹) as well as C/H and C/N ratios.

Table 2 presents the results of the CHN/S elemental analysis for the activated carbons samples (including CAC), as well as calculated values of the C/H ratio.

The CAC is richer in C than the activated carbons prepared by the two methods, which may be due to its preparation process and carbonaceous precursor. Activated carbons prepared by Method 1 (CA14 and CA15) are more C-rich than those prepared by Method 2 (CA24 and CA25). The increase in the C/H ratio values for the activated carbons indicates an increase in the degree of aromaticity after the pyrolysis process and the release of volatiles composed of oxygen and hydrogen, caused by the activation of the materials [37].

The X-ray diffractograms of the activated carbon samples are shown in Figure 4.



Figure 4. X-ray diffractograms of the activated carbon samples (CAC, CA14, CA15, CA24, and CA25).

All samples of activated carbon, including CAC, showed diffractograms with similar graphical profiles due to the formation of wide halos near 25.0° and 44.5°, characteristic of the (002) and (101) reflection planes of the turbostratic structure of graphite microcrystallites, respectively [34,38].

The CAC diffractogram showed the presence of crystalline phases, although the characteristic profile of the amorphous carbonaceous material was observed in a less pronounced way. This is probably due to the industrial activation process of this material, the addition of binders and additives that may have caused the presence of crystalline phases dispersed on the surface of the amorphous matrix [34].

The knowledge of the pH_{PZC} of the adsorbents allows the prediction of the ionization of surface functional groups and their possible interaction with species in the solution. In this sense, the tests performed were useful to estimate the PZC for all samples studied. In general, the mean value of pH_{PZC} for the samples was 7, where three groups of samples could be observed:

(i) Weak acidic character: pH_{PZC} 6.9 and 6.5 for samples CA25 and CA24, respectively;

(ii) Weak basic character: $pH_{PZC} = 7.7$ for the CAC sample;

(iii) Neutral character: $pH_{PZC} = 7$ for samples CA14 and CA15;

3.2. Contact time effect.

Contact time tests were performed to determine the adsorption equilibrium between adsorbent and adsorbate, the removal efficiency, and the adsorption kinetics.

The adsorption efficiency (Rp) was estimated using Equation 1:

$$R_p = \frac{C_0 - C_t}{C_0} \times 100\%$$
 (1)

where C_0 is the initial concentration and C_t is the concentration of the solution at a given time (t).

Figure 5 shows the rates of methylene blue removal as a function of the contact time for the activated carbon samples. The dosage used of activated carbons was 50 mg in 100 mL of 100 mg L^{-1} methylene blue solution.



Figure 5. Adsorption efficiency of samples CAC, CA14, CA15, CA24, and CA25.

For all samples, rapid adsorption is observed during the first 30 min, followed by a slower adsorption rate up to approximately 90 min, when the adsorption equilibrium is reached.

This elevated adsorption of the methylene blue by activated carbons in the first instants of the tests is reported in the literature [39]. Thus, it is possible to infer the existence of a significant amount of active sites distributed on the surface of these materials, which interact with the adsorbate, and the presence of mesopores, which favor the adsorption of molecules into the particles. Over time the adsorption process slows down due to the saturation of the active sites [40].

Among the activated carbons, the CA25 (method 2) and CA15 (method 1) samples had the highest removal rates: 99.3 and 98.2%, respectively. On the other hand, the sample CA14 had the lowest adsorption capability (65.3%). Samples CA24 and CAC presented adsorption efficiency close to 90%, lower than those obtained in samples CA25 and CA15, suggesting that the pyrolysis temperature of 500 °C was determinant for the optimal methylene blue adsorption efficiency.

For the kinetic studies of methylene blue removal, the experimental data were modeled using the linear equations of pseudo-first-order (PFO, Equation 2) and pseudo-second-order (PSO, Equation 3)[41].

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{2}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$
(3)

Thus, Table 3 shows the results of the PFO and PSO adjustments for the activated carbon samples (CAC, CA14, CA15, CA24, and CA25) experimental data.

