

SYNTHESIS AND CHARACTERIZATION OF HYDROXYAPATITE OBTAINED IN DIFFERENT EXPERIMENTAL CONDITIONS

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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 $\text{Ca}(\text{OH})_2$, H_3PO_4 and NH_4OH were used. . In order to study the factors that have an important influence on the chemical precipitation process a experimental platform has been designed for hydroxyapatite synthesis. The experimental platform was designed and developed in order to study the factors involved in chemical precipitation reactions of hydroxyapatite such as synthesis temperature, stirring speed, acid addition rate, aging time of precipitates etc. The proposed method led to obtaining a hydroxyapatite with a high degree of crystallinity. In order to investigate phase composition, crystallinity and crystallite size, the thermal treated powder samples has been characterized by X-ray diffraction*

Keywords: *hydroxyapatite, chemical precipitation, x-ray diffraction, crystallinity.*

1. INTRODUCTION

Among all biomaterials, hydroxyapatite - the mineral component of hard tissues in vertebrates, is the most biocompatible material able to be used in clinical applications of conservation and restoration because of its excellent features such as biocompatibility and bioactivity. Hydroxyapatite shows excellent biocompatibility not only with hard tissue but also with soft tissue.

This material is capable of integrating biologically when directly implanted into a bone defect; furthermore, it produces no harmful effect on the immune system, is not toxic, and features an osteoconductive behavior [1].

Although many routes have been explored for synthesis of hydroxyapatite powders such as hydrothermal methods [2, 3], sol – gel process [4], reactions in solid state [5], microwave processing [6], the chemical precipitation route has proven to be popular, because of its versatile and economical advantages, and thus has been extensively reported [3].

The method proposed in this paper is based on chemical coprecipitation. The hydroxyapatite powders are obtained from the reaction of inorganic oxide chemical solutions.

Chemical coprecipitation involves the use of aqueous solutions. This method leads to obtaining a hydroxyapatite characterized by high specific surface area and small particles size distribution. In most cases deviations from the stoichiometry will occur, at the same time, the amorphous structure is obtained. All these depend on a number of factors such as reactants involved in synthesis, concentration and initial pH of solutions, reaction temperature etc [7].

Wet methods (chemical coprecipitation, sol – gel, hydrothermal etc) involved in synthesis of hydroxyapatite led to obtaining products characterized by a large degree of crystallization, dependent on the conditions of synthesis. These methods are based on two

types of reaction: neutralization (acid - base) or reaction between the two salts.

In the case of hydroxyapatite synthesized by chemical precipitation, obtaining a product characterized by high purity and crystallinity depend on a number of process parameters, such as synthesis temperature, the initial concentration of reactants involved in the synthesis reaction, pH of the environment reaction, the rate of acid addition, the stirring speed of the reactants and the conditions of heat treatment applied to as dried hydroxyapatite powders.

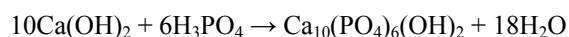
The objective of this work was to obtain hydroxyapatite powders by coprecipitation method, in different experimental conditions. The thermal treated powders were characterized by X-ray diffraction in order to identify the phase composition, crystallinity and crystallite size.

2. MATERIALS AND METHODS

2.1. Hydroxyapatite synthesis

Hydroxyapatite was synthesized via the chemical precipitation method, in according with procedure described in other papers [8, 9]. As the starting reagent, analytical grade $\text{Ca}(\text{OH})_2$, H_3PO_4 and NH_4OH were used.

The chemical equation that describes the reaction is:



Chemical precipitation is performed by first preparing a suspension of calcium hydroxide, $\text{Ca}(\text{OH})_2$, 168 g in 114 ml distilled water and orthophosphoric acid, H_3PO_4 , 9ml in 78 ml distilled water. Ammonium hydroxide, NH_4OH , were used to adjust the solution to raise the pH greater than 10.5, in order to obtain a stoichiometric hydroxyapatite (Ca/P = 1.67).

