Valorization of residue from agro-industrial cocoa production in the preparation of activated carbon for CO_2 capture

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Abstract

Carbon dioxide (CO_2) represents the majority of greenhouse gas emissions. Thus, CO_2 capture is an alternative to mitigating thise environmental impact. The objective of this work is to study the feasibility of transforming the cocoa residue into activated carbon as adsorbent in CO_2 capture. Initially, the potential of cocoa residue for the production of adsorbents was evaluated through the following characterizations: Immediate analysis, WD-XRF, XRD and SEM. In sequence, activated carbon from cocoa residue was characterized by WD-XRF, XRD, SEM, textural analysis and evaluated in CO_2 capture. The cocoa residue presented 25% of fixed carbon and 61.67% of potassium oxide in its composition. The activated carbon presented a significant surface area ($685.7 m^2.g^{-1}$), favoring the adsorption of 6.7% CO_2. These results prove that cocoa residue has high potential for application as activated carbon in CO_2 capture.

Keywords: Adsorption; activated charcoal; cocoa residue; CO_2.

1. Introduction

Carbon dioxide (CO_2) represents approximately 60% of greenhouse gas emissions [1]. This has contributed to the increase in global warming over the centuries. Thus, CO_2 capture is an alternative to mitigate the environmental impacts caused by the gas and consequently to avoid the return to the atmosphere.

There are different types of CO_2 capture technologies, one of which is adsorption, a process that separates compounds by adhesion to the surface through chemical and/or physical interactions. Adsorption through activated carbon is a consolidated technique in the literature, as it's a material that has a porous structure, highly specific surface area and chemical stability [2,3]. However, the search for the development of low-cost materials is still a challenge.

The raw material used in the production of charcoal must come from organic materials rich in carbon. In this sense, agricultural residues are interesting precursors for the preparation of activated carbons because they come from renewable organic sources and low-cost materials [4].

Cocoa (*Theobroma cacao*) is the fruit of a tree plant originating in South America, with chocolate being the most widespread derivative throughout the world [5]. The state of Bahia is the largest cocoa producer in Brazil, producing almost 110 thousand tons per year [6]. This production generates a large amount of waste, since most of the fruit is discarded inappropriately (shell) and only the pulp is used.

Therefore, the objective of this work is to study the feasibility of transforming cocoa residue into activated carbon as adsorbent in CO_2 capture.

2. Experimental

2.1 Pre-processing and characterization of cocoa residue (shell)

The cocoa residue (shell) was subjected to successive washing, crushed, dried at 100ºC and sieved in the range of 100-200 mesh.

The immediate analysis of the cocoa residue was carried out using Shimadzu-60H thermogravimetric analysis equipment, according to ASTM E1131.

Elemental analysis was performed by wavelength-dispersive X-ray fluorescence (WD-XRF) on a Bruker XRF S8-Tiger instrument, which operates with a voltage of 40 kV and a current of 30 mA.

The X-ray diffractogram (XRD) of the cocoa residue was collected on a Shimadzu XRD-6000 device, which operates with CuKα radiation at 40 kV, 30 mA and graphite monochromator, in the 2theta region ranging from 5 to 80° at a scanning speed of $2°.min^{-1}$.

The micrographs were collected on Hitachi model S-3400N equipment at different magnifications. The most representative image of the sample was selected.

2.2 Preparation of activated carbon

A charcoal was produced from cocoa residue, the sample was subjected to pre-pyrolysis under N_2 atmosphere with flow of 100 mL.min^{-1} (10ºC.min^{-1}) at 400 ºC for 2 hours and then washed with distilled water, filtered with a vacuum pump and dried in an oven at 100 ºC for 24 hours. To activate the charcoal, this pre-pyrolyzed sample was subjected to chemical impregnation with a KOH solution (1:1), on a heating plate at 80ºC with constant stirring (75 rpm) until the volume of water present was reduced.

In sequence, the material was dried in an oven at 100ºC. Finally, the sample was pyrolyzed at 700ºC under N2 atmosphere with flow of 100 mL.min^{-1} (10ºC.min^{-1}) for 2h, washed with a solution of HCl diluted at 1mol.L^{-1} and warm water to remove residues and inorganic compounds, and dried again at 100ºC.

2.3 Characterization of activated carbon

Activated carbon was characterized by XRF, XRD and SEM according to previously established methodology. In addition to textural analysis by N_2 physisorption obtained in equipment from Micromeritics (ASAP 2020 model).

