Proceedings of the International Conference on Industrial Engineering and Operations Management
Monterrey, Mexico, November 3-5, 2021

Preparation and characteristics of synthesized hydroxyapatite from bovine bones and by co-precipitation method

Saida Bouyegh, Samira Tlili, Kotbia Labiod and Mohamed Hassani
Research Center in Industrial Technologies CRTI
P.O. Box 64, Cheraga 16014 Algiers, Algeria
s.bouyegh@crti.dz; s.tlili@crti.dz; k.labiod@crti.dz; m.hassani@crti.dz

Mohamed Grimet and Oussama Bensalem
Chemistry Department
Badji Mokhtar -Annaba University
grmtmhmd@gmail.com; oussaoussa750@gmail.com

Abstract
Hydroxyapatite (HA, $(Ca_{10}(PO_4)_6(OH)_2)$ is a widely studied bioceramic due to its biocompatibility, bioactivity, and chemical similarity to the mineral component of bone. Generally, hydroxyapatite can be made from several natural and synthetic sources. The objective of this study is to prepare hydroxyapatite powders from different precursors (natural or chemical). Hydroxyapatite was synthetized by co-precipitation method, the chemical precursors of which are $[Ca(NO_3)_2.4H_2O$, $(NH_4)_2HPO_4]$ and the natural source was bovine bone. Bovine hydroxyapatite (BHA) was extracted from the bovine bone bio-waste via thermal method and milling process. Synthesized HA (SHA) was prepared by co-precipitation method with the pH 10.0 of mother liquor. The prepared powders were characterized using various analytical techniques such as XRD, FTIR spectroscopy, thermogravimetry (TG), and scanning electron microscope (SEM). These techniques provide information about the structural, chemical, morphological and physicochemical of each of the prepared powders. The use of co-precipitation method produced a low crystallinity of HA while the thermal method increased crystallinity. On the other hand, the results showed that the Ca / P ratio of synthetic hydroxyapatite (SHA) as well as that of bovine bone source (BHA) was also stoichiometric.

Keywords
Hydroxyapatite, Bovine bone, Synthesis, Co-precipitation, thermal decomposition.

1. Introduction

Bioceramics based on calcium phosphates (CaP) have developed considerably in recent decades due to their excellent biocompatibility and bioactivity. Hydroxyapatite (HA) is a mineral species of the phosphate family, the chemical formula $Ca_{10}(PO_4)_6(OH)_2$ (Elliott et al. 1994), with a molar ratio equal to 1.67 (HA stoichiometric). However, Hydroxyapatite (HA), a calcium phosphate bioceramic, is the primary material for applications in bone replacement. It is a material that exhibits an absence of local and systemic toxicity, an absence of inflammatory responses and an apparent capacity to bind to the host tissue (Silva et al. 2012). It has been widely used for biomedical applications, including orthopedics, dentistry, and as a coating material for metal implants (Hendi 2017).
In recent decades, hydroxyapatite (HA) has received considerable attention as a biomaterial due to its similarity to human bone. The hydroxyapatite (HA) preparation for medical purposes must meet specific criteria in terms of repeatability, raw material composition, and finished product purity (Bernard et al. 1999). Generally, the physicochemical properties and morphology of hydroxyapatite (HA) depended on the origin and methods of preparation (Sobczak-Kupiec et al. 2012). Indeed, the physicochemical properties of materials depend mainly on their production processes. Due to the interesting properties of hydroxyapatite (HA), various techniques have been and are being developed to produce hydroxyapatite. There are two main ways to obtain hydroxyapatite; one is by inorganic

synthesis (synthetic), and the other is to obtain hydroxyapatite (HA) from natural sources. Extensive attempts have been made to create high-quality HA with appropriate biocompatibility while looking for cost-effective and non-polluting technologies (Sadat-shojai et al. 2013) (Huang et al. 2011). Indeed, some researchers have attempted to synthesize hydroxyapatite from biological materials. Corals (Manjubala et al. 2000), eggshells (Ibrahim et al. 2015) (Siva Rama Krishna et al. 2007) and ostrich eggshells (Dupoirieux et al. 1999), seashells (Shavandi et al. 2014), coral (Dorozhkin et al. 2009), nacre (Dorozhkin et al. 2009) and bovine bones (Herliansyah et al. 2009) have been used to produce hydroxyapatite.
However, a problem with natural hydroxyapatite (HA) is the transmission of disease when proper preparation is not followed to remove all proteins (Goller et al. 2006). Above time, various methods have been developed to synthesize hydroxyapatite (HA) suitable for different applications. Hydroxyapatite (HA) can be also manufactured synthetically by using number of different methods. The process for the preparation of synthetic hydroxyapatite comports reactions in solid state (Arita et al. 1995), co-precipitation (Gentile et al. 2015) (Ignjatovic et al. 2004), sol-gel process (Jafari et al., 2018, Padmanabhan et al. 2009, Ramanan et al. 2004), microemulsion (Ma et al. 2016, Koumoulidis et al. 2003), and hydrothermal method (Ashok et al. 2007, Yoshimura et al. 2004). Nevertheless, the preparation and synthesis of HA from different sources with characteristics that are nearly identical to stoichiometric HA (Ca/P = 1.67) has not been understood fully, and research in this field is still wide open.
This work is part of the understanding of the synthesis, shaping and structural characterization of hydroxyapatite composition. Variations in the parameters which affect synthesis are necessary in order to produce hydroxyapatite (HA) particles of the required size, crystallinity, and composition. This research is of particular interest for the understanding of hydroxyapatite preparation (quantity and crystalline structure) under controlled physico-chemical conditions. One of the major objectives lies in the preparation of hydroxyapatite powders and their control by a simple and reproducible process.

