XRD Study Of Crystalline Phases In Activated Carbon Obtained From Cocoa (*Theobroma Cacao*) Shell

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Abstract:

Background: The cocoa (Theobroma cacao) shell has no specific technical use, and it could be used to prepare activated carbon (AC). The AC represents a feasible adsorbent substrate for the removal of heavy metals, organic and inorganic compounds from solutions. In this work, the formation of crystalline phases due to the activation process in activated carbon obtained from cocoa shell is reported.

Materials and Methods: In this work, cocoa (Theobroma cacao) shells were used as a low-cost precursor for production of activated carbons. The raw materials were carbonized at 300 °C and 350°C. The activation process was realized using H_3PO_4 and KOH at two activation temperatures (500 °C and 600 °C) during 1 h. The startingmaterials were analyzed by the Proximate analysis, as well as, TGA/DSC analysis, FTIR spectroscopy, RAMAN spectroscopy and XRD technique. The crystalline phases in the final compounds were solved by the XRD technique.

Results: The proximate analysis results indicated that the cocoa shell contains values of moisture (~7.95%), high volatile matter (83.34%), ash content (~8.34%) and fixed carbon (9.19%). FTIR spectroscopy identified diverse functional groups, such as, water, alkenes, hydroxyl groups and carboxylic functional groups. RAMAN spectroscopy showed the presence of signals at ~1353 cm^{-1} and ~1578 cm^{-1}, which are related with the D and G band of carbon. XRD technique displayed the cellulose signals around ~15° and 22° in 2θ range in the raw materials, as well as the formation of other carbon-related phases in the carbonized samples. In addition, this technique confirmed the formation of diverse crystalline phases in the activated carbons due to the activation process.

Conclusion:The samples activated with H_3PO_4 displayed crystalline phases in the XRD spectrums compared with the activation using KOH. The correct identification of crystallin phases in the activated carbons could contribute to explain the adsorption or photocatalytic response of some applications of activated carbons.

Key Word: Activated Carbon; Cocoa shell; Activation process; XRD; Crystalline phases.

I. Introduction

In recent years, activated carbon (AC) represents a feasible adsorbent substrate for the removal of heavy metals, organic compounds from solutions[1-2]. The AC can be defined as a class of carbonaceous porous material prepared through the carbonization of any material rich with elemental carbon. Some sources to prepare the AC are coal, agricultural wastes, as well as diverse lignocellulosic materials[3]. In this sense, several authors have been reported the successful synthesis of activated carbon using agricultural wastes, such as, orange peel[4], sugarcane bagasse[4], coconut[5], bamboo[6], banana peel[7], cocoa shell[8], among others. However, it is important to mention that the adsorbing quality of the final activated carbon is influenced by the carbonization temperature, activating reagents, activation time, impregnation ratio, the presence of inorganic impurities and crystalline phases in the material[3].

The cocoa is one of the fastest-growing crops worldwide with an estimated world production of more of 5k million tons[9] and in Mexico, the Tabasco state is the major producer with the ~63 % of the cacao production in the country[10]. The cocoa shells correspond to the 90% of the fruit and it is mainly composed of pectic polysaccharides (45%), hemicelluloses (20%), cellulose (35%) and contain lignin[11]. In addition, cocoa shell has no specific technical uses and it shall have a huge disposal problem[11].

In this work, cocoa (*Theobroma cacao*) shells from the Tabasco state were used as a low-cost precursor for production of activated carbons using two temperatures of carbonization (300°C and 350°C). The materials were characterized by proximate analysis, TGA/DSC analysis, FTIR spectroscopy, RAMAN spectroscopy and the XRD technique. The effect of the activation process using H_3PO_4 and KOH on the formation of crystalline phases is reported.

II. Material And Methods

Raw materials

The precursor used to obtain the activated carbon was the cocoa (*Thebroma cacao*) shell obtained from the municipality of Comalcalco in the Tabasco state of Mexico (Fig.1). The raw material was sliced into strips of ~50 mm x 6mm and it was sun dried before the carbonization.

Figure 1. (a) Cocoa fruit, (b) cocoa shell and (c) activated carbon.

Proximate analysis

The proximate analysis was realized to the precursor material based on the ASTM standards; moisture[12], volatile matter[13], ash content[14] and fixed carbon.

TGA/DSC analysis

Thermal decomposition of the cocoa shells was observed in terms of mass loss through LABSYS Evo TG thermogravimetric analyzer. The cocoa shell was pulverized, and 17 mg was collocated in a sample holder. Before the thermal decomposition analysis, a high purity argon stream with a flow rate of 60 mL min^{-1} was continuously passed into the furnace to prevent any undesired oxidative decomposition. The analysis was realized from room temperature to 700°C using a heating rate of 10 °C min^{-1}.

