Activated Carbon from Brazilian Babassu Nutshell using Physical Route and Microwave Radiation

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ABSTRACT
The Activated charcoal - AC is a carbonaceous material with high carbon content in its structure, it can be obtained from biomaterials such as: coconut shell, wood, bamboo, etc. Its pores are highly developed, have high adsorption capacity and have a microcrystalline form capable of selectively purifying liquids or gases. All the ACs have micro, meso and macro pores in their structure, but the relative proportion depends on the precursor and production process. In carrying out this work, activated carbon was produced from the charcoal of the babassu endocarp prepared via microwave radiation. The physical activation process took place in the atmosphere of CO_2 via microwave radiation at room temperature 235 °C and activation time corresponding to 50 minutes. The characterizations of the AC were performed with the following techniques: Scanning electron microscopy - SEM; Surface area analysis - BET and porosity; Thermogravimetric analysis - TGA; Analyzes of methylene blue adsorption in the region UV-Vis. The data obtained in this research shows that babassu activated carbon produced at low temperatures and high activation time has better methylene blue adsorption characteristics than AC produced at high temperatures and less time.

Keywords: *Activated charcoal, Adsorption, Microwave oven, Uv-Vis.*

1. INTRODUCTION

Babassu is the name given to oil palm trees referring to the Palmae family and complementary to the Orbignya and Attalea genera. Babassu stands out among the palm trees found in Brazilian territory in the states of Maranhão, Piauí and Tocantins, which concentrate the largest extensions of forests where babassu predominates, forming, often and spontaneously. Maranhão concentrates approximately one-third of the total area of babaçuais (or cocais) found in the Brazilian territory, constituting one of the main vegetal riches of this state and also of Piauí. However, its industrial use is limited to oil almonds. Grace and beauty of the structure that is characteristic of it: reaching between 10 and 20 meters in height. Babassu is found in Brazil [1].

The babassu coconut endocarp is the raw material used to carry out this research, with which activated carbon was produced. The babassu fruit, a native fruit from Brazil, has an ovoid shape, with an approximate size of 9 cm, a width of 5.4 cm and a mass of 133.2 g. It has four constituents: The fibrous and thin layer called the epicarp, responsible for surrounding the secondary layer, the mesocarp that is popularly known with the fruit powder and the rigid endocarp that contains a significant amount of lignin and houses the almonds inside. Today, it is becoming increasingly common to use shells in the manufacture of charcoal, both for domestic purposes and industries. Recently, many studies have reported the production of activated carbon (AC) from residues such as: Rice husk, Green Coconut Shell, Babassu coconut, [2, 3]; Residues of babassu, Coffee waste, Oil palm, etc. Many studies have discussed the great potential of lignocellulosic as a renewable feedstock for the preparation of Activated Carbon. [4], removal of Copper from Bioleachate of Electronic Waste using Banana-Activated Carbon (BAC) and Comparison with Commercial-Activated Carbon (CAC).

The utilization of agricultural waste biomass such as from the pineapple (Ananas comosus) industry offers an interesting alternative based on its potential to be converted into activated carbon. [5], prepared activated carbon from the pyrolysis of pineapple waste biomass (leaves, stem, crown) impregnated with ZnCl2. Resulting activated carbon with the highest surface area was chosen and evaluated for its dye removal efficiency using methylene blue (MB), the study demonstrated the potential of using pineapple waste biomass as efficient raw materials which produce activated carbon for dye removal from wastewaters.

The search for lower costs in the production of activated carbon has led to the search for new precursors and forms of pyrolysis. In the conventional heating process, heat transfer occurs by conducting energy from the material's surface to its interior. Unlike conventional methods, in microwave heating the frequencies promote interactions between the chemical constituents of the materials and the electromagnetic field, such intermolecular frictions generate heat internally to the material. Thus, microwave radiation has been reported as a promising technique, as the process occurs in shorter times, allowing more effective control of the process due to the less pronounced heat gradient [6].

