THE EFFECT OF CALCIUM SUSPENSION CONCENTRATION ON THE HYDROXYAPATITE STRUCTURES AND PURITY

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The presented work aimed to the hydroxyapatite (HAP) preparation through the wet precipitation method, which consists of drop-wise phosphoric acid addition to stirring calcium suspension. For this, the materials called CPW10, CPW50, CPW100 and CPW200 were obtained by using the concentration of the calcium suspension as variable. To characterize the obtained materials, XRD, FTIR, SEM/EDS and TGA analysis were carried out.

The results obtained showed that the calcium suspension concentration plays a crucial role for the structure and purity of the prepared materials. It found that low reagent dispersion *i.e.* high concentration leads to the formation of carbonated hydroxyapatite with secondary phases including the un-reacted calcium source. Moreover, low suspension concentrations promote the formation of the carbonated hydroxyapatite as a single-phase. Indeed, the results demonstrate that the increase in the calcium concentration is accompanied by an increase of the carbonate contents in the final materials.

INTRODUCTION

Calcium phosphate (CP) is a family of minerals divided into several crystalline structures with various chemical formulas. CP is a major focus because it can be found in many living organisms, in bone minerals and tooth enamel. The most similar crystalline structure to the mineral present in the organisms is the hydroxyapatite (HAP, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$). Hydroxyapatite is also the most thermodynamically stable crystalline phases in the calcium phosphate family with an excellent osteoconductivity, bioactivity and adsorption properties. For this, HAP has many applications in the medical field.¹

The general importance of the hydroxyapatite (HAP) has led to the development of many synthetic routes of the mineral. HAP can be prepared by various methods such as solid-state reaction, soil gel, molten salts, liquid-solid solution, electrochemical deposition, hydrothermal technique, hydrolysis and chemical precipitation and neutralization. Chemical precipitation and neutralization in aqueous solution is one of the most widely used techniques because of its relative simplicity and its low cost with a high product yield.²

Moreover, several studies proved that various calcium phosphate phases could be presented during the hydroxyapatite formation, which leads to a mixture of hydroxyapatite with secondary

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phases such as brushite (DCPD), octacalcium phosphate (OCP) and tricalcium phosphate (TCP).³⁻⁵ For this, the control and the optimization of the operating conditions are necessary to obtain hydroxyapatite as a single-phase.

Some reported studies focus on the experimental synthesis conditions that affect the properties of the hydroxyapatite such as temperature and pH, reaction time and flow of phosphoric acid addition, reagent concentration, calcination and sintering temperature.⁴⁻⁷ These studies show that the experimental conditions change the hydroxyapatite properties including its purity.

For this, the presented work is devoted to the study of another experimental factor that can affect the hydroxyapatite properties; this factor concerns the calcium suspension concentration. Different powders CPWX (CPW10, CPW50, CPW100 and

CPW200) were prepared by wet chemical precipitation using a mixture of calcium hydroxide $\text{Ca}(\text{OH})_2$ and calcium carbonate CaCO_3 and using phosphoric acid H_3PO_4 as starting reagents. The effect of calcium aqueous suspension concentration on the properties, composition and structures of un-calcined and calcined CPWX was evaluated by using different characterization techniques.

EXPERIMENTAL

CPWX preparation

CPWX powders were synthesized via chemical wet precipitation method with stoichiometric initial molar ratio calcium/phosphate $\text{Ca/P} = 1.67$. The chemical equation describing the reaction is shown below:

The precipitation was performed by first preparing a suspension of calcium. For this purpose, 0.67 mole of a mixture of 80% calcium hydroxide ($\text{Ca}(\text{OH})_2$) and 20% calcium carbonate (CaCO_3) were dispersed in the desired volume of double-distilled water and stirred during 24 hours. Then, 0.04 mole of phosphoric acid (H_3PO_4) solution having the concentration of 0.8 M was added to the calcium aqueous suspension, drop-wise, at a rate of 2 mL/min.