Yield and carbonization of cocoa shell

The cocoa shell was carbonized to evaluate the carbonization temperature on yield. In this sense, 100 g of different samples of cocoa shell were sintered in a furnace at diverse temperatures (200, 250, 300, 350, 400, 500 and 600 °C) using a heating rate of 5 °C min^{-1} during 30 min in air atmosphere.

Experimental design

A full factorial experimental design (FED) 2^4 (two levels (low and high) and four factors) was used to obtain the interactions among diverse parameters (Table 1). The factor A represents the activation temperature (500 and 600 °C); factor B, time (1 and 2 h); factor C, cocoa carbonization temperature (300 and 350°C); factor D, activating agent (H_3PO_4 or KOH).

Table 1. Full factorial experimental design (FED) 2^4 used for the preparation of the activated carbon

Activation Agent C	Carbonization temperature (°C) D	Temperature of activation (°C) A	500		600	
		Activation time (h) B	2	3	2	3
H_3PO_4	300		C CCA$_{11}$	C CA$_{12}$	C CA$_{13}$	C CA$_{14}$
	350		C CA$_{21}$	C CA$_{22}$	C CA$_{23}$	C CA$_{24}$
KOH	300		C CA$_{31}$	C CA$_{32}$	C CA$_{33}$	C CA$_{34}$
	350		C CA$_{41}$	C CA$_{42}$	C CA$_{43}$	C CA$_{44}$

Fourier transform infrared spectroscopy (FTIR)

FTIR spectroscopy was used to study the changes in the functional groups of the raw material and after the carbonization process. This technique was realized in a Thermo Scientific Nicolet IS50 spectrophotometer from 4000 to 400 cm^{-1} (32 scans, resolution =4).

RAMAN spectroscopy

Raman spectroscopy was realized to detect the formation of carbon in the samples. The Raman spectroscopy measurements were carried out at RT in a Raman system from XploRA plus model (Horiba Jobin Yvon IBH Ltd, Glasgow, Uk) with λ = 532 nm and data collected in the range 100-700 cm^{-1}.

X-Ray Diffraction technique (XRD)

The crystalline structure of the raw material, the effect of carbonization process, as well asthe effect of the activation process were observed by the XRD technique. The X-ray diffraction analysis was carried out using a D2 phaser 2nd Gen diffractometer (Bruker brand) coupled with Lynxeye detector using Cu K$_\alpha$ radiation (λ = 1.5406 Å) at 30 kV and 10 mA.

III. Results

Proximate analysis

The chemical composition of the cocoa (*Theobroma cacao*) shell was obtained from proximate analysis based on the ASTM standards: D2867-09[12], D5832-98[13] and D2866-04[14] (Table 2). The analysis indicates that the cocoa shell contains about ~7.95 % of humidity, ~88.34% of volatile matter, ~8.34 % of ash and ~3.32 % of fixed carbon.

Table 2. Proximal analysis of cocoa shell.

Proximate Analysis	Humidity (%) ASTM D2867-09	Volatile Matter (%) ASTM D5832-98	Ash (%) ASTM D2866-94	Fixed carbon (%)
Cocoa shell	7.95	88.34	8.34	3.32

TGA/DSC analysis, yield and carbonization of cocoa shell

The TG/DTA analysis displayed the loss of mass of the cocoa shell. The TG spectrum shows 4 stages[6] which are identified in the Fig. 2a. The first stage occurs attemperatures below ~150 °C where a mass loss of ~15% is observed at 135°C. This loss can be attributed to the evaporation of moisture and volatile matter of the cocoa shell. The second stage started around 115°C and finished at ~220°C, where no significant mass loss can be observed at 220 °C (only ~2%). In this range, occurs the decomposition of lignin[6]. The third stage occurs between ~220 °C and ~340 °C, where the cocoa shell showed a loss mass of ~58% at 280°C. This effect is normal considering that in this temperature range occurs the decomposition of the hemicellulose (~220-315 °C), cellulose (~315-400 °C) and lignin (~160-900 °C). Finally, the fourth stage considers the gradual decomposition of the lignin and cellulose (~350-700°C).
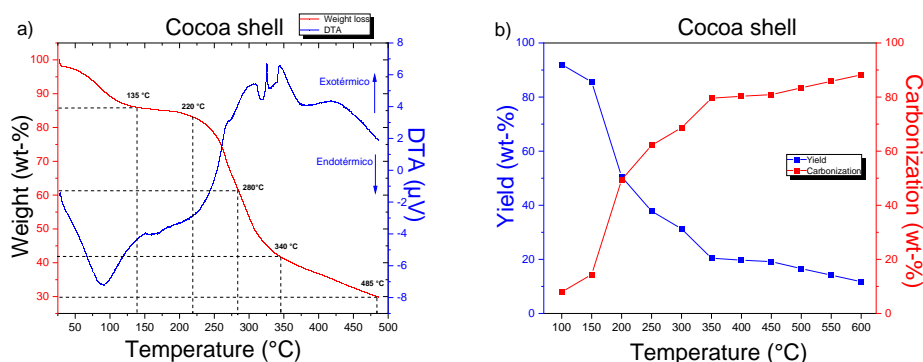

