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Preparation of bone chars by calcination in traditional furnace

N. Slimani Alaoui [1], A. El Laghdach[1], E. Manuel Cuerda Correa [2],
M. Stitou [1], F. El Yousfi [1], N. Jbari [1]

[1]*Laboratoire De l'Eau, d'études et des analyses environnementales, Département de chimie, Faculté des sciences Université Abdelmalek Essaâdi, B.P. 2121, Mhannech II, 93002 Tétouan, Maroc*
[2]*Département de chimie organique et inorganique, Faculté des sciences, Université d'Extremadura, Avda d'Elvas S/N, E-06071, Badajoz, Espagne*

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**Corresponding author: Email: slimanialaouinabila@gmail.com; Tel :(+212 661 316 209)*

Abstract

This work aims to prepare adsorbents based on low cost cattle bones. The bones have sustained a carbonization in inert atmosphere at two different temperatures 400°C and 600 °C in a traditional furnace, followed by activation by hydrochloric acid. The charcoals obtained were characterized by X-ray diffraction (EDX) and scanning electron microscopy (SEM), infrared spectroscopy (FT-IR) and Brunauer-Emmett-Teller technique (BET). The results showed that the specific surface area of these coals reached 83 m^2/g, in addition to a considerable mesoporous texture that has been developed, the dominance of calcium and phosphorus detected by EDX and the presence of functional groups of carbonates and hydroxyl, with a dominance of phosphate ions (PO_4^{3-}) shown by FT-IR. The previous results have clearly showed that the coals can be used for the adsorption of various organic pollutants that derive from industrial discharges.

Keywords: Bones, Carbonization, Activation, Characterization, Adsorption

1-Introduction

The various industrial sectors are considered to be large consumers of water. This excessive use generates consequently large flows of industrial wastewater. These waters are extremely heterogeneous, their quantity and quality vary depending on the operated process used. They often present a wide spectra of chemical pollutants, consisting of solid or dissolved state, organic-inorganic materials, dyes, metals, hydrocarbons, solvents, oils, fats, salts, ... at various levels of toxicity and which are mostly discharged into the environment [1].

The evacuation of these effluents without preliminary treatment harms the environment, particularly the Oueds and the groundwater, which introduces an imbalance of the ecosystems. Several techniques were used to eliminate the pollution contained in these effluents. According to their physico-chemical characteristics, we can design various processing chains, namely, biological treatment, physicochemical, coagulation-flocculation, filtration, oxidation, etc....

Adsorption is one of the most techniques used for treatment of industrial discharges, stemming from food industry, textile industries and those that generate heavy metals. It is an easily practicable technique; that defines the property of some materials to fix their surface molecules extracted from the liquid phase or the gas phase in which they are immersed [2].

The activated charcoal is one of the most used materials for the adsorption of organic pollutants. Its elaboration has been the subject of several studies; it can be obtain from different natural sources (coal, lignite, anthracite, fibers of palm trees, oil shale, coconut, peat, pine wood, bone, etc...) [2, 3].

Coals prepared from bones were used for a long time by food industry, for the purification of sugars, and it has proven efficiency for discoloration of syrups, wine, vinegar, without destroying them [4] and discoloration of acids [5]. This coal was also used for the removal of mercury [6], copper [7] and the fluorides which can be present in abundance in water table [8], and used for adsorption of contaminated air and water by microbial contaminants [9,10].

The present work has as objective to test the efficiency of two coals prepared with cattle bones, in a traditional furnace, at two different temperatures, by characterizing them by various techniques of characterization, to verify the possibility of their use for the discoloration of some industrial discharges.

2 - Materials and Methods:

2-1 Preparation of coals:

Carbonization:

Bones used in this work are bones of beef, resulting from a slaughterhouse in Meknes city.

A first, the Bones are degreased with boiling water in a cooking pot for 1hour, and dried in a steam room at 110°C. They are then placed in a closed vase and introduced in a traditional oven (400 to 600° C) in absence or limited presence of oxygen [4, 11]. The carbonized materials were recovered after one hour of carbonization.