2.4 CO_2 capture

The CO_2 capture using method TSA (Temperature swing adsorption) was carried out using Shimadzu - DTG60H equipment. The samples were conditioned at a heating rate of 10ºC.min^{-1}, up to 200ºC for 30 min in a N_2 flow (50 mL.min^{-1}), after which they were cooled to 30ºC for 110 min and finally a CO_2 flow (50 mL.min^{-1}) was introduced at 30ºC for 30 min.

3. Results and discussion

3.1 Characterization of cocoa residue (shell) and activated carbon

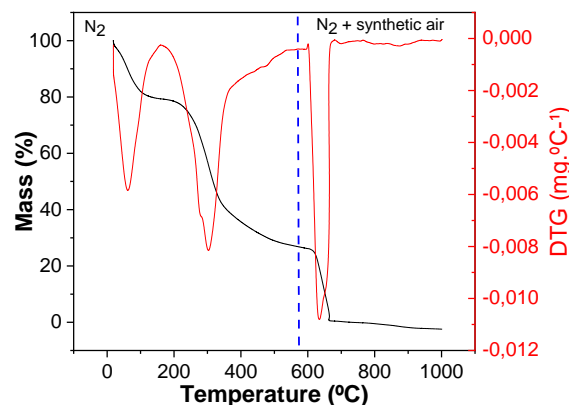The result of the immediate analysis of the cocoa residue is presented in Fig. 1 and Table 1.

Fig. 1. Immediate analysis of cocoa residue

Table 1. Immediate analysis of cocoa residue according to ASTM E1131

	Measure (%)
Highly volatile	20.67
Medium volatile	53.16
Fixed carbon	25.90
Ashes	0.28

The Figure 1 shows a mass loss event up to 200ºC attributed to loss of moisture and highly volatile materials, which represents 20.67% of the initial mass (Table 1). The most significant mass loss event begins at around 200ºC to 460ºC attributed to the decomposition of hemicellulose and cellulose. In the range of 460ºC–600ºC lignin decomposition occurs [7]. This event refers to the decomposition of moderately volatile material, around 53.16%. Between 600 and 700ºC the change to an oxidizing atmosphere occurs, this event highlights the percentage of fixed carbon in the biomass residue (25.90%). After this temperature, the material is completely decomposed, and only 0.28% ash is considered.

The amount of fixed carbon after the end of the analysis is associated with the decomposition products of hemicellulose, cellulose and mainly lignin, in addition to inorganic compounds originating from biomass [8]. The percentage of fixed carbon in the cocoa residue in the present work (25.90%) was close to those obtained in the literature for different biomasses, such as the yellow mombin fruit stones (23.72%) and the banana pseudostem (24,38%), so it can be inferred that cocoa residue has great potential for the production of activated carbon [9,10]

The elemental analysis of cocoa residue and activated carbon is presented in Table 2. There is a

predominance in the composition of the cocoa residue of 61.67% potassium oxide, this oxide remaining in a significant percentage in the active carbon. The presence of residual potassium in the precursor, as well as the insertion of a greater quantity of the element after activation, favors an increase in the microporosity of the coal [11]. According to Cordeiro (2022), potassium as an activating agent improves textural properties with an increase in surface area.

Table 2. Elemental analysis by WD-FRX of cocoa residue and activated carbon

Oxides	Cocoa residue	Activated charcoal
K_2O (%)	61,50	21,11
CaO (%)	12,17	24,10
MgO (%)	5,50	13,94
SiO_2 (%)	5,20	22,96
Others	15,36	17,61

The XRD results of the precursor and activated carbon are shown in Fig. 2. Lignin and hemicellulose are amorphous macromolecules, cellulose can be crystalline or amorphous, depending on the structural order.
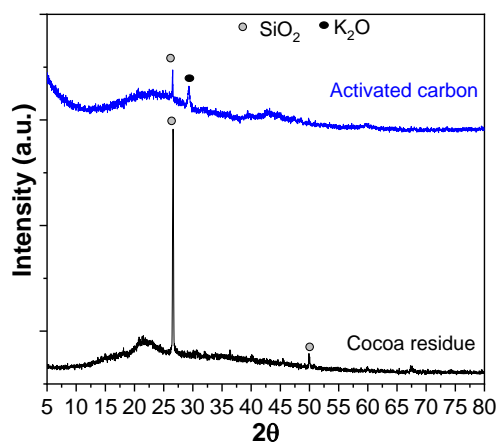

Fig. 2. Diffractograms of cocoa residue and activated carbon

The cellulose present in these samples presents a low structural order, as observed in Fig. 2, which indicates a predominantly amorphous structure. However, a high intensity peak is noted at $2\theta = 26.61$ referring to SiO_2 in the cocoa residue, which remains less intense in activated charcoal even after successive washing. The peak at $2\theta = 29.37$ in activated carbon refers to K_2O originating from the percussor and the activating agent. This result corroborates those obtained by WD-FRX.