Sample	PFO				PSO			
	q_e $k_1 \times 10^{-2}$		R^2		$k_2 \times 10^{-3}$	q_e	R^2	
	(mg g ⁻¹)	$(mg g^{-1} s^{-1})$			$(s mg g^{-1})$	$(mg g^{-1})$		
CAC	60.9	2.42	0.8409		2.948	175.4	0.9997	
CA14	68.2	1.93	0.8448		1.365	131.1	0.9962	
CA15	60.7	2.56	0.8304		3.370	194.9	0.9997	
CA24	93.2	2.15	0.9114		1.319	187.6	0.9985	
CA25	19.8	2.94	0.6059		2.881	195.3	0.9999	

 Table 3. Kinetic parameters obtained for the methylene blue adsorption on samples CAC, CA14, CA15, CA24, and CA25.

It was observed that linear PSO adjustments were superior, as R^2 values for all the prepared samples were higher than 0.97. The R^2 values for the PFO-adjusted data ranged from 0.6059 (CA25) to 0.9114 (CA24), showing a significant linearity shift. Therefore, the adsorption kinetics of these samples was better represented by the PSO model. The maximum adsorption capacity was found for the CA25 sample, equal to 195.3 mg g⁻¹.

3.3. Adsorption isotherms.

The experimental adsorption data was adjusted by the Langmuir and Freundlich isotherm models in non-linear form. The results for the activated carbon samples are shown in Figure 6, which shows the adjustments of the isotherm models for the experimental data of methylene blue adsorption.

Comparing the isotherms for the activated carbons (except CAC) it is evident that the type of the activation process generates great changes in the amount of adsorbed methylene blue. In this study, Method 2 must be highlighted, as it led to porosity development through the deepening and/or enlargement of the existing porous structure [42].

The parameters and the correlation coefficients obtained through the Langmuir and Freundlich isotherm models are shown in Table 4.

Sample	Langmuir					Freundlich	
	q_e	KL	R ²		п	K_F	R^2
	$(mg g^{-1})$	$(L mg^{-1})$				$((mg g^{-1}) \times (mg L^{-1}))$	
						$(1)^{1/n})$	
CAC	182.4	14.491	0.9871		7.9	145.9	0.7261
CA14	106.2	0.189	0.9186		4.3	39.8	0.7273
CA15	178.4	8.072	0.9647		7.2	137.2	0.8328
CA24	171.0	6.584	0.9354		5.9	128.8	0.9222
CA25	181.3	38.068	0.9603		8.9	159.4	0.8566

Table 4. Langmuir and Freundlich parameters for samples CAC, CA14, CA15, CA24 and CA25.

The correlation coefficients (R^2) for the Langmuir isotherm model are significantly higher than those of the Freundlich model. Thus, the Langmuir model represents the experimental data more accurately.

These results, combined with the adsorption kinetics of PSO, shows that the mechanism of methylene blue adsorption occurs predominantly by monolayer adsorption of methylene

blue in the activated carbon surface [43], which can be represented by the reaction (Equation 4):

$$CA(s) + MB(aq) \rightarrow CA-MB(s)$$
 (4)

where CA(s) represents the activated carbon (fine and homogeneous particles), MB(aq) represents the solubilized methylene blue, and the CA–MB(s) is the adsorption complex generated during the process.



Figure 5. Adsorption isotherms for samples CAC, CA14, CA15, CA24, and CA25, fitted by Langmuir and Freundlich models.

4. Conclusions

Regarding the thermal properties of the activated carbons developed, the TGA curves indicate reasonable thermal stability. Sample CA25 showed a specific surface area equal to $1236 \text{ m}^2\text{g}^{-1}$, which is twice the surface area found in the commercial activated carbon used as reference. The XRD results indicated that the materials have a non-crystalline structure. The adsorption kinetics data were better adjusted by the pseudo-second-order model, with a maximum adsorption capacity of 195.3 mg g⁻¹ for the CA25. The Langmuir isotherm model best described the adsorption process. Among the activated carbons, CA25 presented the

highest adsorption efficiency, even when compared to the commercial activated carbon, which highlights the applicability of this material in adsorption processes.

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Conflicts of Interest

The authors declare no conflict of interest.

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