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amina ghedjemis (amina.ghedjmis@yahoo.com)  
Mohamed El Bachir El Ibrahim University  https://orcid.org/0000-0002-7079-7954

Riad ayech  
Mohamed El Bachir El Ibrahim University

Ali BENOUADAH  
University of Algiers

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A COMPARATIVE STUDY ON PROPERTIES OF HYDROXYAPATITE PREPARED FROM BOVINE AND DROMEDARY BONE

A. GHEDJEMIS*, R. AYECH¹, A. BENOUADA²

¹laboratory of characterization, valorization of natural resources, department of biological sciences, Mohamed El Bachir El Ibrahim University, Bordj Bou Arreridj, Algeria

²Faculty of Sciences, University of Algiers 1, Algeria

ABSTRACT

The recovery of agro-food waste is at the heart of the challenges of the 21st century, in this context that this research work comes. A biomaterial is prepared from a significant resource such as dromedary bone and bovine bone by heat treatment at different temperatures and characterized by physico-chemical techniques in order to have the effect of bone type on the physico-chemical properties of hydroxyapatite. The results of FTIR and DRX show the removal of all organic matter and the production of pure hydroxyapatite without any additional phase for both bone types. Analyzes by SEM and laser particle size analyzer show that the particle size of hydroxyapatite is increased with increasing temperature. From the results of XRF, bone type is a direct effect on the concentration of hydroxyapatite compounds in hydroxyapatite prepared from dromedary bone compared to hydroxyapatite prepared from bovine bone.

Keywords: dromedary bone, bovine bone, physico-chemical properties, hydroxyapatite
1. INTRODUCTION

The materials used by humanity to treat and repair the human body back to antiquity. Natural materials such as wood were utilized for try to structurally replace tissue lost due to diseases or accidents. At the start of the 20th century, synthetic polymers, ceramics and metal alloys take the place of materials of natural origin, which offer better performance, grew functionality and greater reproducibility than their natural origin occurring counterparts. Practical and representative metallic biomaterials can be classified into the following groups; cobalt-based alloys, stainless steel (316L) and titanium-based alloys. Early research and fortuitous accidents linked the chemistry of materials to biological response, provided a rational basis for the development of biologically inert substrates, and provided a scientific basis for biomaterials as an intellectually distinct discipline. Calcium phosphate is a group of biominerals containing orthophosphate anions (PO$_4^{3-}$) and calcium cations (Ca$^{2+}$). These compounds have been the subject of much research in recent years, especially due to their dominant role in various applications. They are used as biomaterials for biomedical applications, also as adsorbents for the treatment of polluted water. One of the most interesting formulas of calcium phosphate is hydroxyapatite because of its physico-chemical similarity to the mineral phase found in hard tissues such as teeth and bone. Its stoichiometric formula is Ca$_{10}$(PO$_4$)$_6$(OH)$_2$, with a hexagonal structure, a density of 3.156 and a Ca / P ratio of 1.67. The development of hydroxyapatite in the medical or environmental field requires several modes of synthesis, which are two families of methods either by chemical attitude or by natural attitude.

In recent years, the valorization of by-products represents the major interests targeted by the world. Among the under-used products accompany the production of food and available in Algeria, camel bone and bovine bone which are these two sources used in this article for the preparation of
hydroxyapatite powders and studied the effect of the source of bone on the physico-chemical properties of hydroxyapatite.

2. EXPERIMENTAL PROCEDURE

2.1 Presentation and location
The femurs of the dromedary and bovine bone constitute the part used in this study. Both types of bones were collected from the butcher shop. The breeding of the two animals is located in the south-east region of Algeria, in Oued Souf city.

2.2 Préparation de l’hydroxyapatite
The extraction of bone mineral matter is carried out from the dromedary and bovine femur bones by the calcination method. The preliminary stage of the preparation is the treatment of two types of bones with a gas torch to remove the fatty material present on the surface and reduce the smell of gases given off during their calcination. The bones are then ground into powder by a mechanical grinder at a speed of 300rpm for one hour to ensure complete calcination. The bone powders are calcined in oven air (Nabertherm) at different temperatures (600, 800, 900 and 1000 °C) for 3, 6, 9 and 12 hours with a heating rate of 10°C/min. After calcination, the prepared powder is cooled slowly inside the oven.

2.3 Yield determination
In order to determine the yield of hydroxyapatite, the raw bone is weighed before and after calcination at room temperature (28 ± 2 °C). The efficiency (Y) is evaluated according to the following equation (1) 4.