2. Experimental Procedure

2.1. Synthesis of HAP powders

In this study, to prepare hydroxyapatite (HA) two sources (natural and synthetic) were used. The natural source is bovine cortical bone because it is morphologically and structurally similar to human bone. In addition, this natural source is easy to obtain, inexpensively and available in unlimited quantities. The second aspect relates in particular to the synthesis of hydroxyapatite by co-precipitation route in order to optimize the synthesis protocol and to develop the purest possible ceramics for their characterization.

2.1.1 Synthetic hydroxyapatite (SHA) by co-precipitation route

The precipitation experiments were performed by mixing the solutions of calcium nitrate and diammonium hydrogen phosphate. Figure .1 shows an experimental setup for the preparation of synthetic hydroxyapatite. Figure 1 shows the typical steps for fabrication of HA powder using the chemical precipitation.
Synthetic hydroxyapatite (SHA) obtained by co-precipitation uses Calcium nitrate tetrahydrate ($Ca(NO_3)_2.4H_2O$) salt with a purity of 98% and dibasic ammonium phosphate ($(NH_4)_2HPO_4$) as precursors of the reaction. Solutions of distilled water 0.5 M $Ca(NO_3)_2$ and 0.3 M $(NH_4)_2HPO_4$ (to meet the stoichiometric Ca / P = 1.67) were prepared. The phosphate solution ($(NH_4)_2HPO_4$) was added drop wise to the solution of calcium nitrate, with stirring at temperature (80 °C). The speed of adding the phosphate solution to the calcium solution must be low enough to limit the formation of calcite in the precipitates. In addition, the pH of the mixture was regulated to 10 by dropwise addition of 25% v / v ammonium hydroxide solution (NH_4OH), with continuous and vigorous magnetic stirring (500tr/min), giving an opaque suspension.
The reaction involved during this synthesis is designated by the equation below (1) (El-Kholy et al. 1998):

$$10\ Ca(NO_3)_2 + 6\ (NH_4)_2HPO_4 + 8\ NH_4OH \rightarrow Ca_{10}(Po_4)_6(OH)_2 + 20\ NH_4NO_3 + 6\ H_2O \qquad (1)$$

The precipitates formed were aged (maturation) overnight (24 hours) at room temperature. At the end of the maturation, the final precipitates collected were filtered, washed several times with distilled water to remove all the sub products. Then the precipitates were dried in an oven in air for 8 hours at 100 °C. The dried powders were crushed with a pestle mortar and the ground powders were calcined at the temperature 850 °C at a speed of 10 °C min^{-1} for 2 h before proceeding to a new characterization. This method of SHA preparation has been repeated several times and found to be reproducible.

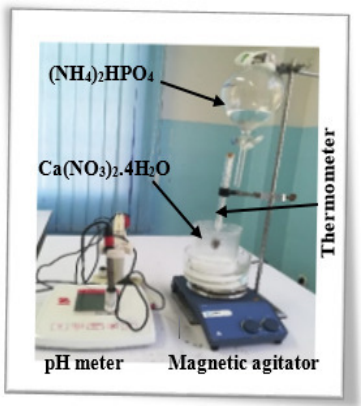

Figure 1. Preparation of synthetic Hydroxyapatite (SHA) by co-precipitation method

2.1.2 Extraction of HA from bovine bone by thermal decomposition

HA can be obtained from biogenic sources such as bovine bone by means of calcination at high temperature.
In this study may be used to extract hydroxyapatite from biowaste bovine bovine femur. In order to ensure the homogeneity of the material, a sufficient quantity of bovine femurs was collected. Initially, to eliminate the organic matter from the bovine femur (marrow, tissue), the bone has been submitted to a deproteinisation process. Figure 2. Photographs of natural bone condition after degreasing, deproteinization and pulverizing treatments.

