

# Synthesis and Characterization of Hydroxyapatite Nanopowders by Chemical Precipitation

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**Abstract:** - In this paper we present a synthesis method for obtaining hydroxyapatite nanopowders by chemical precipitation. As the starting reagents, analytical grade  $\text{Ca}(\text{OH})_2$ ,  $\text{H}_3\text{PO}_4$  and  $\text{NH}_4\text{OH}$  were used. The proposed method led to obtaining a hydroxyapatite with a high degree of crystallinity and purity. The synthesized samples were characterized by X-ray diffraction (XRD), Fourier transformed-infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) techniques.

**Key-Words:** - hydroxyapatite, chemical precipitation, X-ray diffraction, FT-IR spectroscopy, microstructure, heat treatment, rheology

## 1 Introduction

Hydroxyapatite is a major mineral component of bone tissue. HA is biocompatible with the human organism and is capable of integrating biologically into bone tissue [1].

Hydroxyapatite belong to the apatite family. Apatite is the name given to a group of crystals of the general chemical formula  $\text{M}_{10}(\text{XO}_4)_6\text{Z}_2$ , where  $\text{M} = \text{Ca}^{2+}, \text{Sr}^{2+}, \text{Ba}^{2+}, \text{Na}^+, \text{Pb}^{2+}, \text{La}^{3+}$ , and many rare earth elements;  $\text{XO}_4 = \text{PO}_4^{3-}, \text{VO}_4^{3-}, \text{SiO}_4^{4-}, \text{AsO}_4^{3-}, \text{CO}_3^{2-}$ ;  $\text{Z} = \text{OH}^-, \text{Cl}^-, \text{F}^-, \text{CO}_3^{2-}$  [2]

The molar ratio of calcium to phosphorus  $\text{Ca}/\text{P}$  varies from 1.2 to almost 2 in HA. The stoichiometric molar ratio of HA is 1.67; however, this is not the value observed in the organism because small amounts of other materials such as carbon, nitrogen, iron and another elements are incorporated [3].

This biomaterial is widely used to repair, fill, extend and reconstruct damaged bone tissue. It can also be used in soft tissue. Hydroxyapatite can be manufactured synthetically by using a number of different methods. The processes for the preparation of hydroxyapatite and any other calcium phosphate powders may be classified under two main headings: synthesis from mammal bones or coral and in the lab, in this case it can be synthesized by reactions in solid state [4], coprecipitation [5, 6], hydrothermal methods [7], sol-gel process [8], microwave processing [9], among others.

The most popular methods are chemical coprecipitation from water solutions containing the ions  $\text{Ca}^{2+}$ ,  $\text{PO}_4^{3-}$ , and  $\text{OH}^-$ , which in conditions of  $\text{pH} > 7$ , form primary crystallites of insoluble hydroxyapatite [10].

The objective of this work is hydroxyapatite powders synthesis by coprecipitation method. The heat treated powders were characterized by X-ray diffraction in order to identify the phase composition and crystallinity of the calcium phosphate compounds. For estimation of hydroxyapatite powder quality has been used Fourier transformed infrared spectroscopy (FTIR) techniques, the morphology of synthesized powders has been studied by scanning electron microscopy (SEM), as well rheological properties has been studied .

## 2 Experimental procedure

### 2.1 Hydroxyapatite synthesis

Chemical precipitation is performed by preparing a suspension consist in 75 g calcium hydroxide,  $\text{Ca}(\text{OH})_2$ , in 510 mL distilled water and a solution of 40 ml orthophosphoric acid,  $\text{H}_3\text{PO}_4$ , in 200 ml distilled water.

In order to obtain a hydroxyapatite slurry,  $\text{H}_3\text{PO}_4$

suspension was added by dropwise, for 3 hours over the alkaline solution based on  $\text{Ca}(\text{OH})_2$ , in conditons of intense stirring.