Two types of coal were obtained further to the variation of the temperature, the first one that was carbonized at 400°C, is black, and the second one, carbonized at 600°C is grey. Coals were kept in closed flasks to prevent any interaction with air.

The carbonized materials were then grinded in a mortar, and sieved through 1 mm sieve, in order to have uniform particles.

Activation:

The activation of both types of coals was realized using concentrated hydrochloric acid with a ratio of 10ml per 50g, and a contact time of 4 hours under host. The carbons were washed with distilled water until obtaining a neutral medium (pH = 7), to eliminate the excess of acid, then were filtered using a vacuum pump, and were dried at 100°C in the steam room for 2 hours. The Powder obtained from the activated charcoals has a diameter of 0.1 to 0.5 mm, and can be used for the adsorption.

2-2 Characterization of coals:

Four types of coal were prepared; they are named and grouped according to the following table:

Table 1. Nomenclature of carbonaceous materials prepared

Material	Preparation Temperature	Nomenclature
Raw coal	400 °C	CBN-400
Activated charcoal	400 °C	CAN-400
Raw coal	600 °C	CBG-600
Activated charcoal	600 °C	CAG-600

The samples were dried at 120 ° C for 24 h and characterized by the following various methods:

- The acquisition of the SEM images with the EDX spectra was carried out using 3D Quanta FEG equipment (FEI Company, Hillsboro, 169 USA). Measurements were made in the high vacuum working mode, using an accelerating voltage of 15 kV. The secondary detector (DTE) was used and the working distance was 10 mm.
- The samples were texturally characterized by gas adsorption (N_2, -196ºC), mercury porosimetry and mercury and helium density measurements. The samples were always first oven dried at 120ºC for 24 h.
- The adsorption isotherms of N_2 (purity > 99.998%) at -196ºC were collected using an adsorption apparatus (Autosorb-1, Quantachrome). Approximately 0.15 g of sample was used in each adsorption experiment. Adsorbents were placed in a glass container and degassed at 10^{-3} Torr at 120ºC overnight prior to the adsorption measurements.
- A Quantachrome porosimeter, Autoscan-60, was used to obtain the mercury intrusion curves. The values of surface tension and contact angle used in the computational program of the porosimeter were 0.480 N m−1 and 140º, respectively.
- Samples were also characterized in terms of surface chemistry by FT-IR spectroscopy. The FT-IR spectra were recorded to IR-300 spectrophotometer Thermo Nicolet in the range of wave numbers 4000-450 cm^{-1}. 32 scans were collected at 4 cm^{-1} resolution. Disks were prepared in a ratio sample: KBr = 1:500. The total mass was 250 mg. The dispersion of the sample with the KBr was placed in a Perkin-Elmer hydraulic press, and a charge of 10 tons was applied for 3 min. A background spectrum was registered previously, using a KBr disk with the same mass and thickness as for the samples.

3- Results and discussion

3-1 Elemental Analysis CHNS:

The elemental analysis (CHNS) for both carbonaceous materials showed that the carbon content is significantly different, it is reduced for the coal calcined at 600°C, compared to the one calcined at 400°C whose content in carbon is extremely high. From these data it may be concluded that the mineralization degree of all samples is high, as a consequence, the carbon content of all samples is very low. The same observation was made in the case of nitrogen. While in the case of hydrogen and sulfur; a slight decrease in CBN-400 to CBG-600, was recorded. After activation of the calcined carbon, by hydrochloric acid, it was observed that there was no significant change between the coal charred at 400°C and the coal charred at 600° C for all elements.

Table 2. CHNS Elemental analysis of samples

Sample	Element	Weight %	Sample	Element	Weight %
CBG-600	C	1.138±0.254	CBN-400	C	5.474±0.045
	H	0.897±0.110		H	0.928±0.013
	N	0.241±0.098		N	0.886±0.011
	S	0.036±0.022		S	0.056±0.006
CAG-600	C	2.317±0.096	CAN-400	C	3.426±0.143
	H	0.515±0.002		H	0.681±0.012
	N	0.283±0.037		N	0.361±0.042
	S	0.028±0.001		S	0.029±0.004

3-2 Characterization of carbonaceous materials by SEM (Scanning Electron Microscope)

The observation of samples by SEM (Figure 1), allowed us to get an idea about the texture of carbonaceous materials obtained. It was observed that there is a variety of forms, recorded for all coals, some are sharp and others are pointed and rounded, it is essentially due to the presence of several particles in coals, this will be explained later, by the analysis of diffraction of the X-rays and infrared spectroscopy.