Figure 2. Photographs of bovine femur: (a) Raw state; (b) washed and cleaned; (c) pulverized

Bovine bones (femur) were cleaned from the meat with a knife, boiled in distilled water to remove fat. The bone cooking treatment was performed in a domestic stainless steel pressure cooker with water covering the bones. Pressure cooking of the bones was performed in potable (tap) water, while degreasing and deproteinization treatments used distilled water. The bones, cleaned and dried in an oven at 100 °C, then fragmented into small pieces using a pestle mortar. Calcination of the powder at a temperature of 900 °C/3h to improve the crystallinity and to check the purity of BHA powders. Before grinding of the powder using a planetary mill (Fritsch, Pulverisette 7), for a period of 4 hours at a speed of 350 rpm. finally, the sieving of the ground powder to obtain an adequate particle size fraction as required.

2.2 Physicochemical characterization of HAP powders

Different investigative techniques were used in this study for the preparation of hydroxyapatite (HA): differential thermal analysis (DTA), X-ray diffraction (XRD) analysis was carried out, Fourier transform infrared (FTIR), scanning electron microscopy (SEM) coupled with energy dispersive x-ray spectroscopy (EDX), and a laser particle size analyser. The existing phase's analysis was performed by X-ray diffraction (XRD) with a Rigaku device, Ultima IV (CuKα radiation λ = 1,5406Å). The spectra were recorded in the 2θ interval of 10°-90° (0.05° step and time in 5s step). The microstructure and the morphology of prepared hydroxyapatite powder was examined using a scanning electron microscope (SEM/EDS) type QUANTA 250 and Chemical analysis was carried out using an EDX at 20 kV. Analysis of the functional groups of the prepared powders were characterized utilizing an IRAfinitty-1S (Shimadzu) Fourier transform infrared (FTIR) spectrometer and the measurements were carried out in the transmission mode with wave numbers from 400 cm^{-1} to 4000 cm^{-1} with a resolution of 1 cm^{-1}, averaging 100 scans. TGA-DSC analysis (SDT Q600 equipment) was used to evaluate the thermal changes of bovine bone produced by temperature between 25 and 1200 °C, at a heating rate of 10 °C / min, in a nitrogen atmosphere. A laser particle size analyser (Partica LA960) was utilized to determine the particle size distribution of the prepared hydroxyapatite (HA) powder.

3. Results and Discussion

3.1 DSC /ATG analysis

Moreover, in order to evaluate the calcination temperature, sample of bovine femurs was investigated by thermogravimetric analysis. The thermal transformation process of bovine bone and the hydroxyapatite thermal stability were studied by using a TGA/DSC analyzer. The TG/DSC analysis of as-received bovine bone are shown in Figure 3. During treatment at different temperature, the percentage of weight loss of bovine change. The removal of the organic portion from bovine bone confirmed by TGA analysis. It can be see no weight loss was observed from room temperature to 600 °C (no decomposition), furthermore, at the temperature ranging from 600 to 800 °C, the extensive weight loss was perceived; this was related to exothermic reaction or the evaporation of carbon dioxide gas. After that, no weight loss was detected at temperatures ranging from 800 °C to higher, implying that the change was complete. So the calcination temperature should be set from 800 °C, and it was essential to note that percent weight loss was estimated to be 55 %. However, in several other articles (Chraïbi et al. 2016, Buasri et al. 2013), the calcination temperature was found to be higher than 800 °C.

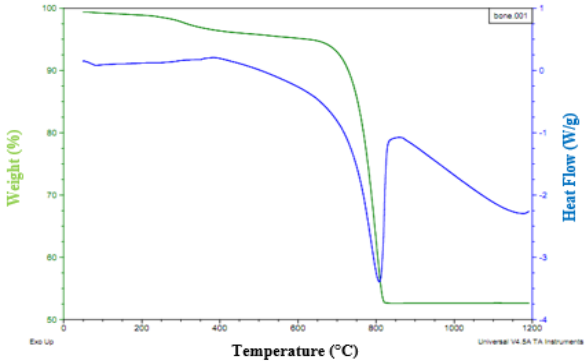

Figure 3. Differential thermal analysis of raw bone

3.3 XRD analysis

The phase composition and purity of the prepared hydroxyapatite (HA) were determined by X-ray diffraction (XRD). The XRD patterns obtained of the HA powder synthesized are identified by comparison with the references of the International Center for Diffraction Data - Powder Diffraction Files (ICDD-PDF) file (Figure 4). Powder diffraction patterns of HA powder prepared from bovine bone wastes and synthetic HA are illustrated in Figure 4. The as-prepared HA powders shows broad peaks and is identified as HA based on JCPDF 9-432. This is a typical characteristic of the HA. Figure 4a shows the diffraction patterns of the bovine bone waste. According to this figure, the natural HA exhibits higher crystallinity than the synthetic HA. By performing the calcination, the diffraction lines become more refined and become more and more resolute and intense. Analysis indicates that the crystallinity of apatite is only clear at a temperature of 850 °C.