During the addition the pH was kept at 9.5 – 10, by using concentrated aqueous ammonia solution,  $\text{NH}_4\text{OH}$ , in order to obtain a stoichiometric hydroxyapatite ( $\text{Ca}/\text{P} = 1.67$ ).

After the complete addition, the reaction mixture were kept during 48 hours for aging. In order to remove any impurities, the precipitate was separated from the suspension by vacuum filtration, washed

with distilled water and ethanol. The filtered cake was oven dried at  $130^\circ\text{C}$  for 24 hours and then ground to a powder in an mortar and pestle.

In the next step, hydroxyapatite powders was heat treated at  $200^\circ\text{C}$ ,  $600^\circ\text{C}$  and  $1200^\circ\text{C}$  for 2 hours. Finally, powders was then ball milled, using a porcelain mill pot with tungsten carbide balls, for 1hour. The procedure for preparing hydroxyapatite powder, in agreement with procedure above mentioned, is schematically illustrated in Figure 1.

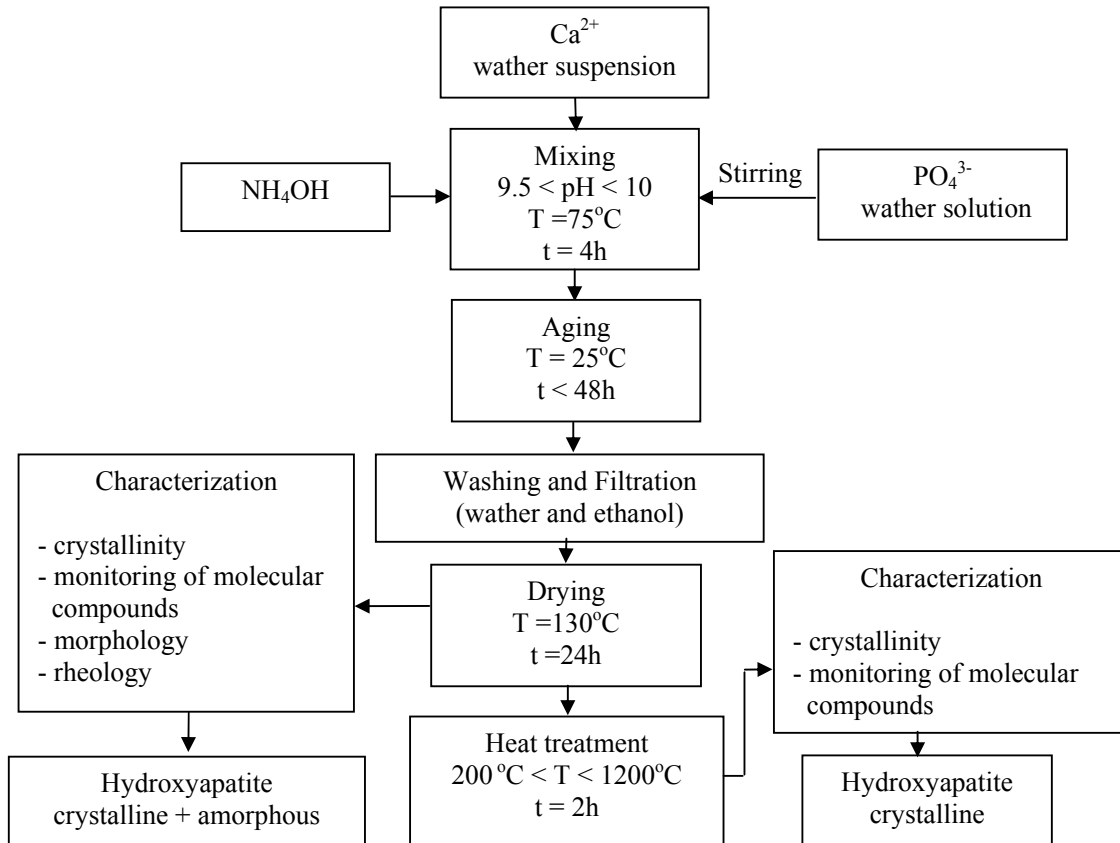


Fig. 1. Flow chart for the synthesis of hydroxyapatite by precipitation process

## 2.2 Characterization Techniques

The structural characterization was carried out by X-ray diffraction using a Bruker AXS D8 ADVANCE diffractometer with  $Cu_{k\alpha} = 1.5405\text{\AA}$  radiation generated at a voltage of 40 kV and a current of 30 mA. Data were collected in the  $2\theta$  range of  $20\text{--}60^\circ$ , with a step size of  $0.04^\circ 2\theta$ . X-ray analysis was used to assess the present phases, the degree of crystallinity and size of crystallites, in case of hydroxyapatite studied.

Identification of phases was achieved by comparing the diffraction patterns of hydroxyapatite obtained in

laboratory with ICDD – PDF2 (The International Centre for Diffraction Data - Powder Diffraction File 2) standards.

Table 1. Phases identifications present in samples obtained by chemical precipitation

Calcium phosphate compound and their chemical formula	PDF files
Hydroxyapatite - $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$	00-009-432
Calcium Phosphate - $\beta\text{-Ca}_3(\text{PO}_4)_2$	00-009-169
Calcium Phosphate - $\alpha\text{-Ca}_3(\text{PO}_4)_2$	00-009-348