The micrographs of the cocoa residue and activated carbon are shown in Fig. 3. The presence of a fibrous structure is verified, with parallel fibers

as shown in Figure 3(a) that are ruptured after activation with KOH and a carbon is formed activated with dense and irregular surface clusters, Figure 3(b).

According to GUO et al. (2000), activation with KOH can change the morphology of the material, as carbon is oxidized to obtain potassium carbonate, which subsequently decomposes into carbon dioxide and elemental potassium, developing porosity to the material.
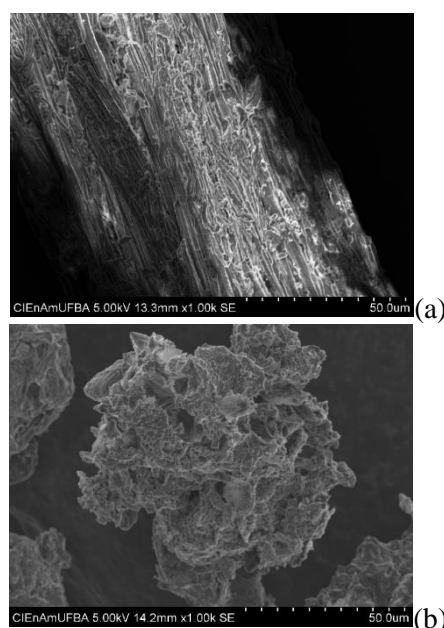

Fig. 3. Micrograph of cocoa residue (a) and activated carbon (b)

The textural properties of activated carbon are shown in Table 3. The data in the table show a promising result for activated carbon, with S_{BET} of 685.7 $m^2.g^{-1}$ and a high micropore area of 1085.9 $m^2.g^{-1}$, which favors the physisorption of CO_2. In the literature, S_{BET} were obtained for coals prepared from cocoa residue of 619 and 642 $m^2.g^{-1}$ [12,13].

Table 3. Textural properties of activated charcoal

Textural properties	Activated carbon
$S_{BET}{}^a$ ($m^2.g^{-1}$)	685.7
$S_{mic}{}^b$ ($m^2.g^{-1}$)	1085.9

[a] S_{BET}, surface area calculated by BET
[b] Smic, surface area calculated by Dubinine-Astakhov method

3.3 CO_2 capture

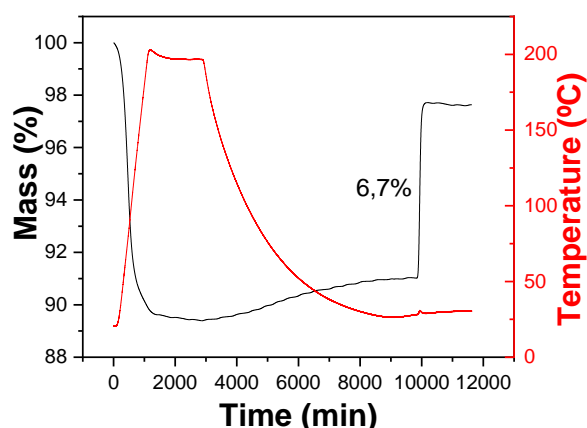The result for the CO_2 capture test is shown in Fig. 4.

Fig. 4. CO_2 capture on activated carbon prepared from cocoa residue.

Initially, a mass loss event was observed until approximately 2000 minutes, in which the impurities adsorbed on the coal surface were removed, for which the sample was heated to 200ºC, under a flow of N_2. The coal was then cooled to 30ºC to favor the adsorption temperature. Finally, the CO_2 flow started to capture the CO_2. A mass gain event (6.7%) is observed between 8000 and 1200 minutes, which represents the amount of CO_2 adsorbed by the coal.

The result obtained by Fiuza Jr. et al. (2016) for the adsorbed amount of CO_2 in carbon samples activated with KOH, obtained from yellow mombin fruit stones, was 6.3% with a surface area of 246 $m^2.g^{-1}$. While Rashidi et al. (2014) obtained 2.7% CO_2 capture, with a surface area of 370.7 $m^2.g^{-1}$ in coal from coconut shells.

The activated carbon prepared in the present work showed a greater CO_2 adsorption capacity (6.7%) than the aforementioned works, in which the coals were also prepared from biomass. This better performance may have been favored by the high percentage of potassium in the coal precursor and the greater surface area obtained.

5. Conclusion

The adsorption capacity of the activated carbon prepared in this study was 6.7%, so it can be concluded that cocoa residue has potential as a raw material for the preparation of activated carbon and application in CO_2 capture.

6. References

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