The initial pH is basic without any base addition. The pH values represented in Table 1 indicate the release of hydroxyl groups from $\text{Ca}(\text{OH})_2$ implying the total dissolution of H_3PO_4 . The resulting mixture was agitated at 750 rpm for 24 hours at room temperature and normal atmospheric pressure. After 24 hours, the mixture was filtered and dried at 70°C for 12 hours. The obtained CPWX were named CPW10, CPW50, CPW100 and CPW200; where X is the volume of water used in the preparation of calcium suspension, respectively 10 mL, 50 mL, 100 mL and 200 mL, as shown in Table 1.

Characterization

The synthesized powders were calcined at 800°C using a Wise Therm06-314 furnace with the heating rate of 5°C/min

for 2 hours. Calcined and un-calcined powders were characterized using infrared spectra recorded on an Agilent Technologies Cary 600 Series Fourier Transform Spectrometer (FTIR) with a resolution of 4 cm^{-1} . FTIR was used to confirm the formation of HAP and to potentially investigate the presence of other calcium phosphate phases. X-Ray Diffraction (XRD) profile of CPWX samples was studied at room temperature with a diffractometer Rigaku Ultima IV using $\text{CuK}\alpha$ irradiation at 1.54 Å and scanning rate of 0.02° (2θ/S). The angle of diffraction was varied from 3° to 70°. The phases presented in each CPWX were determined by means of International Centre for Diffraction Data (ICDD) reference XRD patterns. Morphological observation and surface atomic percentage composition were performed using the JEOL JED-2300 Scanning Electron Microscopy instrument coupled with Energy Dispersive X-ray Spectroscopy (EDS/SEM). The thermogravimetric analysis (TGA) were carried out in TA SDT Q600 instrument in nitrogen atmosphere at the scanning rate of 5°C/min in the temperature range of 50°C to 1000°C. TGA was used to study the thermal behavior of CPWX and to determine the weight loss in each powder.

Table 1

Experimental conditions for CPWX synthesis

	Water volume (mL)	Initial pH
CPW10	10	12.2
CPW50	50	11.9
CPW100	100	11.7
CPW200	200	11.4

RESULTS AND DISCUSSION

FTIR analysis

Calcium phosphate undergoes different transformations to obtain hydroxyapatite [HAP, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$], pass through dicalcium phosphate dihydrate [DCPD, brushite, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$] and/or dicalcium phosphate anhydrous [DCPA, monetite, CaHPO_4] and/or octacalcium phosphate [OCP, $\text{Ca}_8(\text{PO}_4)_4(\text{HPO}_4)_2 \cdot 5\text{H}_2\text{O}$].^{3,6,8}

The Figure 1 (a-d) represents FTIR spectra of CPWX materials. The Figure shows the presence of broad envelope between 2600 cm^{-1} and 3700 cm^{-1} in CPW50, CPW100 and CPW200 spectra. The obtained broad envelope involve the O–H stretching vibration of adsorbed water and O–H stretching vibration of the hydroxyapatite crystals. For the spectrum corresponding to the CPW10 material (Figure 1 a), the above-mentioned broad envelope was obtained in the same range of wavenumbers but with the existence of several peaks at 3560 cm^{-1} , 3483 cm^{-1} , 3271 cm^{-1} , 3156 cm^{-1} and 2957 cm^{-1} . These peaks are due to the O–H stretching of water in DCPD structure according to the studies done by Mandel and Tas 2010 and by Amer *et al.* 2014.^{9,10} The very small peak at 3566 cm^{-1} showed in Figure 1 (b-d) is assigned to stretching mode of O–H groups that exist on the surface of the hydroxyapatite crystals. Moreover, the peak observed at 1636 cm^{-1} for all samples [Figure 1 (a-d)] is attributed to the bending mode of water.¹¹