We noticed that the form of coals has no sudden of modifications, either before or after chemical treatment, which explain the role of hydrochloric acid, which allows the preservation and stability of coals.

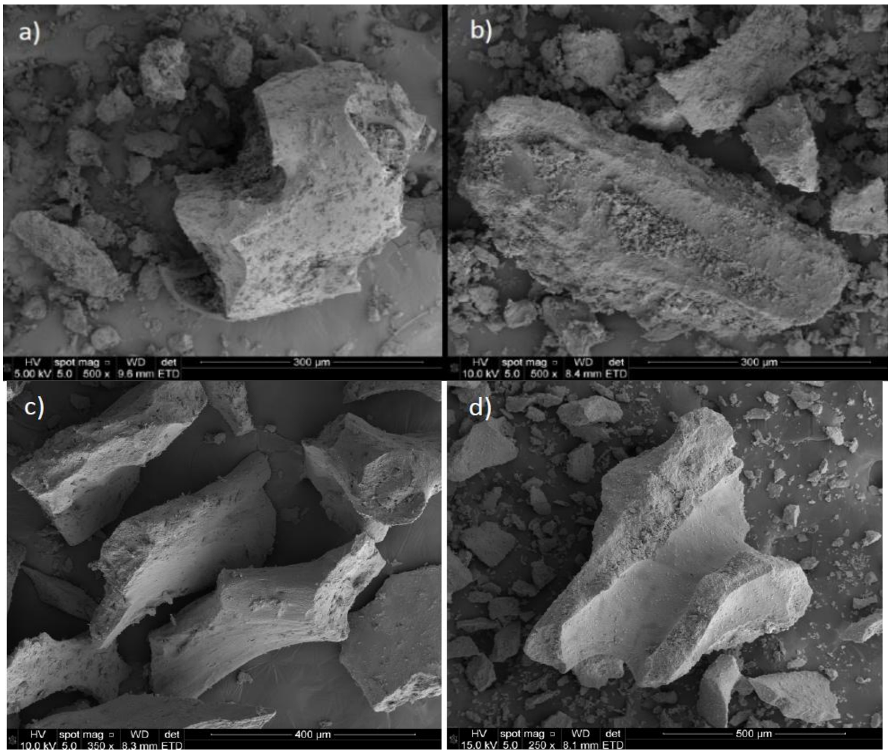

Figure 1. SEM images of Samples CBG-600 (a), CBN-400 (b), CAN-400 (c) and CAG-600(d)

3-3 Characterization by X-ray (EDX):

The study of EDX elemental analysis of carbonaceous materials showed the presence of several elements. The Calcium, phosphorus, carbon and oxygen are the most abundant elements in these materials. According to the data summarized in Table 3, we notice that the phosphorus content is practically the same for all the samples; the calcium is slightly lower for the CAG-600. Carbon is more abundant in the CBN-400, while the oxygen content increases regularly passing from the CBG-600 to CAG-600 and from the CBN-400 to CAN-400. After the calcination of bones at 600 °C, the content in chlorine and in potassium increases in a remarkable way, compared to the bones calcined at 400 ° C. In fact, after activation with hydrochloric acid concentration this content decreases.

By analyzing these results, we notice that the calcination of bones at high temperatures, introduces the combustion of organic carbon and the mineralization of the nitrogen, while the activation by acid does not act on its elements.