2.4 Physico-chemical characterizations
The hydroxyapatite powders are characterized by Fourier Transform Infrared Spectroscopy (FTIR from KBr pellet method, Bio-Rad Win-IR Pro), the analyzes of which are carried out in the
wavelength range from (400-4000 cm$^{-1}$) to distinguish the presence or absence of organic matter in the powders of two types of bones prepared at different times and temperatures.

The analysis of the crystalline phases present in the powders is carried out by X-ray diffraction (XRD). The diffractograms are acquired with the Kα radiation of copper (CuKα 1.54056 Å) on a diffractometer (Bruker D8 Advance), the spectrum of which is taken at 2θ: 10°-80° with a step of 0.02.

The size of the crystals is determined according to the Scherrer equation $^{10}$.

Inorganic chemical elements in oxide form present in the sample are analyzed by X-ray fluorescence spectrometer (Bruker AXS GmbH).

The pycnometer is used to determine the density of HA powders prepared from the two types of bone (bovine and dromedary) using the following equation (3) (Lal 2006):

The thermal behavior of HA powders prepared at 600 °C was followed by thermogravimetry and differential. These analyzes were performed by the SHIMADZU 60H DTG apparatus. For this analysis, the rate of rise and fall of temperature is set at 5 °C / min in air and sample analyzes are set up to 1500 °C.

Hydroxyapatite powders prepared from dromedary bone are analyzed by laser particle size analysis (Cilas, Particle Size Analyzer 1090) to determine the effect of temperature on the size distribution of their particles.

The characterizations by SEM scanning electron microscopy of hydroxyapatite were carried out on a Leo 1530 type apparatus, (Carl Zeiss, Germany). The samples were coated with a thin layer of gold using a CRESSINGTON SPUTTER COATER 108 AUTO to reduce the electrostatic charges of the samples and improve the emission of electrons (improved conductivity).
3. RESULTS & DISCUSSION

3.1 General observation

The determination of the optimum temperature for the preparation of hydroxyapatite from two types of bone is carried out by heat treatment at different temperatures (600, 800, 900 and 1000°C). We first determined the optimal preparation time by calcining the bones at different time intervals (3, 6, 9 and 12 h) at 600 °C. The ashes of bovine bones calcined for 6 hours became white but the color of the ashes of dromedary stayed gray, up to 12 hours of calcination, it becomes white. According to some bibliographic data, hydroxyapatite is characterized by a distinct white color and the gray color is due to the presence of significant amount of carbon in the material. This means that the calcination time of 6h at 600 °C is insufficient. The elimination of the organic matter and the obtaining of the biomaterial "hydroxyapatite" from the dromedary bone is required 12 hours at a temperature of 600 °C (Figure 1). Obtaining the color white means total elimination of organic matter, this elimination can be confirmed by infrared spectroscopic analysis.

![Fig 1: Color variation color of the ashes after calcination of the dromedary bone at 600 °C for 12 hours.](image)

3.2 Weight change (Yield):

The yield of hydroxyapatite prepared from two types of bone at different temperatures is shown in
Figure 2. The yield of hydroxyapatite prepared from dromedary bone at 1000 °C for 12 hours is (69%). It is greater than the yield of hydroxyapatite prepared from bovine bone (61.2%). In fact, the yield of hydroxyapatite prepared from bovine bone agrees with that in the literature (62.5%) \(^{12}\) and differs from others \(^{7}\), which indicates that the average yield of hydroxyapatite prepared from bovine bone is 66%. This variation in rate of return can be explained by several factors, including age, sex, type of bone and region of farm. In the light of the results obtained by our research \(^{13}\), we can conclude that the origin of the bone is the main factor of variations in the yield of hydroxyapatite.

![Figure 2: The yield of hydroxyapatite prepared from two types of bone at different temperatures.](image)