In addition, the two bands at 1100 cm^{-1} and 575 cm^{-1} correspond to the bending mode of phosphate groups^{11,12} can denote the formation of the hydroxyapatite. In fact, the absorption bands at 984 cm^{-1} , 1050 cm^{-1} and 1143 cm^{-1} obtained in CPW10 spectrum (Figure 1 a) suggests the phosphate groups vibrations of brushite (DCPD) crystals.¹⁰ The small band observed at 480 cm^{-1} in all samples is attributed to the symmetrical distortion of PO_4 .^{3,4}

Other bands of CPW50, CPW100 and CPW200 spectra *i.e.* 1422 cm^{-1} , 1456 cm^{-1} and 875 cm^{-1} reveal to the carbonate existence. Guo *et al.* 2013, Giardina *et al.* 2010 and Anwar *et al.* 2016^{5,13,14} reported that the stretching mode of the carbonyl from carbonate groups appears around 1550 cm^{-1} , 1457 cm^{-1} and 880 cm^{-1} when CO_3^{2-} substituted some hydroxyl groups. In this case, the hydroxyapatite is called hydroxyapatite type A. They also reported that stretching mode gives values around the following bands 1462 cm^{-1} ,

1418 cm^{-1} , 876 cm^{-1} for the hydroxyapatite type B when CO_3^{2-} substituted some phosphate groups. In our research, following the wavenumber of the carbonate bands (Figure 1 b-d); we have the type B substitution.

The two bands specific to the hydroxyapatite type B substitution, were replaced by a single large band at 1434 cm^{-1} in the CPW10 (Figure 1 a). The band observed for CPW10 at 2360 cm^{-1} also characterize the presence of carbonate anions CO_3 .²⁻¹⁵

By comparison, the smaller carbonate bands were found in CPW200 prepared with the lowest concentration of calcium leading to the most diluting suspension. Furthermore, the higher bands of carbonate were observed for CPW10 prepared by using the highest concentration of calcium source. In addition, the FTIR spectrum corresponding to CPW10 material clearly shows the presence of un-reacted calcium carbonate (CaCO_3). The presence of CaCO_3 can certainly be presented because the calcium hydroxide is more alkaline and more soluble than calcium carbonate. Therefore, the added phosphoric acid to the calcium source preferentially consumed the calcium hydroxide and not the calcium carbonate. Consequently, the pH remains at a high value and inhibit the decomposition of the calcium carbonate.

Several studies demonstrate that the calcination have an important effect on the calcium phosphate properties. For this, CPW10 and CPW200 were calcined at 800°C ; the obtained powders were named CPW10800 and CPW200800 respectively. Figure 2 illustrates FTIR spectra of CPW10800 and CPW200800 compared to the un-calcined material (CPW10 and CPW200). For CPW200, the carbonate bands are significantly decreased by heating at 800°C . This decreasing indicate the departure of the carbonate. On the other hand, a simple disappearance of the 2360 cm^{-1} band was observed in CPW10.

According to the Figure 2, the surface area of the band between 2600 cm^{-1} and 3700 cm^{-1} was considerably reduced after the calcination. Indeed, the different bands at 3560 cm^{-1} , 3483 cm^{-1} , 3271 cm^{-1} , 3271 cm^{-1} , 3156 cm^{-1} and 2957 cm^{-1} characterizing the presence of the brushite (DCPD) in the CPW10 material were disappeared and replaced by a small band only. The disappearing of the above-mentioned bands is explained by the structural transformation of the DCPD phase into another thermodynamically more stable calcium phosphate. As well, the band recorded at 1636 cm^{-1} is not observed in CPW10800 and CPW200800 spectra due to the elimination of water molecules by powders dehydration.

Fig. 1 – FTIR spectra of (a) CPW10, (b) CPW50, (c) CPW100 and (d) CPW200.

Fig. 2 – Comparative FTIR spectra. (a) CPW10, (b) CPW10800, (c) CPW200 and (d) CPW200800.