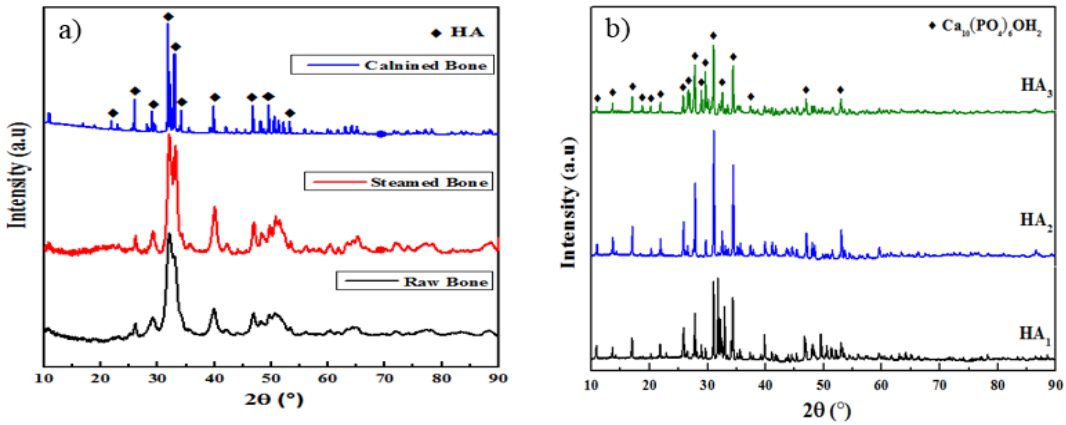

Figure 4. X-ray diffraction pattern of HA powder prepared from a) bovine bone wastes, b) synthetic

3.3 FTIR analysis

FTIR analysis was performed to obtain information about the functional groups of the prepared HA powders. Figure 5. Illustrate the FTIR spectra of hydroxyapatite synthesized from bovine bone and by co-precipitation route. The peaks for the $PO_4^{3-}$and OH^-groups in the hydroxyapatite may be identified in the FTIR analysis in Figure 5. In these spectra, bands placed at 630 and 3600 cm^{-1} corresponding to the hydroxyl (OH^-) vibrational groups, can be identified. Furthermore, bands at 570, 582, 964, 1030 and 1068 cm^{-1} belonging to phosphate groups (PO_4^{3-}) were found. These functional groups are characteristic of stoichiometric hydroxyapatite (Raya et al.2015).

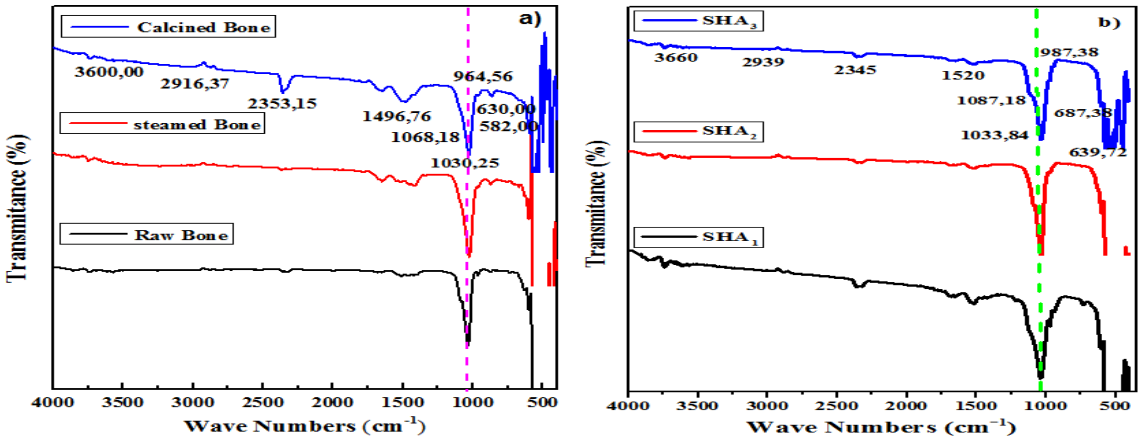

Figure 5. FTIR spectra of the HA prepared from a) Bovine bone, b) by Co-precipitation method

Figure 5 shows the transmittance intensity of the bands at 639 and 400 cm^{-1} belonging to OH^- that is lower in the case of the natural BHA compared to synthetic SHA. This difference can be explained by the fact that the natural HA was obtained by means of physical reactions (thermo decomposition) while the synthetic HA was obtained by means of reactions between two solutions in aqueous medium thus allowing the formation of a large amount of such functional groups.

3.4 FESEM Characterizations

The morphology and texture of the hydroxyapatite powders are revealed by scanning electron microscopy (SEM). The morphology of the HA powder prepared from bovine bone, examined by SEM, is illustrated in Figure 6. Small and large pores can be found in raw bovine bone; however, the microstructure is often dense due to the presence of organic compounds impregnated with the mineral phase present in bovine bones. As can be seen from the particle morphologies, there is a distribution of small particles and large agglomerates. Grains display several sizes and shapes. These agglomerates are made up of very fine particles welded together. So, unlike the raw bovine bone powder, which has a more compacted microsurface, the decomposed powder has numerous pores generated by the dissolution of the organic and mineral phases.