### 3.3 Infrared spectroscopy analysis (FTIR):

Figure 3 shows the infrared spectra of dromedary bone ash before and after calcination at different times. In order to examine the degree of removal of organic matter, the appearance or disappearance of organic matter can be verified by FTIR \(^9\). The bands of the amide functional groups (NH) are 2860, 2929 and 2913 cm\(^{-1}\) \(^{14}\). They are present in the spectrum of dromedary bone ash at 2854 cm\(^{-1}\) and 2924 cm\(^{-1}\). These absorption bands do not disappear before 12 hours of calcination.
The results of the calcination of bovine and dromedary bone for 12 hours at different temperatures (figure 4 and 5) show that all the organic matter contained in the bone is eliminated from a temperature of 600 °C, with the exception of the carbonate groups, inserted in the phosphate and hydroxyl sites corresponding to the transition bands: 871, 1460 and 1417 cm$^{-1}$, which explains the change from the black color to the white color. The presence of a carbonate group in hydroxyapatite has an influence mainly on the behavior of hydroxyapatite in a biological medium. Some data in the literature have shown that the elimination of organic matter present in bone is only done from 800 °C. This difference may be due to the type of bone and its origin or to the calcination time. Carbonate groups (CO$_3^{2-}$) can substitute for the phosphate site (type B) or the hydroxyl site (type A) and both sites (type AB). The typical bands of these substitutions are located at 871 cm$^{-1}$, 1460 cm$^{-1}$ and 1417 cm$^{-1}$ respectively. These bands are present in the spectrum of the two types of bone studied. The bands due to the vibrations of the phosphate PO$_4$: 474, 565, 603, 959, 1031 and 1100 cm$^{-1}$ are presented in all the spectra of bovine and dromedary bone ash, these bands become stronger and
narrower with increasing heat treatment temperature. In addition, the calcination of the ashes induces the hydration of the mineral matter of the two types of bone, the corresponding bands being of 634 and 3572 cm\(^{-1}\), these bands are not present in the raw bone and appear after calcination. The intensity of the peak at 3572 cm\(^{-1}\) increases proportionally with increasing temperature. This is probably due to the increased crystallinity of hydroxyapatite [192, 209]. The water absorption band (3000-3400 cm\(^{-1}\)) [210] disappears after heat treatment at 900 °C and its presence in the dromedary bone may be due to the humidity of the KBr.

Fig 4: FTIR spectrum of heat-treated dromedary bone
3.4 X-ray diffraction analysis (XRD)

The XRD diffractograms of bovine and dromedary bone treated at different temperatures (600, 800, 900, 1000 °C) are shown in Figures 6 (a and b). These results are compared to the JCPDS hydroxyapatite reference 00-009-0432. All peaks on diffractograms of bone calcined at 600, 800, 900 and 1000 °C correspond to the hydroxyapatite phase and no other phase was observed. Certain other studies reveal the presence of two additional phases due to impurities (CaO, NaCaPO₄) in the ashes of bovine bone treated at a temperature above 800 °C and confirm the absence of tricalcium phosphate (TCP) in the ashes treated with 1000 °C ¹³,¹⁸. The DRX results also show the effect of heat treatment on crystallinity and grain size: the ash peaks treated at 600 °C are broad and therefore have low crystallinity and big grains, which is probably due to the presence of carbonate which is identified in the FTIR analysis. At high temperature, the peaks became narrower, hence better crystallinity of hydroxyapatite and small grains ¹⁹.
The widening of the peak is an important parameter for the evaluation of the change in structural characteristics with increasing temperature. The width at half height (FWHM) of the specified peaks is used to determine the crystalline phase fraction. As is known, there is an inverse relationship between this parameter and the degree of crystallinity.

From the results of DRX and Scherrer's equation, we calculated the size of the crystals of hydroxyapatite prepared from dromedary bone and bovine bone at different temperatures on (002) plan (Figures 7 a and b). The crystal size of hydroxyapatite prepared from dromedary bone at 600, 800 and 900 °C is 34, 45, 74 and 74 nm and for hydroxyapatite prepared from bovine bone is 34, 68, 70 and 74nm respectively. Crystal size exhibits a linear relationship with calcination temperature, which increases with increasing temperature. The change in crystal size is due to certain chemical factors. Among these is the denaturation of the bone matrix during heat treatment, in which recrystallized
mineral crystals influence the crystal size of the treated bone [9]. These results are consistent with the considerable structural changes in the bone mineral occurring between 600 and 1000 °C, as reported in the literature 10.

Tables 1 and 2 show the FWHM values for the peak (002) located at 25.9° at different temperatures. The value of FWHM decreases with increasing temperature from 600 to 900 °C. This decrease can be explained by the transformation of nanometric crystals to micro-sized crystals 21. Moreover, the increase in the calcination temperature above 900 °C has no influence on the FWHM value. The process of dehydroxylation of hydroxyapatite is carried out at the calcination temperature of 900-1000 °C 22. An increase in FWHM is expected due to the loss of hydroxyl group, but FWHM shows no change in this region. This could be due to the slow dehydroxylation process at these temperatures and due to rehydroxylation by the interaction of the sample with air. These results are in agreement with other works 21.