Table 3. EDX local elemental analysis of samples

Sample	Element	% weight	% Atome	Sample	Element	% weight	% Atome
CBG-600	C	8.08	17.06	CBN-400	C	12.30	24.09
	O	20.83	33.01		O	23.17	34.06
	Na	1.11	1.23		Na	0.51	0.52
	Mg	0.72	0.75		Mg	0.28	0.27
	P	18.47	15.12		P	20.35	15.45
	Cl	8.45	6.04		Cl	1.86	1.24
	K	0.22	0.14		K	0.09	0.05
	Ca	42.12	26.65		Ca	41.45	24.32
	Total	100.00	100.00		Total	100.00	100.00
CAG-600	C	9.42	17.72	CAN-400	C	9.09	17.93
	O	31.91	45.09		O	27.01	40.00
	Na	1.35	1.33		Na	1.06	1.09
	Mg	0.71	0.66		Mg	0.71	0.69
	P	19.62	14.32		P	20.31	15.54
	Cl	0.25	0.16		Cl	0.25	0.17
	K	0.20	0.12		K	0.21	0.13
	Ca	36.54	20.61		Ca	41.37	24.46
	Total	100.00	100.00		Total	100.00	100.00

The presence of large amounts of calcium and phosphorus has also been noticed, which is compatible with the presence in abundance of calcium, phosphate and carbonate in the original material. The activation by HCl doesn't affect the calcium and phosphorus of carbonaceous materials that have been calcined at 400°C, whereas the materials calcined at 600°C, their content has changed (Figure 2).

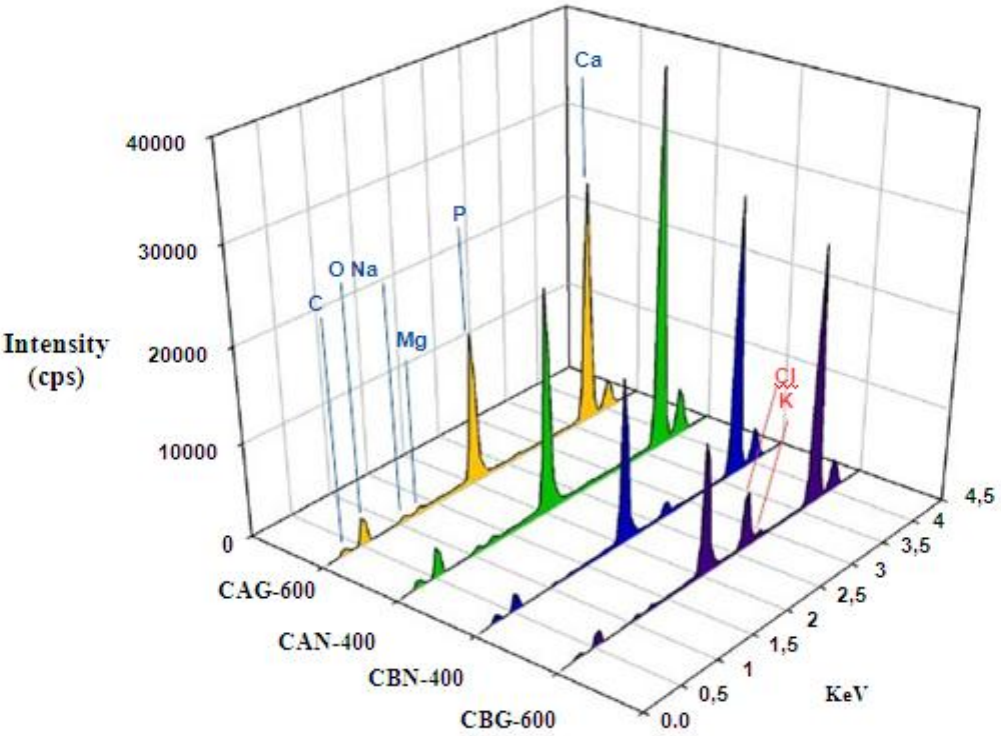

Figure 2. Representation of peaks of diffraction of the X-rays (EDX) in 3D of the various samples

It is observed that the ratio Ca / P of all the carbonaceous materials studied is approximately equal to 1.67, which corresponds to the pure hydroxyapatite of the beef bones, for which the formula is $Ca10\ (PO_4)_6\ (OH)_2$ [10, 11]. This is in agreement with other studies that indicate that the carbonization temperature of bones between 200 ° C and 600 ° C has no influence on the ratio Ca / P of pure hydroxyapatite, whose the melting temperature is 700 ° C [14].