Microwave irradiation has recently exhibited superior performance for some organic chemical transformations when compared to conventional heating methods. This is related to the high efficiency of microwaves in rapidly heating media. Microwave heating has huge potential as an effective method in order to produce activated carbon with high quality, high carbon yield and porosity. The eco-friendly activated carbon prepared via microwave heating can save significant energy and time activation [7]. In this study, the microwave irradiation system was used to produce babassu endocarp activated carbon (BAC) using physical activation with carbon dioxide as an activating agent. The properties of the activated material, such as surface area, pore size and yield were analyzed for the first time for the conditions presented.

2. METHODOLOGY

2.1. Raw Material

The babassu coconut endocarp is the raw material used to carry out this research, with which activated carbon was produced. The babassu fruit has an ovoid shape, with an approximate size of 9 cm, a width of 5.4 cm and a mass of 133.2 g. It has four constituents: The fibrous and thin layer called the epicarp, responsible for surrounding the secondary layer, the mesocarp that is popularly known with the fruit powder and the rigid endocarp that contains a significant amount of lignin and houses the almonds inside. Today, it is becoming increasingly common to use shells in the manufacture of charcoal, both for domestic purposes and industries.

The babassu coconut sample was collected in the urban area of Caxias City, Maranhão, Brazil (4 ° 51'50.8 "S 43 ° 19'47.2" O). Figure 1 shows the location of the babassu fruit collection.

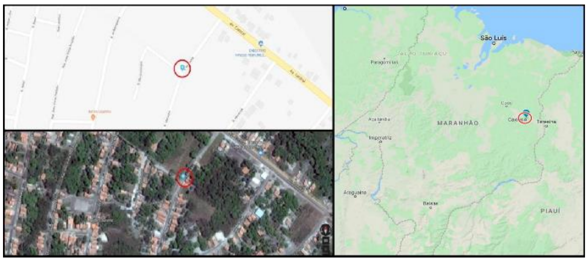

Figure 1. The babassu was collected.
Fonte: GOOGLE MAPS (2018).

The babassu fruit used for the research was collected from just one tree, which can be seen in Figure 2.

Figure 2. Palm oil tree that babassu collects.
Fonte: Author (2018).

The babassu endocarps were first crushed to the size fraction of 5.0-8.0 mm; the particle size plays an important role in microwave heating because the penetration depth becomes significant as the particle size increases [8]. After the grinding of the endocarps was completed, the next procedure was dehydration of the biomass.

2.2. Separation of Coal

The coals used to produce AC were selected from [9]. prepared at low temperature (320 °C) and resident time of 62 min. The babassu endocarp was weighed and then transferred to the reactor installed inside the microwave, which already contained a certain amount of commercial activated carbon, forming a base layer in the reactor. Subsequently, carbonization was carried out at different temperatures using a nitrogen atmosphere. The carbonization temperature varied between 300 ºC to 600 ºC with a processing time of 20 to 65 minutes. Next, the produced coal was weighed to determine the carbonization process yield. Figure 3 illustrates (A) charcoal with dimensions shown in the ruler, (B) charcoal sample and (C) charcoal stored in bottles and cataloged.

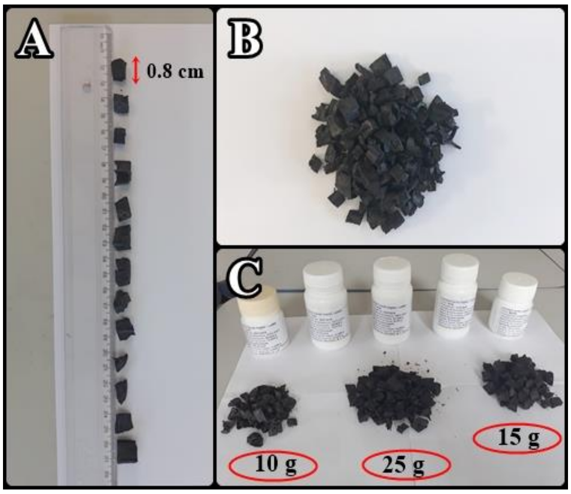

Figure 3. In (A) Dimension of the coal, (B) Coal samples (C) Coals stored in bottles.
Fonte: Author (2018).

2.3. Production of Activated Carbon

The Activated Carbon was produced in the CO_2 atmosphere, with a temperature of 235 °C for 50 min with a heating rate of 50 °C/min and a gas flow of 1 L/min. The temperature was monitored by a thermocouple connected to a data logger, which sent all the temperature information to a laptop with installed software that collected this information and assembled a graph.