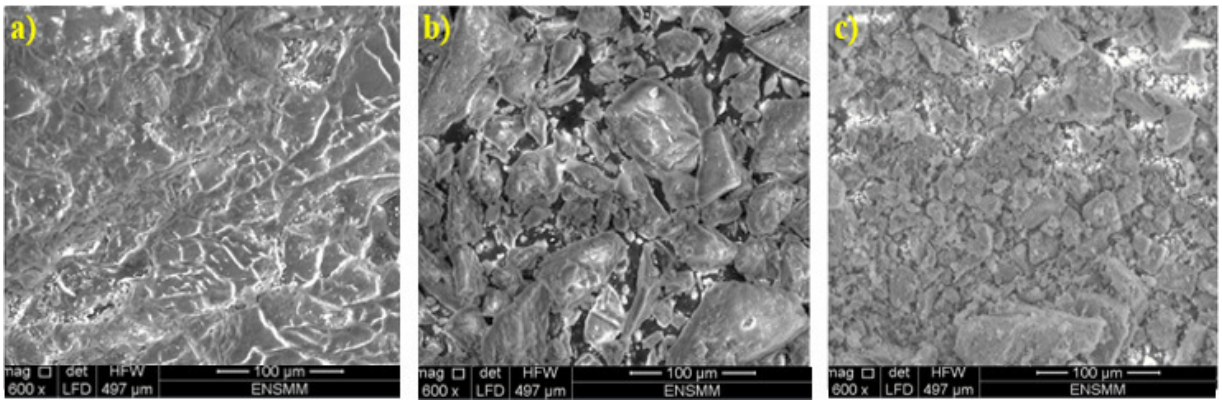

Figure 6. SEM micrographs of bovine bone: (a) Raw material; (b) Grounded; (c) Calcined at 900 °C/3h

The microstructure of synthetic hydroxyapatite (SHA) is shown in Figure 7. The presence of well-distributed macroporous through and microporous within the pore walls can be seen on the figure. The size, morphology, and interconnectivity of pores determine the quality of powders. Figure 7 shows SEM images corresponding to synthetic hydroxyapatite (SHA) at different magnifications [a) X1 000, b) X3 000, c) X12 000]. In these images, the grain distribution can be observed, show semi-spherical shapes, with more homogeneous sizes.

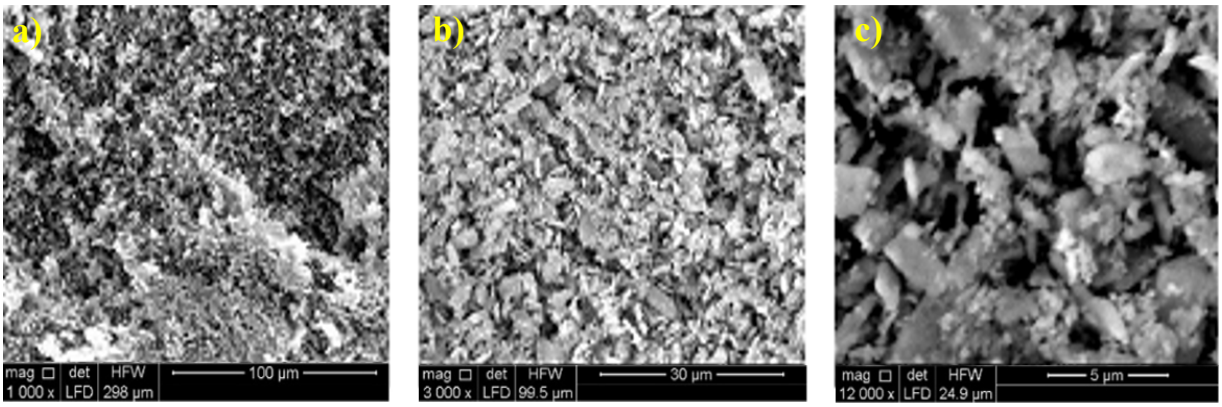

Figure 7. SEM images of SHA powders at different magnifications: a) X1 000, b) X3 000, c) X12 000

3.5 Energy dispersive X-ray spectroscopy (EDX)

Semi-quantitative chemical analysis of the powder to obtain the Ca / P ratio was performed using energy dispersive X-ray spectroscopy (EDX, Oxford, Aztec Energy X-Act). Also, the approximate values of Ca/P molar ratio for BHA powders were calculated from the results of XRF analyses. The theoretical Ca/P molar ratio of pure HA is 1.67. The results of the EDS analysis showed that the Ca/P ratio (18,98 / 11,34) of BHA investigated in this study is about 1,673. This result is relatively close to 1.67 for the stoichiometric HA (Milovac et al. 2014, Huang et al. 2011).