The content in carbon decreased after calcination of bones at 600 ° C, this can be explained by the combustion of organic coal and the persistence of mineral coal only. The activation of carbonaceous materials by hydrochloric acid gives them more oxygen, this is explained by the introduction of the carbonyl groups on the surface of the coal, which are bound in the carbon atom [15].

The content in chlorine decreased after activation by HCl, this can be explained by the fact that after washing by distilled water, there was an elimination of the excess acid that carried off the chlorine.

3-4 Measure of the specific surface area:

From the N_2 adsorption data, the values of specific areas (S_{BET}), micropores volume (Vmi) and mesopores volume (Vme) summarized in Table 4 have been calculated.

Table 4. Surface area and pore volumes of the various samples

	N_2 adsorption		**Hg porosity**	
Sample	**S_{BET} (m^2/g)**	**Vmi (cm^3/g)**	**Vme (cm^3/g)**	**Vme-p (cm^3/g)**
CBN-400	41	0.014	0.095	0.139
CBG-600	36	0.001	0.124	0.160
CAN-400	83	0.028	0.217	0.255
CAG-600	53	0.017	0.180	0.228

It is observed that the values of specific surface areas, obtained after the calcination of beef bones, studied at 400°C and 600°C, are respectively of the order of 41 m^2 / g and 36m^2/g. The temperature of calcination influences slightly the value of the specific surface.

After activation of the materials by the adding concentrated hydrochloric acid (36 N), the surface area of the final materials has increased to reach 83 m^2 / g and 53 m^2 / g , respectively for materials calcined at 400°C and 600°C. This can be explained by the action of the acid on the potential of the basic groups, which occupied pores or their entries, preventing thus the arrival of nitrogen at the bottom of these pores. The results of the local elementary analysis made by EDX, indicates that the mass rate of Cl has decreased after activation of the calcined materials, in fact, it went from 1.86 to 0.25% for CBN-400 and from 8.45 to 0, 25% for CBG-600, which justifies this assumption.

The adsorption isotherms of the carbonaceous materials are depicted in Figure 3, together with their respective DFT plots.

By analyzing these curves, we observe that they are isotherms type II according to BET classification. From the adsorbed volume of N_2 it may be stated that the development of the surface area and porosity of the samples is moderate, particularly in the microporosity range. The porous texture of the samples, mainly constituted by mesopores, is gradually developed from sample CBG-600 to CMN-400, then decreasing slightly for sample CMG-600. The increase of microporosity for all samples can be explained by the beginning of dissociation of groups (CO_2, H_2O, H_2S, NH_3) for example, caused by the pyrolysis of organic substances [16], the passage from 0, 4 to 1 indicates the development of mesopores and the beginning of appearance of macropores [7].

This latter is corroborated from the DFT plots depicted in Figure 3 b. These plots clearly point out a scarce development of microporosity and narrow mesoporosity as well as a wide variety of pore sizes within the range of medium-size to large mesopores. As expected from the N_2 adsorption isotherms, the more significant contribution of mesoporosity corresponds to sample CAN-400**;** the mesoporous volume is about 0.255 cm^3 / g, which is similar to the literature [18], therefore it is the most adopted for the use for adsorption of the organic pollutants.

In order to further analyze the porosity of the samples, mercury intrusion curves were acquired. The Figure 4 depicts such curves as well as the pore size distributions that can be obtained from them. From the shape of the mercury porosimetries (Figure 4a) it may be observed the presence of two tracts showing a remarkable slope. These tracts are located in the ranges of pore radii 50-200 Å and $2{\cdot}10^4$-10^6 Å. Adsorbents contain pores classified into three groups, micropores (<2 nm), mesopores (2-50 nm) and macropores (> 50 nm), the results are represented in Å (angstroms), 1 Å = 0.1 nm [19].