XRD analysis

Figure 3 (a-d) illustrates the diffraction patterns of CPWX materials. The presented phases in each powder were determined by comparing the recorded peaks with those corresponding to each pure phase. Pure phase peaks were checked by means of ICDD (International Centre for Diffraction Data) reference XRD patterns. For all CPWX powders, the XRD diffractograms depicted in Figures 3 suggest the presence of the peaks centered at 26° , 32° , 40° , 50° and 64° , which demonstrate the existence of the hexagonal carbonated hydroxyapatite structure $[\text{Ca}_{10}(\text{PO}_4)_{5.64}(\text{CO}_3)_{0.66}(\text{OH})_{3.03}]$ with PDF card no 01-072-9863.

The presence of carbonate in the hydroxyapatite structure has been observed in Figure 1 (FTIR) when the position of the carbonate bands indicates that we have hydroxyapatite type B substitution. Following the obtained hydroxyapatite formula from XRD, we confirm that the hydroxyapatite presented in the CPWX materials is type B in which the carbonate anions replace some phosphate anions. The presence of carbonate in the

hydroxyapatite structure may be explained by the dissolution of CO_2 released in the reaction (1). The CO_2 dissolution is possible due to the alkalinity of the medium in which the CPWX materials were formed.

Moreover, carbonated hydroxyapatite is the only phase of calcium phosphate presented in CPW100 and CPW200. Concerning the CPW50 material, the pattern represented in Figure 3 (b) shows the presence of all diffraction peaks corresponding to the carbonated HAP phase with the existence of calcium carbonate in which its diffraction peak is screened by the hydroxyapatite diffraction peak centered at 29° .

For the CPW10 material, the Figure 3 (a) shows the presence of the principal diffraction peaks of carbonated HAP with the existence of DCPD (brushite) and OCP (octa calcium phosphate) diffraction peaks. In addition, the peaks centered at 18° and 30° (Figure 3 a) proves the presence of unreacted calcium hydroxide ($\text{Ca}(\text{OH})_2$) and calcium carbonate (CaCO_3).

Fig. 3 – XRD patterns of (a) CPW10, (b) CPW50, (c) CPW100 and (d) CPW200, with $2\theta = 0.02^\circ$.

Giardina *et al.* 2010 reported that a very high pH promotes the formation of HAP without DCPD intermediate or secondary phase.¹³ In fact; it is known that the formation of DCPD requires an acidic medium.¹⁰ Our study showed a surprising result that is, the existence of the DCPD phase in CPW10 despite that the material is prepared in the most alkaline medium with the highest pH. The formation of the brushite (DCPD) is explained by the acidity provided by the addition of H_3PO_4 . Indeed, the calcium suspension used for the preparation of CPW10 is the least dispersed. Therefore, H_3PO_4 reacted rapidly with calcium bication (Ca^{2+}) in the form of hydrogen phosphate ion (HPO_4^{2-}) before its dissolution into PO_4^{3-} leading to the brushite formation and stabilization.

SEM/EDS analysis

The micrographs of CPWX represented in Figure 4 show each one, different morphologies, which were obtained by varying the calcium suspension concentration used in the CPWX preparation. A significant change in morphology and an acquiring surface homogeneity were observed after calcination at 800°C .

The presented surfaces in SEM micrographs were analyzed by EDS technique. As can be seen in EDS graphs given by the Figure 5 (a-f) that the principal elements of carbonated hydroxyapatite structure exist in all samples. These elements are calcium (Ca), phosphor (P), carbon (C) and oxygen (O). From the EDS technique, we can quantify the

molar percentage of each element. Therefore, we can deduce the molar ratio Ca/P of the analyzed surfaces. The obtained results are listed in Table 2. The Table 2 clearly shows that the carbon molar percentage (C(%)) and the molar ratio Ca/P obtained by EDS are depending on the initial water volume *i.e.* calcium suspension concentration.