2.4. Characterizations Activated Carbon

2.4.1. Proximate and Ultimate Analyses

Proximate analysis was carried out by a thermogravimetric analyzer (TGA), SHI- MADZU TGA-51 Thermobalance, before and after carbonization was used a nitrogen atmosphere with a gas flow of 50 mL/min in the Materials Treatment Laboratory-corrosion, Plasma of the Postgraduate Program in Materials Engineering at the Federal Institute of Piauí - PPGEM / IFPI.

The ultimate analysis was used to determine the carbon, hydrogen, nitrogen and sulfur contents of babassu and biochar using an Elemental Analyzer (Vario Micro Cube).

2.4.2. Scanning Electron Microscopy

The SHIMADZU SSX-550 model equipment was the Scanning Electron Microscope (SEM) used to verify the presence of porosity on the raw material, biochar and Activated Carbon surfaces in the Scanning Electron Microscopy laboratory (LabMEV), in partnership with the Materials Engineering Graduate Program of the Federal Institute of Piauí - PGEM / IFPI.

2.4.3. BET – Surface Area

The analysis of the surface area and total pore volume were obtained by measuring their nitrogen adsorption-desorption isotherms at 196 °C. The Brunauer Emmet Teller (BET) model was applied to determine the surface area and S_{BET} (m^2/g) while pore volume and micropore volume were determined using a Surface Area Analyzer (ASAP 2020, V3.04H; Micromeritics) equipment at the University Laboratory Management Unit - UPMU, the University of Technology of Malaysia (UTM).

The BET isotherm equation depends on the following two assumptions [10].

From the second layer, the adsorption energy E has the same value as the liquefaction energy EL in the previous layer, that is, there is no interaction between layers. The multilayer has an infinite thickness in $p/p_0 = 1$ Where we have the emergence of the constant C of the BET equation:

$$C = exp(\frac{E1-E2}{RT}) \quad (1)$$

The BET equation in its standard form:

$$n = \frac{nmCp}{(po-p)[1+\frac{(C-1)p}{po}]} \quad (2)$$

For convenience it is usually expressed in its linear form:

$$\frac{p}{n(po-p)} = \frac{1}{nmC} + \frac{(C-1)}{nmC}(\frac{p}{po}) \quad (3)$$

Where:
n - Volume of gas adsorbed at pressure p;
nm - Volume of gas required to form a monolayer;
p/p_0 - Adsorbate relative pressure;
C - BET constant (related to the adsorption energy of the 1st layer)

Through the BET isotherm format, it is possible to obtain information, such as specific area and porous structure of the material. The constant C is exponentially related to the adsorption enthalpy of the first layer.

2.4.4. Spectrophotometer – UV-Vis

For adsorption isotherms analysis, four different times 10, 25, 40 and 55 min were used, using the SHIMADZU UV-1800 Spectrophotometer. To obtain the adsorption isotherms, 0.1 g of activated carbon was used in contact with a volume of 50 mL of the solution with the methylene blue dye. Then a quantity was removed with a fine needle syringe, inserted in the glass cuvette and sent to Spectrophotometry. The methylene blue dye solution was prepared according to the protocol: 0.05 g of methylene blue was placed in the beaker, then it was made up to 1000 mL with distilled water. The solution stored in the volumetric flask, showing a high concentration, with the purpose of decreasing its acidity was separated 100 ml of this concentrate in another volumetric flask and distilled water adding 1000 ml was added. The determination of the dye adsorption capacity on activated carbon was determined from the Equation.

$$Qt = \frac{(Co-Ct)V}{m} \quad (4)$$

Where:
Qt – Absorption capacity of the dye on adsorbent medium at time t;
Co – Initial concentration of the dye solution (mg/L);
Ct – Dye concentration at time t or equilibrium concentration (mg/L);
V – Volume of adsorbate (L);
m – Mass of adsorbent (g).

The analyzes were performed at the Analytical, Inorganic and Physical - Chemical Laboratory of the Federal Institute of Piauí – IFPI.