In order to obtain a hydroxyapatite slurry, H_3PO_4 solution was added by dropwise, for 10 min. to – 1.4

hours over the alkaline solution based on $\text{Ca}(\text{OH})_2$, in conditons of intense stirring.

After the complete addition, the reaction mixture were kept during 2 to 48 hours for ripening. In order to remove any impurities, the precipitate were separated from the suspension by vacuum filtration, washed with distilled water. The filtered cakes was oven dried at 110°C for 24 hours and then ground to a powder.

In the next step, hydroxyapatite powders was heat treated at 1200°C for 3 hours. Finally, powders have been ball milled, using a planetary mill with tungsten carbide balls, for 1hour.

2.2. Characterization of the samples

The structural characterization of powders was carried out by X-ray diffraction using a Rigaku SmartLab diffractometer with $\text{Cu}_{k\alpha} = 1.5418 \text{ \AA}$ radiation generated at a voltage of 45 kV and a curent of 200 mA. Data were collected in the 2θ range of $10 - 150^\circ$, with a step size of $0.02^\circ 2\theta$.

X-ray analysis was used to assess the present phases, the degree of crystallinity and size of crystallites, in case of hydroxyapatite studied.

Phases identification was achieved by comparing the diffraction patterns of hydroxyapatite obtained with ICDD – PDF2 standards: 09-0432 card for hydroxyapatite, 09-0169 card for β -tricalcium phosphate and 37-1497 card for calcium oxide.

In order to study the factors that have an important influence on the chemical precipitation process and, in the end, on the finished product properties, a experimental platform has been designed for hydroxyapatite synthesis. The experimental platform was designed and developed in order to study the factors involved in chemical precipitation reactions of hydroxyapatite such as synthesis temperature, stirring speed of reaction enviroment, acid addition rate, aging time of precipitate etc.

The main components of experimental platform (Fig. 1.) designed for synthesis of hydroxyapatite by chemical coprecipitation are thermostated bath (1), peristaltic pump (2) mechanical stirrer (3) and portable pH meter (4). The experimental conditions for the synthesis of hydroxyapatite powders are presented in Table 1.

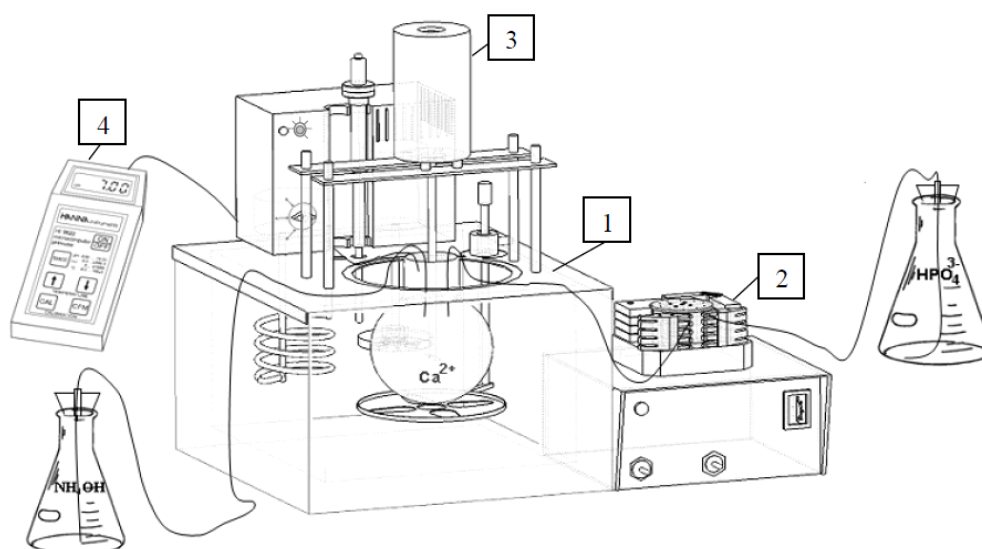


Fig. 1. Design of experimental platform for hydroxyapatite synthesis

Table 1. Experimental conditions for hydroxyapatite synthesis

Experiment	Concentration [mol/l]	Temperature [$^\circ\text{C}$]	Addition rate [ml/min]	Stirring speed [rpm.]	Aging time [h]
E1	2	75	1	1000	48
E2			10	1000	48
E3			1	300	2
E4			10	300	2

3. RESULTS AND DISCUSSION

The X-ray diffraction results of the synthesized precipitates heat treated at 1200°C are shown in figure 2. The pattern of sample E1 illustrated in figure 2a shows that the only phase present in powder synthesized in according with experimental conditions presented in table 1, is hydroxyapatite.