Tetracalcium phosphate - $\text{Ca}_4(\text{PO}_4)_2\text{O}$	00-025-1137
Calcium Oxide - $\text{CaO}$	00-037-1497

The fraction of crystalline phase ( $X_c$ ) of the hydroxyapatite powders was evaluated by the following equation [11]

$$X_c = 100 \cdot \frac{I_{300} - V_{112/300}}{I_{300}}, [\%] \quad (1)$$

where  $I_{300}$  is the intensity of (300) diffraction peak and  $V_{112/300}$  the intensity of the hollow between (112) and (300) diffraction peaks of hydroxyapatite. The crystallite size,  $\tau$ , of hydroxyapatite powder has been calculated based on Scherrer's equation [12]:

$$\tau = \frac{K \cdot \lambda}{W \cdot \cos(\theta)}, [\text{nm}] \quad (2)$$

where:  $K$  = constant dependent on crystallite shape,  $0.8 < K < 1.1$ ;  $K = 0.94$  for FWHM of spherical crystals with cubic symmetry;  $\lambda$  is the wavelength of monochromatic radiation ( $\lambda_{\alpha_1} = 1.5405 \text{ \AA}$ ).  $w$  is defined as the full width of peak from the intensity distribution pattern measured at half of the maximum intensity value. This value is the difference between two  $2\theta$  values, in radians; and  $\theta$  is the Bragg angle, in degree.

The chemical characteristics of powders, after heat treatment at different temperatures were analyzed by FTIR absorption spectroscopy within the range

between  $4000$  and  $600 \text{ cm}^{-1}$ , by using a Fourier transformed infrared spectrometer (FTIR- Spectrum GX Perkin Elmer), equipped with ATR (attenuated total reflectance) crystal. The sample was placed over the ATR crystal to cover the crystal surface. Scans in the range of  $600\text{--}4000 \text{ cm}^{-1}$  were accumulated for each spectrum at a spectral resolution of  $4 \text{ cm}^{-1}$ . Morphology of the hydroxyapatite powders was studied using scanning electron microscopy (SEM) on Philips XL-30-ESEM TMP (accelerating voltage,  $25\text{--}30 \text{ kV}$ ). The rheological characteristics in the sense of determination of flow rate of hydroxyapatite powders were determined in accordance with ASTM B213-03.

### 3 Results and Discussion

#### 3.1 X-Ray Diffraction (XRD)

Figure 2 shows the X - ray diffraction patterns for hydroxyapatite samples, in according with experimental procedure above described.