3. RESULTS AND DISCUSSION

3.1. Raw Material – Babassu

The Thermogravimetric Analysis (TGA) of the fresh endocarps in figure 4 shows a significant loss of mass between 300 and 580 ºC, which corresponds to the elimination of the substances present in the babassu coconut endocarp. In the first stage, despite dehydrating for 1 hour and removing almost 90 % of liquid, there is still residual water. The 300 ºC peak corresponds to the decomposition of cellulose and hemicellulose molecules. This thermal event has a maximum speed of 580 ºC with a loss of mass of 63 %. For the peaks corresponding to the temperature of 300, 340, 380 and 580 ºC the loss of mass is due to the combined decomposition of hemicellulose and cellulose. The decomposition of cellulose contributes to the subsequent peak at 430 ºC and lignin to a peak of 380 ºC. These results are compatible with [2].

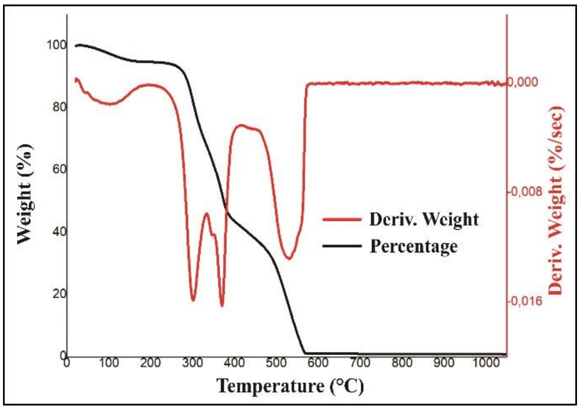

Figure 4 . TGA raw babassu endocarp.

3.1. Activated Carbon from Babassu Biomass

Only 25 g of babassu charcoal was used to produce the activated carbon, after activation the mass was reduced to 19.5 % of the previous mass, which is equivalent to 4.88 g of activated carbon.

The temperature and activation time is essential to define the quality of the activated carbon, so during the entire activation time, the process was monitored through the longer peak connected to a Laptop. The peaks shown in Figure 5, were obtained in the range of 200 to 235 ° C, with a time of 50 min. The heating ramp took approximately 5 min to reach the peak.

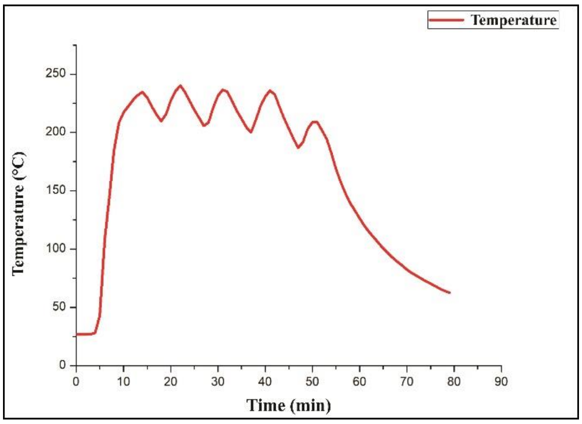

Figure 5. Temperature profile during activation.

3.2. Thermogravimetric Analysis

The thermogravimetric analysis of the CA is shown in Figure 6, where it is noticed that the high rate relative to the loss of mass occurs between temperatures of 400 - 580 ° C and these losses, which are usually sudden, can be explained with the elimination of the substances that form the babassu endocarp. Usually, the main components are cellulose, lignin and hemicellulose [11].

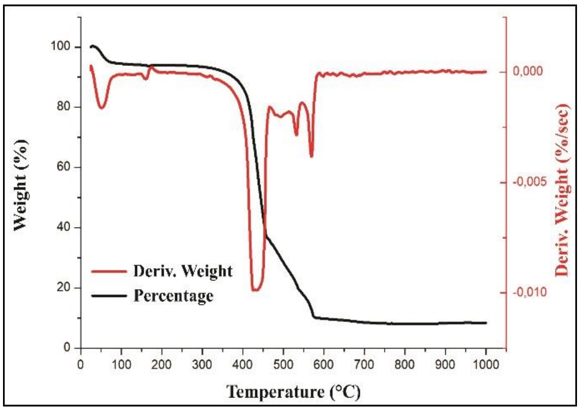

Figure 6. TGA curves of activated carbon.