Figure 2. (a) TG/DTA analysis of cocoa shell and (b) Yield and carbonization graphs of cocoa shell.

On the other hand, the Fig. 2b displays the yield vs carbonization graph of the cocoa shell. The material shows a yield of 50% at the temperature of 200 °C, however the percentage of carbonization is low. A good percentage of carbonization was achieved at 350 °C (~80 %), however the yield is around 20%. For the above, the selected temperatures for the preparation of the activated carbons were 300 and 350 °C.

Fourier transform infrared spectroscopy (FTIR)

The FTIR spectra (Fig. 3) shows typical signals of lignocellulosic precursors[4]. The water content in the raw cocoa shell is related with the band in ~3250 cm^{-1}, that correspond to the -OH signals of H_2O[15]. In addition, some signals are observed between ~1500 and 1650 cm^{-1} that are related with weak bonds of carbon (C=C). The signals related with the hemicellulose (C-H, C-C and C-O) were observed in ~1000, ~1242, ~1325, ~1426 and ~1595[16]. It is important to mention that the carbonization temperature promoted that some signals were reduced, however, some bands related with the cellulose and lignin are observed, because they need higher temperatures to decompose[6].
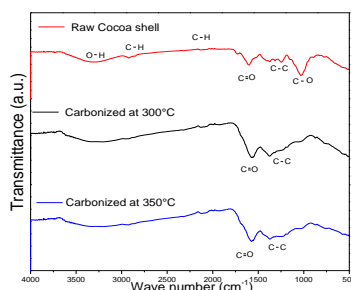
Figure 3. FTIR spectra of the cocoa shell.

RAMAN spectroscopy

The formation of carbon due to carbonization process was observed by RAMAN spectroscopy (Fig. 4). The wor characteristic oscillations of carbon are observed in the RAMAN spectra. The first vibration is in ~1353 cm^{-1} (D band) and it is related to the defects and disorders in the graphite structure of carbons. The second signal is in ~1578 cm^{-1} (G band) and it is related to the stretching of the Sp^2 bond between carbons in graphite configuration[17]
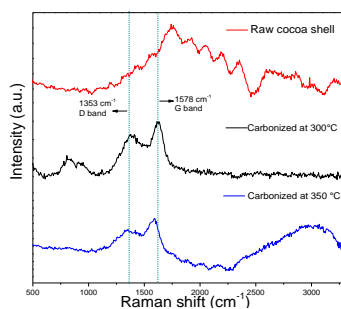

Figure 4. Raman spectra of cocoa shell samples.

X-Ray Diffraction (XRD)

X-Ray powder diffraction is one of the most potential characterization tools as well as non-destructive technique for characterizing carbon-based materials and their composite properties[18]. The raw cocoa shell (Fig. 5) showed the characteristics wide peaks of the cellulose (ICDD-09-0289) in ~14° and 22° in 2θ range. On the other hand, the carbonization process at 300°C and 350 °C favored the reduction of the cellulose peaks due to its decomposition and provoked the formation of extra peaks that match-well with diverse crystalline phases related with carbon (ICDD-001-0640, ICDD-089-8493, ICDD-007-2136, ICDD-082-2779). The above confirmed the signals of carbon observed in RAMAN spectroscopy.
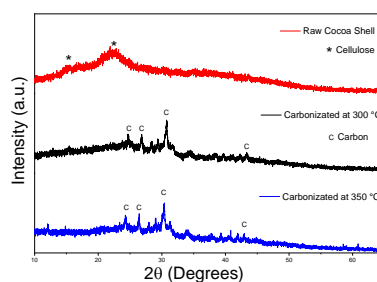
Figure 5. XRD patterns of cocoa shell samples before the activation.