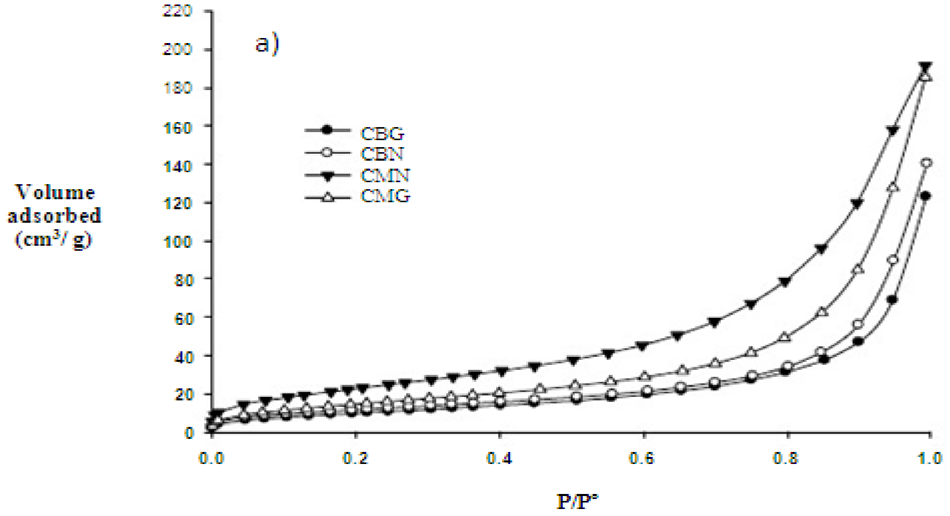

Figure 3a. N_2 adsorption isotherms

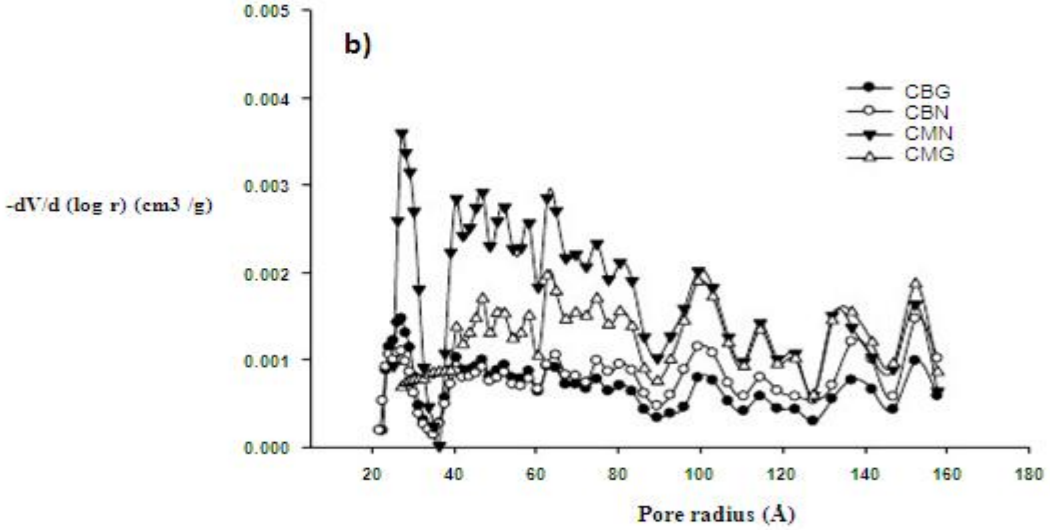

Figure 3b. Pore size distribution obtained by DFT of samples

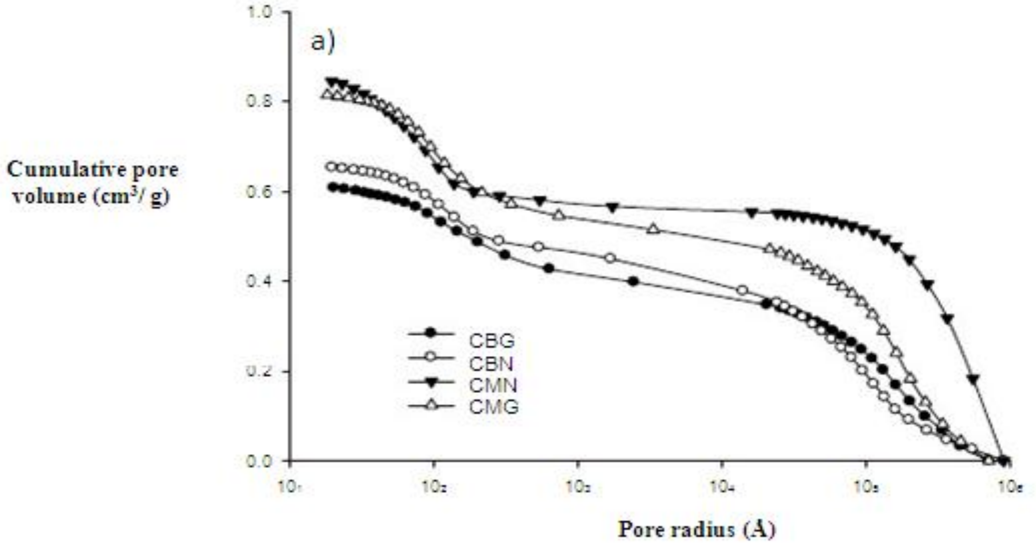

Figure 4a. Mercury intrusion curves

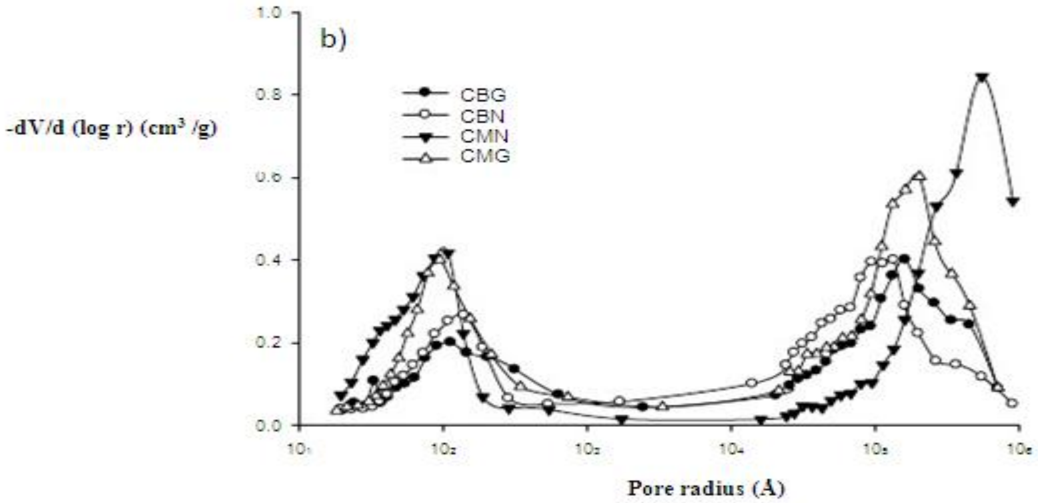

Figure 4b. Meso- and macropore size distributions of samples

Hence, it may be concluded that the pores showing pore radii in these intervals contribute to the wide mesoporosity and macroporosity, respectively, to a larger extent. This assertion is corroborated from the pore size distributions shown in Figure 4b, where two broad peaks appear in the corresponding intervals. All the above exposed is in good agreement with the values of the meso- and macropore volumes (Vme-p and Vma-p) summarized in Table 4.

By referring to literature, we find that the percentage of total porosity of the cattle bones is about 5.20% [13], this value is extremely increased, reaching 84% after the heat treatment of coals. This can be explained by the evaporation of water and the combustion of organic substances contained in the bones, only the mineral part persists [20].

3-6 Analysis by infrared spectroscopy:

The surface chemistry of the samples has been analyzed by FT-IR spectroscopy. Several spectra were recorded; they are shown in Figure 5. The analysis of these spectra allowed us to have a clear idea about the composition of the materials after carbonization and activation with chloridric acid.