In case of sample E2 and E3 presented in figure 2b and 2c, X-ray diffraction patterns reveal that hydroxyapatite is not only phase. A small amount of calcium oxide (CaO) was identified as secondary

phase. Calcium oxide presence was revealed by the diffraction lines situated at 37.4 2θ and 53.95 2θ.

In case of sample S4, pattern presented in figure 2d, reveals presence of β-tricalcium phosphate, β-Ca₃(PO₄)₂ and calcium oxide as secondary phases. The presence of β-Ca₃(PO₄)₂ is evidenced by the diffraction lines located at 27.87 2θ, 29.79 2θ, 31.13 2θ, 34.5 2θ, 41.2 2θ, 44.93 2θ, 45.34 2θ and CaO by diffraction line located at 37.4 2θ and 53.95 2θ. An estimate regarding the proportion of each phase analyzed in powders structure was achieved by comparison experimental results with AMCSD database has been presented in figure 3.

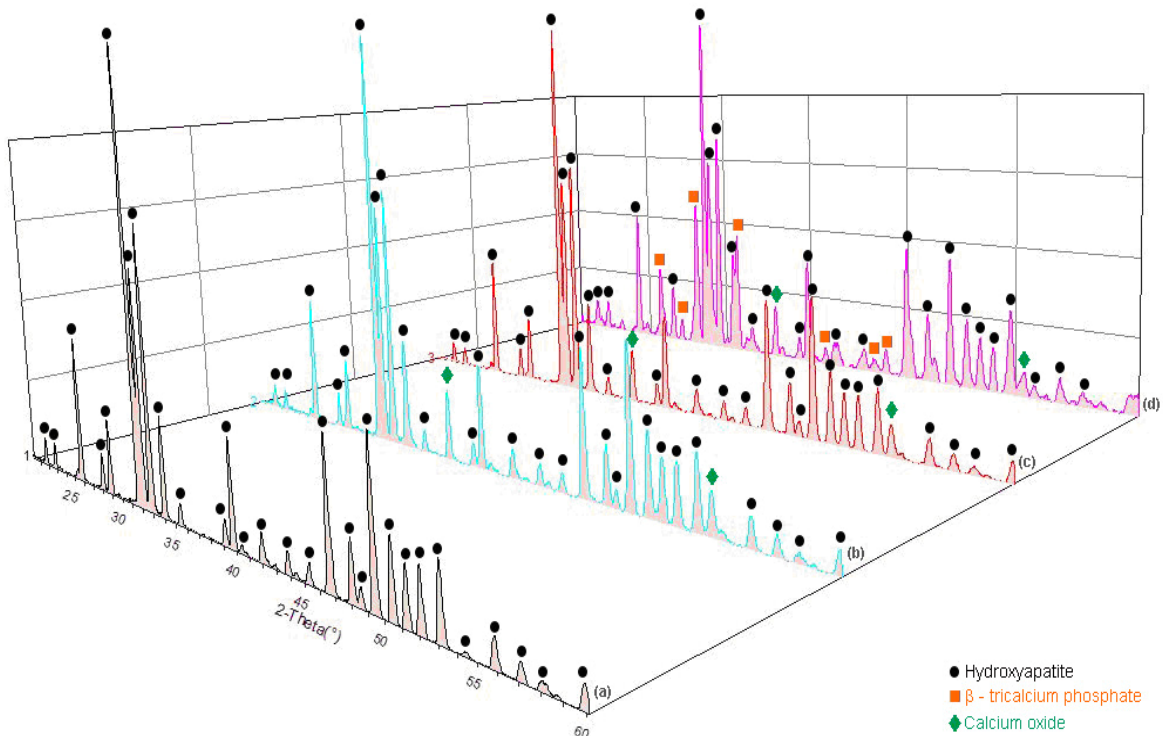


Fig. 2. X-ray diffraction patterns of hydroxyapatite samples synthesized in according with experimental condition above mentioned