For CPW10 material, we can see that the Ca/P value is superior to the initial stoichiometric ratio. This value (1.71) can be explained by the presence of unreacted $\text{Ca}(\text{OH})_2$ and CaCO_3 as was observed by XRD (Figure 3 a). The Ca/P values recorded for the materials CPW50, CPW100 and CPW200 were inferior to the stoichiometric ratio (1.67) indicating the formation of calcium-deficient hydroxyapatite (Ca-DHAP).³

As found in the XRD analysis that HAP phase presented in the CPWX materials is defined by the formula $\text{Ca}_{10}(\text{PO}_4)_{5.64}(\text{CO}_3)_{0.66}(\text{OH})_{3.03}$. The Ca/P ratio in the above-given formula is 1.77 that is superior to the stoichiometric Ca/P ratio because some phosphate ions were replaced by the carbonate anions. These phosphates replaced by the carbonate ions are considered as an excess covers the calcium atoms on the CPWX surface, leading to a negative deviation of the Ca/P values detected with EDS analysis. Based on this finding, we confirm that Ca-DHAP was presented only at the surface of the materials. After calcination, the CPW200 Ca/P ratio increases from 1.40 to 1.47, indicating that a thermal transformation to an hydroxyapatite more stoichiometric was produced.

Fig. 4 – SEM micrographs of (a) CPW10, (b) CPW50, (c) CPW100, (d) CPW200 (e) CPW10800 and (f) CPW200800 at 10 μm.

Fig. 5 – EDS graphs of (a) CPW10, (b) CPW50, (c) CPW100, (d) CPW200, (e) CPW10800 and (f) CPW200800.

Table 2

Calcined and un-calcined CPWX elements molar percentage (Ca (%), P (%), O (%) and C (%)), Carbon to Phosphor molar ration (C/P) and Calcium to Phosphor molar ration (Ca/P) obtained by EDS

	Ca (%)	P (%)	O (%)	C (%)	C/P	Ca/P
CPW10	17.45	10.19	57.35	15.01	1.47	1.71
CPW50	17.78	12.57	55.60	14.05	1.12	1.41
CPW100	16.30	11.67	58.26	13.77	1.18	1.40
CPW200	16.74	11.94	57.44	13.88	1.16	1.40
CPW10800	18.90	10.57	54.84	15.69	1.48	1.79
CPW200800	24.65	16.76	53.93	4.66	0.28	1.47

Table 2 also illustrates that the high carbon percentage (C (%)) recorded for un-calcined CPWX is 15.01%, obtained in CPW10. The calcination of this material (CPW10) at 800°C for two hours shows that the carbonates remain in the structure. Further, when CPW200 has been calcined at 800°C for two hours, the C (%) decreases from 13.88% to 4.66%, which shows that this material eliminates carbonates from its structure. These results are with good agreement with the results obtained from FTIR spectra as was represented in Figure 2.

By combining XRD and EDS results, we confirmed that the surface and the interior of CPWX materials do not have the same mineral structure. Indeed, the structure defines our carbonated hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_{5.64}(\text{CO}_3)_{0.66}(\text{OH})_{3.03}$) show that the carbon to phosphor ratio (C/P) is 0.11 (0.66/5.64). On the other hand, the C/P determined by EDS give values more important than 1 for all un-calcined CPWX powders (Table 2). The presence of this high amount of carbon in CPWX material is not possible because this important quantity of carbon does not exist in the starting reagents (see equation 1).

Fig. 6 – TGA thermograms of (a) CPW10, (b) CPW50, (c) CPW100 and (d) CPW200 obtained with 5°C/min heating rate.

Table 3

Table represents the weight loss achieved at 300°C (W_{T300} (%)) and at 1000°C (W_{T1000} (%)), the rapid weight loss at the temperature T_{Tr1} (W_{Tr1} (%)), the rapid weight loss at the temperature T_{Tr2} (W_{Tr2} (%)) and the rapid weight loss at the temperature T_{Tr3} (W_{Tr3} (%)) determined from TGA curves

	W_{T300} (%)	W_{T1000} (%)	W_{Tr1} (%)	W_{Tr2} (%)	W_{Tr3} (%)
CPW10	12.04	27.39	6.95	1.65	11.96
CPW50	3.87	10.59	/	/	3.44
CPW100	3.61	6.83	/	/	0.5
CPW200	3.95	8.04	/	/	0.88

From this, we deduce that the high amount of carbon determined from EDS technique is found only on the surface of CPWX materials. Furthermore, it is known that hydroxyapatite has a strong affinity for all kinds of CO_2 and water molecules. For this, we explain the presence of the high percentage of carbon by the adsorption of carbonate ions and CO_2 molecules generated from the equation (1).