**Fig 7:** Effect of temperature on crystal size of hydroxyapatite prepared from a. bovine and b. dromedary bone.
Table 1: crystal size and FWHM of hydroxyapatite prepared from dromedary bone at different temperatures 600, 800, 900 and 1000 °C for 12 h.

| Treatment temperature (°C) | FWHM (°) | Crystal size (nm) |
|---------------------------|----------|------------------|
| 600                       | 0.2401   | 34               |
| 800                       | 0.1801   | 45               |
| 900                       | 0.1102   | 74               |
| 1000                      | 0.1102   | 74               |

Table 2: crystal size and FWHM of hydroxyapatite prepared from bovine bone at different temperatures 600, 800, 900 and 1000 °C for 12 h.

3.5 XRF Analysis:

The analysis of the chemical composition of minerals in the oxide form of hydroxyapatite prepared from dromedary and bovine bone is carried out by X-ray fluorescence. As shown in Table 3, calcium and phosphorus are the main constituents. Other minor components in naturally occurring hydroxyapatite, such as sodium and magnesium, as well as sulfur, strontium, zinc and potassium are in trace amounts.

Compared to some studies carried out on the composition of bovine bone, and our results, we see that the rate of strontium and zinc obtained is relatively high in dromedary bone 0.131% and 0.024%, unlike bovine bone whose the rates are around: 0.015% and 0.02%. Strontium is naturally present in the structure of bone. Its behavior in the body is very similar to that of calcium. Substitution of dental enamel for calcium by strontium improves resistance to chemical attack. Research has shown that this mineral element (strontium) improves the mechanical properties of bone and plays a very important role in the biocompatibility of hydroxyapatite.
better bond between hydroxyapatite coatings and tissues \textsuperscript{16}. Strontium enriched hydroxyapatite crystals are more stable. In vitro studies comparing calcium silicate ceramics substituted with Mg\textsuperscript{2+}, Zn\textsuperscript{2+} or Sr\textsuperscript{2+} have shown that the presence of strontium stimulates the differentiation of osteoblasts and significantly increases the expression of osteoblastic markers such as alkaline phosphatase compared to doping with magnesium or zinc \textsuperscript{23}.

The Ca/P molar ratio of hydroxyapatite obtained from dromedary bone and bovine bone is 1.62 and 1.64 respectively. These results are in agreement with the results of research carried out on the Ca/P ratio of bovine bone obtained by other research \textsuperscript{4}, they however lower than the molar ratio of hydroxyapatite obtained from pig bones (1.95), human teeth (1.84) \textsuperscript{26} and bovine bone (2.23) \textsuperscript{27} and theoretical hydroxyapatite (1.67) \textsuperscript{13}. This difference may be due to biological factors such as nutrition, sex, age, breed of animal and the presence of disease \textsuperscript{28}.

| Source of bone \textsuperscript{3} | CaO (wt %) | P\textsubscript{2}O\textsubscript{5} | Na\textsubscript{2}O | MgO | SO\textsubscript{3} | SrO | ZnO | K\textsubscript{2}O | Ca/P |
|-----------------------------------|------------|-------------------------------|-----------------|-----|-----------------|-----|-----|--------------|------|
| B (wt %)                          | 54.044     | 42.092                        | 1.346           | 1.2 | 0.102           | 0.015| 0.02 | 0.01        | 1.64 |
| D (Wt %)                          | 54.192     | 41.842                        | 1.258           | 1.126| 0.159           | 0.131| 0.024| 0.021       | 1.62 |

3.6 Density:

The densities of hydroxyapatite prepared from dromedary and bovine bone are very close (3.178 g/cm\textsuperscript{3}) and (3.186g/cm\textsuperscript{3}) respectively. Note that the density of synthetic hydroxyapatite is 3.16 g/cm\textsuperscript{3} \textsuperscript{29}. These results reveal a very insignificant difference between the density of naturally occurring hydroxyapatite and synthetic hydroxyapatite \textsuperscript{30}.

3.7 TGD / DTA differential thermal and thermogravimetric analysis
The thermogravimetric curves of the two samples (bovine and dromedary hydroxyapatite) calcined at 600 °C are illustrated in Figures 8 (a and b), as well as the corresponding heat flux profiles, from 20 to 1500 °C. For the two samples, three mass losses are distinguished as a function of temperature with a continuous mass loss throughout the rise in temperature. The first mass loss of 0.6% for the powder prepared from bovine bone and 0.8% for the powder prepared from dromedary bone is observed between room temperature and 300 °C. This loss is due to the dehydration of the hydroxyapatite (removal of free water contained in the pores or on the surface of the hydroxyapatite).