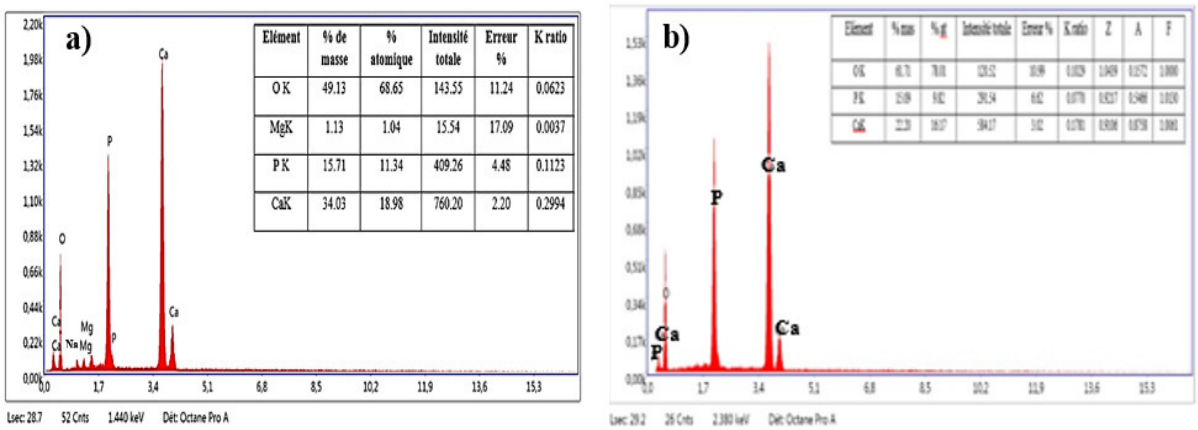

Figure 8. EDS analysis of of the HA prepared from a) Bovine bone, b) by co-precipitation method

According to the EDS results, the predominant elements in both prepared powders are P, Ca and O; furthermore, the spectrum of natural BHA reveals the presence of impurity traces of Mg and Na. These impurities are not present in the synthetic (SHA).

3.6. Particle size analysis

The particle-size distribution (PSD) of the powder was determined by the Laser scattering particle size distribution analyzer. Figure 10 shows the particle size distribution of SHA powder calcined at 850 °C for 2 hours. The average diameter of the hydroxyapatite powder produced by co-precipitation was estimated to be 20.52 µm.

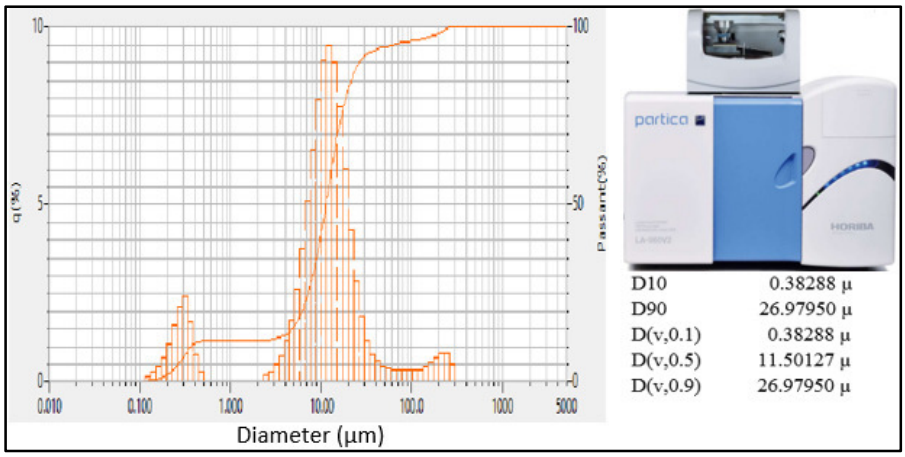

Figure 10. Particle size analysis of SHA calcined at a temperature of 850 °C prepared by co-precipitation

4. Conclusion

According to the results obtained from the above analyzes, it was found that hydroxyapatite can be successfully produced by the co-precipitation process as well as from bovine bone by thermal decomposition but each route has advantages and disadvantages. The method of preparing the powders must be reproducible and, as far as possible, simple to implement. Varied processing characteristics of synthesizing HA particles can result in different morphologies. Thus, it can be concluded that:

- The nature of the precursors plays a very important role in obtaining hydroxyapatite.
- The main difference between SHA derived from the chemical processing route and that of natural-biological origin (bovine bone) is the presence of other minerals such as Na and Mg in BHA from natural source.
- Synthetic process parameters such as pH, temperature, calcination temperature and aging period are important factors that control the purity of the prepared SHA.
- Synthetic hydroxyapatite (SHA) is more commonly used because it is more readily available and free from disease transmission.
- Bovine bone can be considered a promising biomaterial to be used to produce hydroxyapatite. As, there is an economic and environmental incentive due to the sheer volume of agricultural waste or other types of bone available to find value-added applications for these materials in biomaterials.
- According to the method, reagents and variables adopted, it is possible to obtain with diverse characteristics and properties on the intended application.