TGA analysis

The TGA thermograms illustrated in Figure 6 make possible to identify the presented phases in CPWX materials because of their specific thermal behavior. A total weight loss of 27.39%, 10.59%, 6.83% and 8.04% was achieved for CPW10, CPW50, CPW100 and CPW200 respectively. Therefore, we can see that the most important weight loss was obtained for CPW10 thermogram in which we observe three rapid weight losses that

are W_{Tr1} (%) recorded at 189.73 °C, W_{Tr2} (%) recorded between 390 °C-454 °C and W_{Tr3} (%) recorded from 600°C to 700°C.

The W_{Tr1} (%) is associated with the water molecules released by DCPD and OCP phases. Sadat-Shojai *et al.* 2012 expressed that dicalcium phosphate dihydrate (brushite, DCPD) is transformed into anhydrous dicalcium phosphate (monetite, DCPA) in solid-state at a temperature between 120°C and 200°C.⁴ In addition, Nelson and McLean 1984 reported that dehydration of octacalcium phosphate (OCP) results in solid-state, transformation to the hydroxyapatite.¹⁶ In our work, following the Figure 6 (a), these transformations occur between 185°C-195°C, according to equations (2) and (3). In addition, the weight loss from 390 °C to 454 °C (W_{Tr2} (%)), as shown in Table 3, is allotted to the dehydration of HPO_4^{2-} containing in the monetite crystals (DCPA) according to the equation (4).¹⁷

Furthermore, the un-reacted calcium carbonate presented in CPW10 occur thermal transformation to calcium oxide with the release of CO_2 molecules according to the equation (5). This transformation is accompanied with important weight loss represented in Figure 6 (a) in the region of the third rapid weight loss (W_{Tr3} (%)).

CPW50, CPW100 and CPW200 thermograms showed similar weight losses until 300 °C (W_{T300} (%)) associated with the release of adsorbed and confined water molecules in CPWX powders.

In fact, we can see in the Figure 6 (b) the presence of an important weight loss 3.44 % (W_{Tr3} %) recorded at 770.83 °C due to the calcium

carbonate (CaCO_3) existence. By comparison, the heat necessary to CaCO_3 decomposition contain in CPW50 is higher than the heat observed for CPW10. This result indicates that CaCO_3 is coated with carbonated hydroxyapatite that is the principal phase in CPW50.

On the other hand, CPW100 and CPW200 also show a slight rapid weight loss in the range of 719°C to 776 °C attributed to the decarbonation of the carbonated hydroxyapatite structure. At a temperature of 780 °C and above, as represented in equation (6), the OH^- apatite ions can react with $\text{P}_2\text{O}_7^{4-}$ leading to the release of water molecules. The dehydration of HAP crystals is also possible, according to equation (7).¹⁸

CONCLUSION

Different CPWX materials of different compositions and morphologies were obtained by a simple chemical precipitation reaction. The concentration of the calcium suspension i.e. the water quantity is an important parameter for large production of hydroxyapatite and leads to the following results:

High concentration of calcium suspension leads to obtaining carbonated hydroxyapatite with secondary phases as OCP, DCPD, and un-reacted calcium source reagents. On the other hand, the better dispersion and low concentration of calcium suspension imply the formation of carbonated hydroxyapatite as single phase.

From the literature, the DCPD formation requires an acidic medium. In the presented work, a surprising result was obtained concerning the brushite (DCPD) formation in the most alkaline media.

By combining EDS and XRD results, we deduce that the surface and the interior of the carbonated hydroxyapatite have not the same mineral structure.

The FTIR and SEM characterizations of CPW10800 and CPW200800 confirm that the calcium suspension concentration affects the properties of CPWX without and with calcination.

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