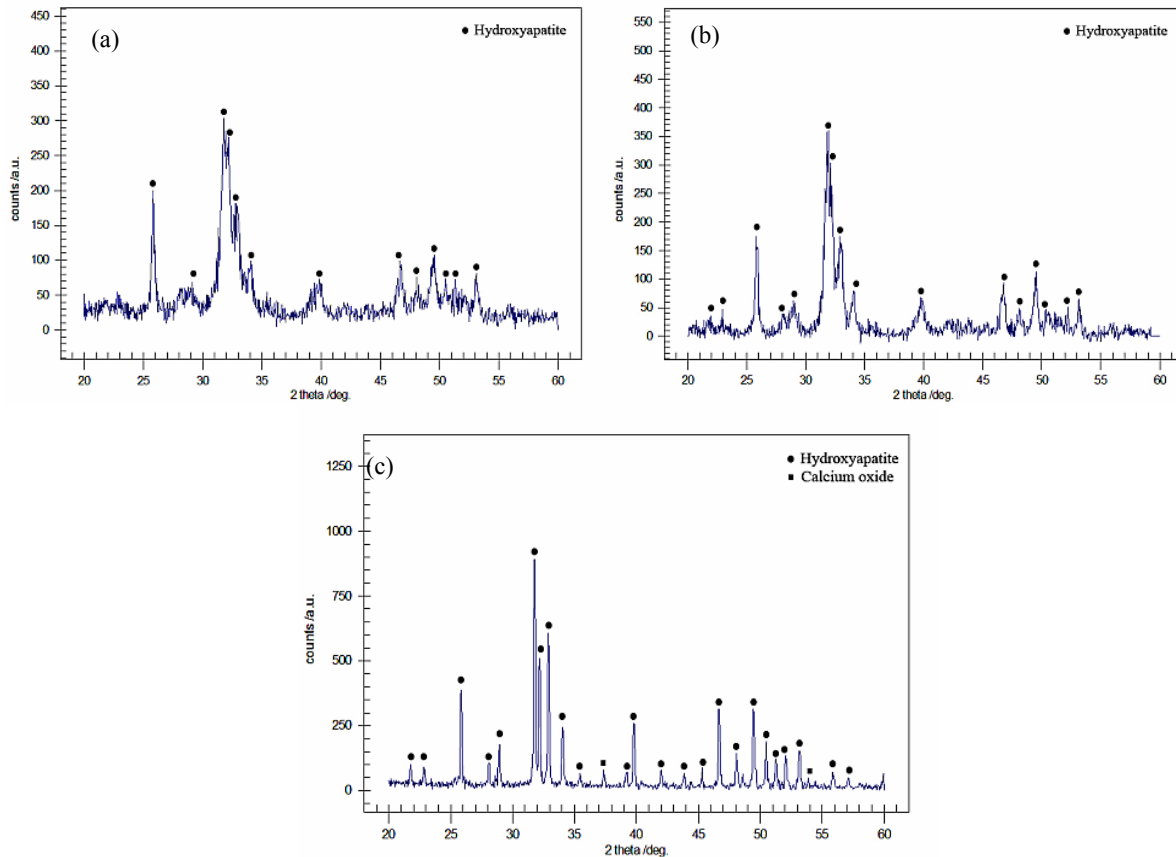


Fig. 2. X- ray diffraction patterns of hydroxyapatite powders heat treated at different temperatures: (a)  $200^\circ\text{C}$ ; (b)  $600^\circ\text{C}$ ; (c)  $1200^\circ\text{C}$

All XRD patterns shows diffraction lines characteristic of hydroxyapatite, both present in standards and in literature. The major phase, as expected, is hydroxyapatite, which is confirmed by comparing data obtained with the ICDD - PDF2 card: 00-009-0432. In case of sample heat treated at 200°C, XRD pattern revealed the presence of an important amorphous phase. The proportion of amorphous phase decreases with increasing of heat treatment temperature, as are presented in figure 2b and figure 2c. When the temperature was increased, the hydroxyapatite peaks became sharper, due to crystal growth. An estimation related to crystallites size for hydroxyapatite powders, according to Scherrer's formula reveals a proportional increase of crystallite size from 22 nm to 53 nm with increasing

of the heat treatment temperature from 200 – 1200°C. The estimated crystallites size of hydroxyapatite are in according with data obtained regarding the crystallinity degree. The crystallinity degree increases from 26% to 38% and 96% with increasing of heat treatment temperatures from 200°C to 600°C, respectively, 1200°C. The XRD pattern of sample heat treated at 1200°C show that only secondary phase present is calcium oxide (CaO), identified at 37.37 and 53.86 (2 $\theta$ ).