Acknowledgements

This work is supported by the research of URMA-CRTI.

References

Elliott, J. C., Structure and chemistry of the apatites and other calcium orthophosphates. Series Amsterdam, *Elsevier. Editor*, 1994.

Silva, A. C., Aparecida, A. H., and Braga, F. J. C., Dispersed hydroxyapatite bioglass 45S5 composites: comparative evaluation of the use of bovine bone and synthetic hydroxyapatite, *Materials Science Forum*, pp. 727-728, 2012.

Hendi, A. A., Hydroxyapatite based nanocomposite ceramics, Journal Alloy and Compounds, Vol. 712, pp. 147–151, 2017.

Bernard, L., Freche, M., Lacout, J. L., and Biscans, B., reparation of hydroxyapatite by neutralization at low temperature-influence of purity of the raw material, *Powder Technology*, Vol. 03, pp. 19–25, 1999.

Sobczak-Kupiec, A., Malina, D., Kijkowska, R., and Wzorek, Z., Comparative study of Hydroxyapatite prepared by the authors with selected commercially available ceramics, Digest, *Journal of Nanomaterials and Biostructures*, Vol. 7, pp. 385-391, 2012.

Sadat-shojai. M., KhorasanI, M. T., and dinpanah-khoshdargi, E., Synthesis methods for nanosized hydroxyapatite with diverse structures, *Acta Biomaterialia*, Vol. 9, pp. 7591-7621, 2013.

Huang, Y. C., Hsiao, P. C., and Chai, H. J., Hydroxyapatite extracted from fish scale: Effects on MG63 osteoblast-like cells, *Ceramics International*. Vol. 37, pp. 1825-1831, 2011.

Manjubala, I., Siva Kumar, M., Sampath Kumar, T. S., and Panduranga Rao, K., Synthesis and characterization of functional gradient materials using Indian corals, *Journal of Materials Science: Materials in Medicine*, Vol. 1, pp. 705-709, 2000.

Ibrahim, A., Zhou, Y., Li, X., Chen, L., Hong, Y., Su, Y., Wang, H., and Li, J., Synthesis of rod like hydroxyapatite with high surface area and pore volume from eggshells for effective adsorption of aqueous Pb(II), *Journal of Materials Research*, Bulletin 62, pp. 132–141, 2015.

Siva Rama Krishna, D., Siddharthan, A., Seshadri, S. K., and Sampath Kumar, T. S., A novel route for synthesis of nanocrystalline hydroxyapatite from eggshell waste, *Journal of Materials Science: Materials in Medicine*, Vol. 18, pp. 1735-1743, 2007.

Dupoirieux, L., Ostrich eggshell as a bone substitute: a preliminary report of its biological behaviour in animals-a possibility in facial reconstructive surgery Br, *Journal of Oral and Maxillofacial Surgery*, Vol. 7, pp. 467-471, 1999.

Shavandi, A., El-Din, A., Bekhit, A. Ali b, and Sun, Z., Synthesis of nano-hydroxyapatite (nHA) from waste mussel shells using a rapid microwave method, *Materials Chemistry and Physics*, pp. 1-10, 2014.

Dorozhkin, S. V., Nanodimensional and Nanocrystalline Apatites and Other Calcium Orthophosphates in Biomedical Engineering, Biology and Medicine, *Journal Materials*, Vol. 2, 19752045, 2009.

Herliansyah, M. K., Hamdi, M., and Ide-Ektessabi, A., The influence of sintering temperature on the properties of compacted bovine hydroxyapatite, *Journal of Material Science Engineering*, Vol. 29, pp. 1674–1680, 2009.

Goller, G., Oktar, FN., Agathopoulos, S., Tulyaganov, DU., Ferreira, JMF., Kayali, ES., and Peker, I., Effect of sintering temperature on mechanical and microstructural properties of bovine hydroxyapatite (BHA), *Journal Sol- Gel Science Technology*, Vol. 37, pp. 111-115, 2006.

Arita, I. H., Castano, V. M, and Wilkinson, D.S., Synthesis and Processing of Hydroxyapatite Ceramic Tapes with Controlled Porosity, *Journal of Materials Science: Materials in Medicine*, Vol. 6, No. 1, pp. 19-23, 1995.

Gentile, P., Wilcock, C. J., Miller, C. A., Moorehead, R., and Hatton, P. V., Process optimization to control the physico-chemical characteristics of biomimetic nanoscale hydroxyapatites prepared using wet chemical precipitation, *Materials*, Vol. 8(5), pp. 2297–2310, 2015.

Ignjatovic, N., Suljovrujic, E., Budinski-Simendic, J., Krakovsky, I., Uskokovic, D., Evaluation of hot-pressed hydroxyapatite/poly-L-lactide composite biomaterial characteristics, *journal of Biomedical Material Research part B*, Vol. 71, pp. 284, 2004.