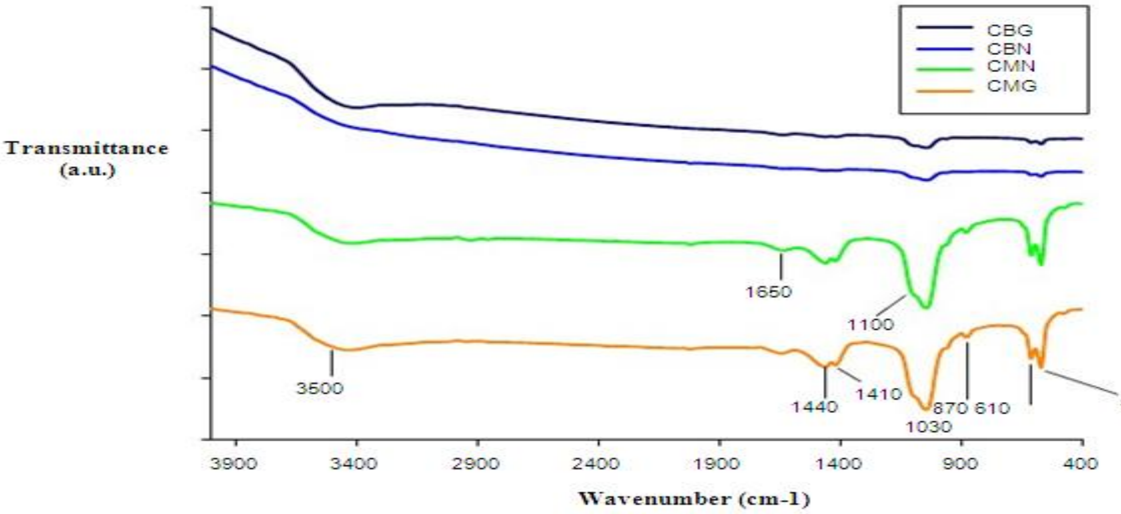

Figure 5. FT-IR spectra of samples

From the FT-IR spectra it may be stated that all sample exhibit similar features in terms of bands position. However, remarkable differences exist regarding the intensity of bands. Thus, for samples CBG-600 and CBN-400 the bands centered around 620-550 cm^{-1} and another band at approximately 1030 cm^{-1} are very weak, corresponding both to PO_4^{3-} ions [6], another band at 3500 cm $^{-1}$ corresponding to hydroxyl groups, recorded for CBG-600 only .

After activation of carbonaceous materials by hydrochloric acid other bands have been recorded. In fact, there is a band between 620-550cm^{-1} and another one, sharper, around 1030 and 1100 cm^{-1}, these two bands correspond to the PO_4^{3-} ions [4]. A weak band at 870 cm^{-1} corresponding to aromatic rings [17] has also been identified. A band at 1410 and 1440cm^{-1} can be characteristic of C = C and O- H. The band at 1650cm^{-1} can be attributable to the molecule C = O while the one at 3500 cm^{-1} corresponds to hydroxyl groups (-OH) [21], this band is slightly concave for the CAG-600, the hydroxyl groups increase with the increase of temperature, until reaching very high temperatures (1000C °),then, they decrease again [12].

Table 5. Assignation of the main spectral features for samples

Band position (cm^{-1})	**Functional group**
560 610	PO_4^{3-}
870	Aromatic rings
1030 1100	PO_4^{3-}
1410 1440 1650	C=O, C=C, O-H
3500	O-H

Conclusion

The main object of this work was to carbonize some materials based on cattle bones in a traditional furnace, at two different temperatures (400C° and 600C°), subsequently activated with concentrated hydrochloric acid. The characterization of these carbonaceous materials by BET showed that they have developed a large surface area and a significant mesoporous texture. The infrared analysis has determined their chemical composition, where they have kept their phosphate groups characteristic of pure hydroxyapatite, and have developed other functional groups resulting from thermal and chemical treatment.

The use of these carbonaceous materials for the adsorption of organic pollutants turned out interesting, considering that it will be easily applied at attainable conditions with a very low cost, which will encourage manufacturers to integrate into the sustainable development.

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