At 170 °C there is a small drop in the graph which is explained by the decomposition of the remainder of hemicellulose, at temperature 400 °C there is a more pronounced drop due to the elimination of lignin and finally at a temperature of 600 °C it presents similar thermal stability such as the coal produced by [2], leaving only 8.4 % of ash.

3.3. Scanning Electron Microscopy

In the microstructural analyzes carried out in the SEM, a high level of porosity is observed when observing the formed craters seen in Figures 7 and 8. It is observed that the dark spots shown in these images are the pores, and may even be micropores developed during the activation of the activated charcoal which can be attributed to the oxidation of organic compounds in the carbonization step Similar situation was also reported by [5]. The digital image processing (PDI) techniques can be applied in the SEM micrographs of activated carbon showed the distribution of the pore structure present in the micrographs, being confirmed by the results obtained through conventional characterization, BET. In this study, it was possible to perceive the porosity relationship on a micrometer scale with the internal porosity in nanometers and the complexity of the porous structure of activated carbon produced from babassu biomass. It was observed the abundant existence of micro and mesopores present in the samples and that can play an important role in defining their application, storage and migration of gas or fluid [12].

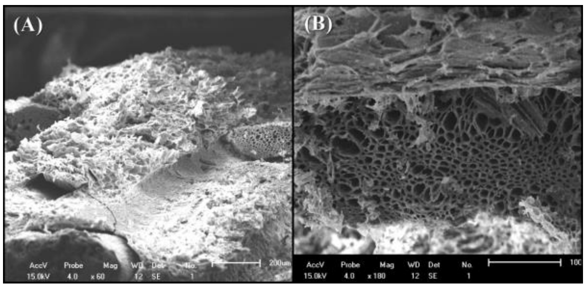

Figure 7. SEM Magnification (A) 60x and (B) 180x.

In Figure 8 due to the 500x and 600x magnifications, the craters formed during activation can be observed more closely, which is a promising result due to the objective of the work through the quality of the AC confirming results obtained by BET analyzes. The purpose of the activation is to provide in a given material, little porous or without porosity, the increase of the surface area, and the increase of the porosity as a result of the oxidation of the carbon atoms. These alternative carbonaceous materials used in the production of activated carbon have, for the most part, a degree of porosity with a surface area ranging from 10 to 15 m²/g, and, after activation, this degree of porosity may have an area close to or greater than 800 m²/g [13].

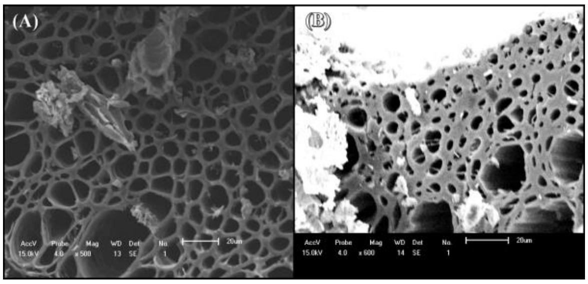

Figure 8. SEM magnification (**A)** 500x e **(B)** 600x.

3.4. Brunauer, Emmett and Teller Method

The BET analysis shows results with a high level of porosity of the activated carbon, its specific pore volume was 0.1308 cm^3/g and it has approximate value of the AC produced by [2] which obtained 0.173761 cm^3/g in AC produced at a temperature of 750 °C. Its surface area was 283.2039 m^2/g and pores of size 1.431764 nm, which is an optimized value of [2] produced at temperatures of 700, 750 and 800 °C. Figure 9 shows the linear parameter of (p/p_0) 0.01 to 0.12 of the surface area. how the same material makes very different biochars when subjected to different pyrolysis methods and the potential of different materials for pyrolysis[14]. This biochar can potentially sequester carbon and improve nutrient and water retention in acidic low-fertility soils like[16]

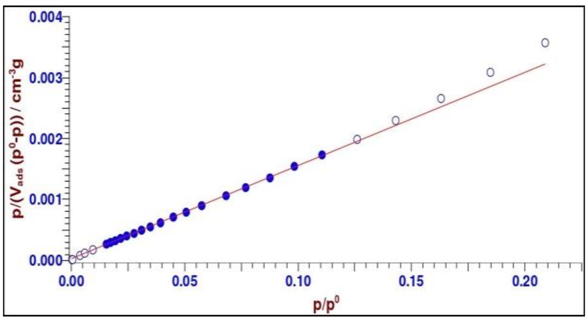

Figure 9. BET linear parameter linear.