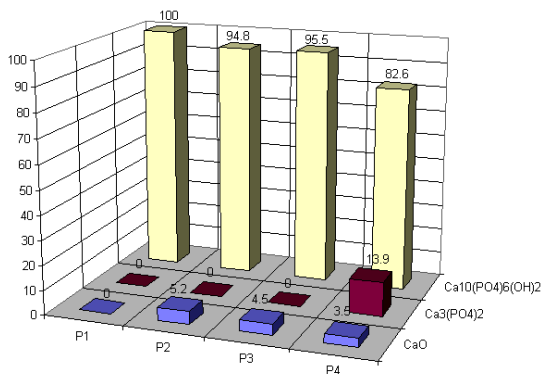


Fig. 3. The estimated value regarding quantitative analysis of hydroxyapatite powders

In table 2 is presented estimated value regarding crystallinity degree and crystallite size, in according with procedures presented in other papers [8, 9].

Table 2. The estimated value regarding crystallinity degree and crystallite size

Samples	E1	E2	E3	E4
Crystallinity, %	97	98	97	92
Crystallite size, nm	41	45	45	37

Data presented in Table 2 are in according with those published in the literature and international standards [10].

The addition rate of phosphoric acid in the alkaline environment plays an important role in obtaining of hydroxyapatite with good stoichiometry. In the case of the use of inappropriate values regarding addition rate of phosphoric acid (10 ml/min.), there is a possibility of formation of secondary phases such as tricalcium phosphate as a result of sharply decrease in pH value near the end of acid addition.

Influence of addition rate on the chemical composition of the precipitate obtained can be explained by changes that occur in the pH. A high rate of addition of acid solution led to a drastic decrease in pH environment reaction. Thus, for an addition rate of approximately 10 ml/min., rapid decrease pH of the reaction, $\text{pH} < 7$, led to an incomplete dissociation of phosphoric acid. The hydroxyapatite precipitation is incomplete in the absence of PO_4^{3-} ions. This explains the presence of undesired byproduct ($\beta - \text{Ca}_3(\text{PO}_4)_2$ and CaO) in the structure of the powders obtained. However, high speed addition of phosphoric acid in alkaline solution can lead to obtain calcium deficient hydroxyapatite.

Stirring speed of reaction environment is another factor that influences the synthesis of hydroxyapatite. In order to obtain hydroxyapatite with a good crystallinity the addition of the reactants required intense stirring of reaction environment. Synthesis of hydroxyapatite in conditions of low mixing speeds (300 rpm) leads to a heterogeneous reaction environment and, consequently, increased local concentration of PO_4^{3-} ions. These drawbacks lead to a decrease in pH value and the formation of soluble precipitated.

The degree of crystallinity of hydroxyapatite may be greatly dependent on the time of maturation of the precipitate. This crystalline behaviour as a function of synthesis and ripening temperature can be explained by the mechanism of crystal growth in solution. It is well known that precipitation of particles involves nucleation and growth from a supersaturated solution. During the aging, the hydroxyapatite crystals are subjected to a process that implies dissolution and recrystallisation. During this stage the smallest crystals disappear in favour of the larger ones, which grow further [8, 11].

4. CONCLUSIONS

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 90%, in case of all samples heat treated at 1200°C.

The XRD patterns reveals that hydroxyapatite is major phase presented in synthesized powders. Thus, in case of sample synthesized in conditions of intense stirring, low addition rate of acid and ripening time up to 48 hours, hydroxyapatite is only phase obtained.

Presence of tricalcium phosphate – β and calcium oxide in powders structure is a result of improper synthesis

parameters setup such as: high addition rate of acid, poor stirring speed of reaction environment and a short time for the aging precipitates.

5. ACKNOWLEDGMENTS

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