The second loss of about 0.6% and 0.5% for hydroxyapatite powder prepared from dromedary bone and bovine bone respectively, observed between temperature 300 °C and 600 °C corresponds to water strongly bound (intracrystalline water). In addition, between 600 °C and 1500 °C the third loss occurs which is about 4.7% (bovine hydroxyapatite) and 4.5% (dromedary hydroxyapatite), which can be attributed to the decomposition of carbonate.

The total loss is approximately 5.9% (dromedary hydroxyapatite) and 5.8% (bovine hydroxyapatite). It should be noted that these losses are relatively low, up to 1500 °C, which indicates the high thermal stability of the samples. These results are in good agreement with the previous FTIR spectra, which showed the presence of very weak bands relating to the carbonate groups.

The two DTA curves relating to apatite prepared from dromedary bone and bovine bone show the presence of an endothermic effect at a temperature between to 900°C and 1000°C for hydroxyapatite prepared from bovine and dromedary bone respectively, attributable to the decomposition of carbonate and the formation of carbon compounds such as carbon dioxide.
3.8 Effect of temperature on particle size

The particle size of the hydroxyapatite powder obtained after heat treatment of the bones can determine the efficiency of the powder for a particular application. The particle size distribution of the powders prepared is measured after the heat treatment of the bovine and dromedary bones at different temperatures (600, 800, 900 and 1000 °C). The statistical data of the particle size distribution of the powder as well as of the specific surface area (SSA) extracted from Figure 9 and Figure 10 are presented in Table 4. According to these data, the particle size of hydroxyapatite prepared from dromedary bone (90%) is 20, 26, 39 and 263μm at 600, 800, 900 and 1000 °C, respectively and 57, 77, 94 and 116μm at 600, 800, 900 and 1000 °C, respectively for hydroxyapatite prepared from bovine bone. These results indicate the presence of a positive correlation between temperature and particle size which is in agreement with the results of others research. The increase in particle size of the powders treated by high temperatures could be explained by the agglomeration of the particles. Our results show that the temperature of bone processing also has an effect on the surface of the particles whose correlation between the temperature and the specific surface of the particles is negative.

Controlling the particle size of hydroxyapatite during synthesis or preparation is very important.
because each specific application corresponds to a given size of hydroxyapatite. Thus, hydroxyapatite
with a size of 32 µm is used as a coating by oxy-fuel and hydroxyapatite. One between 150 and 200
µm in size is used as a plasma spray coating. On the other hand, the desirable surface is also chosen
according to the application. For example, a large surface area of hydroxyapatite improves the
adsorption capacity of heavy metals, or dyes.

Figure 9: Particle size distribution of the hydroxyapatite powder prepared from the dromedary bone (a)
600 °C, (b) 800 °C, (c) 900 °C and (d) 1000 °C
Fig 10: Particle size distribution of the hydroxyapatite powder prepared from the bovine bone (a) 600°C, (b) 800 °C, (c) 900 °C and (d) 1000 °C.

Table 4: Effect of temperature on particle size and specific surface.

| Source of bone | Temperature of extraction | 600°C | 800°C | 900°C | 1000°C |
|----------------|---------------------------|-------|-------|-------|--------|
| dromedary      | size (um)                 | 20    | 26    | 39    | 263    |
|                | Specific surface (cm²/g)  | 21300 | 20936 | 5518  | 4458   |
| bovine         | size (um)                 | 57    | 77    | 94    | 116    |
|                | size (cm²/g)              | 26798 | 23294 | 3582  | 8511   |

4. CONCLUSION

The aim objective of this study was to determine the physical properties of hydroxyapatite prepared from dromedary bone and bovine bone. In the light of the results obtained, several conclusions can be drawn:

- The hydroxyapatite prepared from dromedary and bovine bone particles had a similar morphology in scanning electron microscope images.
The hydroxyapatite prepared from dromedary bone had higher levels of strontium and zinc than the hydroxyapatite prepared from bovine bone.

Based on the result of TGA and DTA, it can be concluded that the thermal stability of hydroxyapatite prepared from dromedary bone bother then the thermal stability of hydroxyapatite prepared from bovine bone.

This works clearly shown that the source of bone affects the physical properties of hydroxyapatite.

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Equations

Equation (1) \[ Y = \frac{(W_{d} - W_{b})}{W_{b}} \times 100 \]

Equation (2) \[ D = \frac{kA}{FWHM \cos \theta} \]

Equation (3) \[ \rho_s = \rho_w \frac{(W_s - W_w)}{(W_{sw} - (W_s - W_w))} \]

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