Jafari, M. M., and Khayati, G. R., Prediction of hydroxyapatite crystallite size prepared by sol–gel route: gene expression programming approach, *Journal of Sol-Gel Science and Technology*, Vol. 86, pp. 112, 2018.

Padmanabhan, S. K., Balakrishnan, A., Chu, M. C., Lee, Y. J., Kim, T. N., and Cho, S. J., Sol–gel synthesis and characterization of hydroxyapatite nanorods, *Particuology*, Vol. 7, pp. 466-470,2009.

Ramanan, S. R., and Venkatesh, R., A study of hydroxyapatite fibers prepared via sol–gel route, *Materials Letters*, Vol. 8, pp. 3320, 2004.

Koumoulidis, G. C., Katsoulidis, A. P., Ladavos, A. K., Pomonis, P. J., Trapalis, C. C., Sdoukos, A. T., and Vaimakis, T. C., Preparation of hydroxyapatite via microemulsion route, *Journal of Colloid and Interface Science*, Vol. 59, pp. 254-260, 2003.

Ma, X., Chen, Y., Qian, J., Yuan, Y., and Liu, C., Controllable synthesis of spherical hydroxyapatite nanoparticles using inverse microemulsion method, *Material Chemistry and Physics*, Vol. 183, pp. 220, 2016.

Ashok, M., Kalkura, S. N., Sundaram, N. M., and Arivuoli, D., Growth and characterization of hydroxyapatite crystals by hydrothermal method, *Journal of Materials Science: Materials in Medicine*, Vol. 18, pp. 895-898, 2007.

Yoshimura, M., F. Koh, P.S., Fujiwara, T., Pongkao, D., and Ahniyaz, A., Hydrothermal conversion of calcite crystals to hydroxyapatite, *Materials Science and Engineering, C 24*, pp. 521-525, 2004.

El-Kholy, M., Khalil, A., and Hashem, A., Thermochemistry of bovine teeth and synthesis of hydroxyapatite, *Interceram*, Vol. 47, pp. 29-32, 1998.

Chraïbi, S., Moussout, H., Boukhlifi, F., Ahlafi, H., and Alami, M., Utilization of Calcined Eggshell Waste as an Adsorbent for the Removal of Phenol from Aqueous Solution, *Journal of Encapsulation and Adsorption Sciences*, Vol. 06(04), pp. 132-146, 2016.

Buasri, A., Chaiyut, N., Loryuenyong, V., Wongweang, C., and Khamsrisuk, S., Application of Eggshell Wastes as a Heterogeneous Catalyst for Biodiesel Production *Sustainable Energy*, Vol. 1(2), pp.7-13, 2013.

Raya, I., Mayasari; E., Yahya, A., et al., Shynthesis and Characterizations of Calcium Hydroxyapatite Derived from Crabs Shells (Portunus pelagicus) and Its Potency in Safeguard against to Dental Demineralizations, *International Journal of Biomaterials*, Vol. 2015, pp. 469176, 2015.

Milovac, D., Gallego Ferrer, G., Ivankovic, M., et al., PCL-coated hydroxyapatite scaffold derived from cuttlefish bone: morphology, mechanical properties and bioactivity, *Materials Science and Engineering: C*, Vol. 34, pp. 437-445, 2014.

Biographies

Bouyegh Saida is a research master in the bioceramics team, ceramics Division, at research center of industrial technologies, Algiers, Algeria. She obtained her engineering degree, her Master's degree in metallurgy and materials engineering at Badji Mokhtar University, Annaba, Algeria. His research focuses on the synthesis of bioceramics and corrosion of materials.

Tlili Samira is project manager in the physical metallurgy team, researcher in bioceramic team, ceramics Division at research center of industrial technologies, Algiers, Algeria. She obtained her engineering degree, her Master's degree and her Ph.D. in metallurgy and materials engineering at Badji Mokhtar University, Annaba, Algeria. His research focuses on the characterization, tribological and corrosion of materials (ferrous, non-ferrous and non-metallic materials) and synthesis of bioceramics.

Labiod kotbia is a research master in bioceramics team, ceramics Division, at research center of industrial technologies, Algiers, Algeria. She obtained her engineering degree, her Master's degree in analytic chemistry and physics at Mentouri University, constantine, Algeria. His research focuses on the valorization of ceramics.

Hassani Mohamed is a research master in materials fiability team, composites Division, at research center of industrial technologies, Algiers, Algeria. He obtained her engineering degree, her Master's degree in mechanical and materials engineering at Badji Mokhtar University, Annaba, Algeria. His research focuses on the characterization and simulation of composites

Mohamed Grimet is master's degree in analytic chemistry at Badji Mokhtar University, Annaba, Algeria. His research focuses on the synthesis of bioceramic and characterization.

Oussama Bensalem is master's degree in analytic chemistry at Badji Mokhtar University, Annaba, Algeria. His research focuses on the synthesis of bioceramic and characterization.