### 3.2 FT-IR Spectroscopy

The FTIR spectra of heat treated powders at 200°C and 1200°C are shown in Figure 3(a, b).

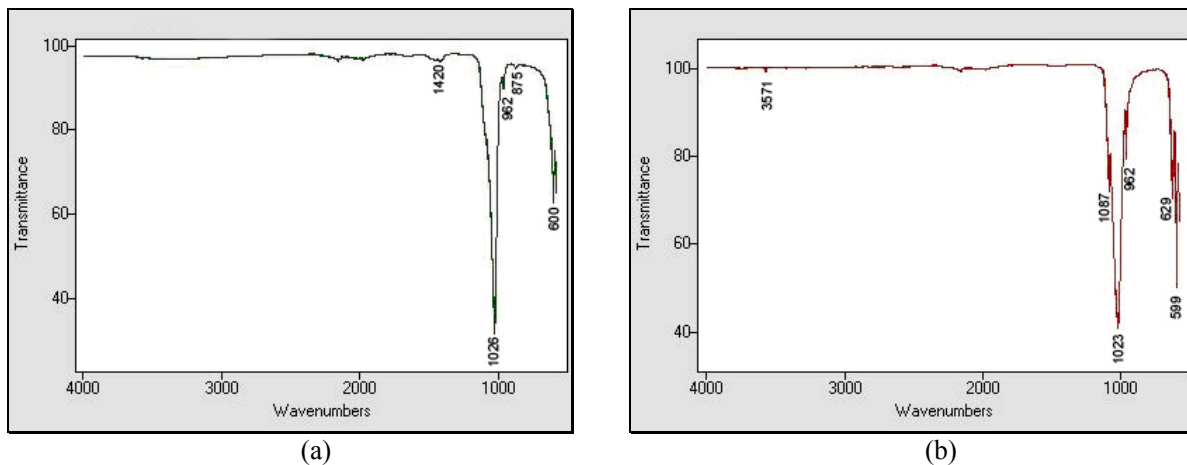


Fig. 4. FTIR spectra of hydroxyapatite synthesized at 75°C and heat treated at 200°C and 1200°C

In case of spectrum presented in figure 4a, the absorption bands at 1420  $\text{cm}^{-1}$  and 875  $\text{cm}^{-1}$  suggest the presence of  $\text{CO}_3^{2-}$  in hydroxyapatite structure [13, 14]. The absorption bands at 1026, 962 and 600  $\text{cm}^{-1}$  detected in the spectra are attributed  $\text{PO}_4^{3-}$  groups [15, 16].

After heat treatment at 1200°C, no peak related to  $\text{CO}_3^{2-}$  group (1420  $\text{cm}^{-1}$ , 875  $\text{cm}^{-1}$ ) was not detected, as shown in figure 4b. Synthesis of hydroxyapatite is revealed by the absence of large peak located at 3550  $\text{cm}^{-1}$ , assigned to the crystallization water, i.e. water molecules trapped in the apatite unit cell [17, 18]. Generally, stoichiometric hydroxyapatite cannot contain water molecules in its unit cell while nonstoichiometric can contain some water molecules [17, 19].

The presence of hydroxyl ion in the apatite lattice are confirmed by absorption bands at 3571  $\text{cm}^{-1}$  and 629  $\text{cm}^{-1}$ , attributed to the stretching and flexural modes of hydroxyl ( $\text{OH}^-$ ) group [20]. The characteristic bands of the  $\text{PO}_4^{3-}$  groups is observed

at 1087, 1023, 962 and 599  $\text{cm}^{-1}$  [15, 16].