The adsorption and desorption isotherms of N_2 with a pore volume of (p/p_0) 0.99 and 0.1307 cm^3/g present in Figure 10, the isothermal curve, and much of the nitrogen absorption occurred at the beginning of the curve where it is most accentuated and that the relative pressure varied from 0.3 to 0.15 cm^3/g, this type of isotherm is particularly known as type I isotherm, which characterizes microporous ACs [2]. In agreement with [15]. Faster development of the micropores was achieved by increasing the activation temperature than by increasing the activation time.

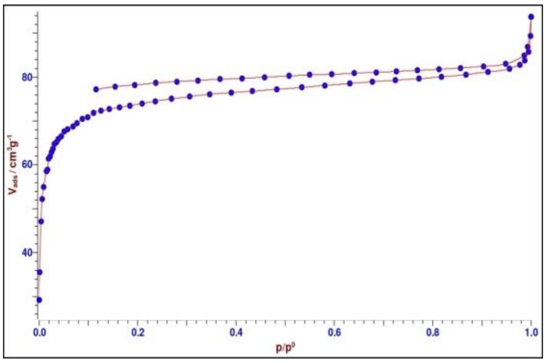

Figure 10. Adsorption/desorption isotherm.

3.5. UV Spectrophotometer – UV-Vis

The adsorption of methylene blue grew gradually with time, tending towards a complete purification of the water after 55 min in contact of the solution with the AC.

To test the effectiveness of activated carbon produced in this research, it was subjected to an analysis of methylene blue adsorption comparing the results with activated carbon produced by [2] via microwave radiation at a temperature of 700 °C and time corresponding to 20 min of activation.

Figure 11 shows that in 40 min the AC produced by [2] has less methylene blue adsorption than that produced in this work and the results are analogous for all tested times. The activated carbon produced at a temperature of 235 °C and a heat treatment time of 50 min, resulted in an AC with greater adsorption.

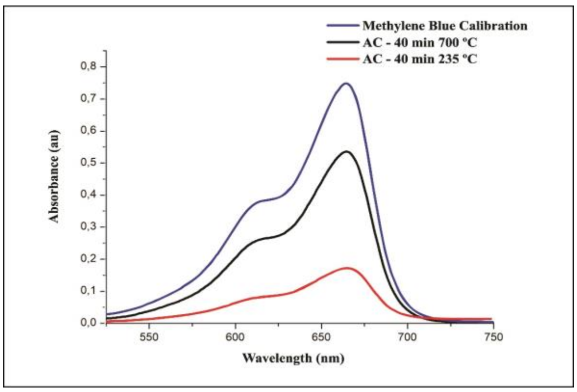

Figure 11. Comparison of the AC produced in this research with data from the literature.

4. CONCLUSION

The data obtained in this research show that activated carbon produced at low temperature (235 °C) and high activation time (50 min) has very promising characteristics and different from those obtained for AC produced at high temperatures (700°C) and in less time (for 20 min).

Activated carbon is efficient in adsorption of methylene blue dye, as confirmed by the results of Uv-Vis analysis. In 40 min the AC produced at 700 °C and activation time to 20 min has less methylene blue adsorption than that activated carbon produced at a temperature of 235 °C and a heat treatment time of 50 min.

The SEM analysis of the AC produced in this work showed a high production of smaller pores, which indicates greater microporous formation, with pore size range: 0,31-1,0 nm duly proven with results of the BET analysis.

This research is relevant for several reasons, among which we can highlight: the first, the environmental importance in the destination the parts of the babassu coconut that are improperly discarded. In the second, why the activated carbon produced from the use of this residue can be efficiently used in the process of treating water contaminated with dyes such as methylene blue.

Thus, the use of biomass from Babassu coconut has an excellent potential to be used in the production of activated carbon, in addition to contributing economically and environmentally to the Babassu production chain.

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