The activation process with H_3PO_4 was applied to the samples carbonized at 300°C and 350°C using the experimental design showed in the Table 1 and the XRD results are shown in the Fig. 6.In the XRD pattern of the C CA11 sample (Fig. 6a) is possible to observe only a peak in ~30.6° in 2θ, which match-well with carbon phase of the ICDD 081-9116 card. However, the increment in the activation time as well as the temperature of activation favored in the C CA12, C CA13 and C CA14 samples the formation of diverse crystalline phases, such as Hydrogen Potassium Phosphate phase (ICDD-013-2371) and Archerite phase (ICDD-002-8835). The activated carbon samples carbonized at 350 °C (Fig. 6b) shown similar behavior compared with the samples carbonized at 300 °C (Fig. 6a). The C CA21 sample was the only one which displayed the carbon phase and the C CA22, C CA23 and C CA24 samples shown the Archerite phase
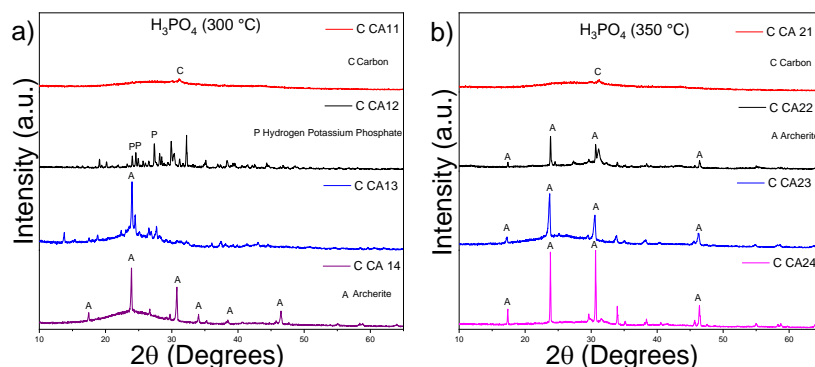

Figure 6. XRD patterns of cocoa shell samples carbonized at 300 °C (a) and 350 °C (b) after activation with H_3PO_4.

The XRD results of the samples activated with KOH are shown in the Fig. 7. The diverse samples carbonized at 300°C (Fig. 7a) displayed extra peaks of diverse crystalline phases, such as Potassium Hydrogen Phosphate Hydrate $((H_2K_3P_3O_{10})(H_2O))$, Potassium Hydrogen Phosphate $(K_2H_2PO_4)$ and Hydrogen Potassium Phosphate $(H_2K(PO_4))$. These phases could be formed by the activation process with KOH and residues on the starting sample at 300°C. Only the samples C Ca32 shown peaks attributed to a crystalline carbon phase. On the other hand, the samples carbonized at 350 °C (Figure 7b) did not shown extra peak a crystalline phase. The C CA42 and Ca44 samples shown signals of the carbon phase possibly to the major temperature time.
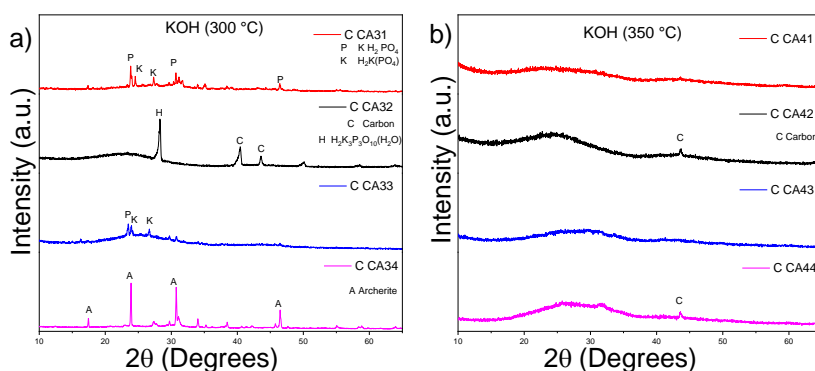

Figure 7. XRD patterns of cocoa shell samples carbonized at 300 °C (a) and 350 °C (b) after activation with KOH.

IV. Conclusions

In the present study, activated carbon from cocoa (Theobroma cacao) shell by acid and basic media were successfully obtained. The yield and carbonization results indicated diverse parameters to taking account to realized diverse series of activated carbon using cocoa shell. The FTIR spectroscopy and RAMAN spectroscopy indicated that the starting samples contained the formation of carbon, and it is expecting that at higher temperatures conserve the carbon contain. The XRD results shown the formation of diverse phases due to the activation process. The samples activated with H_3PO_4 displayed morecrystalline phases in the XRD spectrums compared with the activation process using KOH. It is necessary complement the characterization of these activated carbon samples with BET analysis and SEM characterization to obtain superficial area and

morphology. However, the identification of the crystalline phases in the activated carbons could contribute to explain the adsorption or photocatalytic response of some applications of activated carbons.

Acknowledgments

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