### 3.3 Scanning electron microscopy

The morphologies of the co-precipitated produced powders, heat treated at 200°C, observed by SEM, are shown in Figure 5. This sample mostly consists of the particles with fine grain, homogeneous and uniform distribution of components. Spherical particles obtained will allow a high degree of packing, otherwise most particles are submicron size, as shown in figure 5a, while figure 5b reveals presence of nanometric particles.

Figure 5a reveals microstructural aspects of the sample analyzed at magnifications of 1000x. Figure 5a shows a cluster with various sizes and preferentially associated. High resolution image (10000X) provides details of constituent structure in which particles are mostly spheroidal shape and homogeneous distributed.

A qualitative analysis recorded magnification of 10000X reveals the microstructure of two individual

particles with average diameter of 203 and 193 nm.

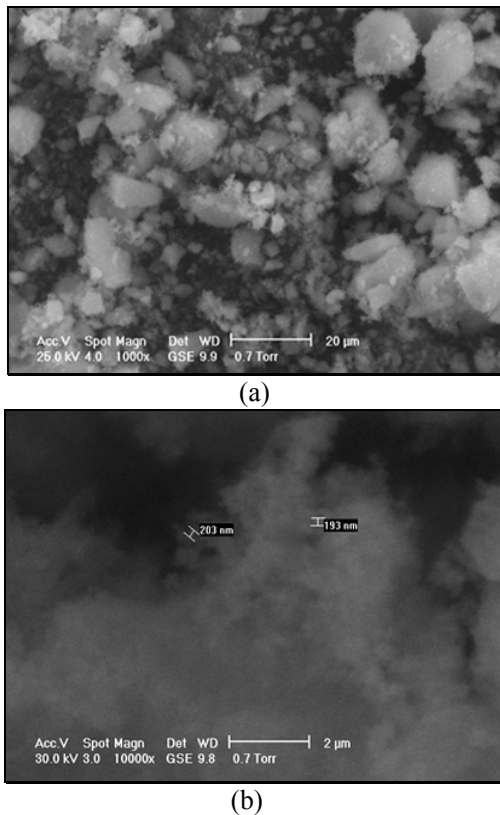


Fig. 5. SEM images of hydroxyapatite powders heat treated at 200°C  
(a) low magnification; (b) high magnification

Other techniques, as atomic force microscopy (AFM) could reveal a rough surface architecture for HA, the predominant size of grains being in the range of 90-100 nm [21]. At higher temperature the deagglomeration of bulk phases and agglomeration of nano phases leads to the nano crystalline hydroxyapatite. As a conclusion, the crystal size distribution depends on the size of the critical nucleus under the super saturation condition.

### 3.4 Rheological study

The ability of hydroxyapatite powder to flow depends on a number of factors, such as: powders density, particle size distribution, specific surface area, particle shape etc. The flow rate decrease with the increasing of moisture in the powder, specific surface and fractions with low average diameter. Since powder particles is considered very small ( $0.47 \pm 0.01 \mu\text{m}$ ), they do not have gravity, which leads to the conclusion that ultrafine powders have high specific surface which will lead to increasing packing and an advanced densification.

## 4 Conclusion

The proposed method for the synthesis of hydroxyapatite powders led to obtaining a product with a high degree of crystallinity and purity. The crystallinity degree was greater than 95%, in case of all samples heat treated at 1200°C. The X – ray diffraction analysis reveal the presence of insignificant amounts of calcium oxide as secondary phases, less than 2%. The IR spectrum confirm the formation of hydroxyapatite. Scanning electron microscopy reveals synthesis of spherical particles hydroxyapatite with fine grain, homogeneous and uniform distribution. Rheological study leads to conclusion that ultrafine powders have high specific surface, therefore an advanced densification.

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