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Physicochemical study of the effect of maturation time on the chemical composition of an oxygenated apatite

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Abstract

This study aims to evaluate the effect of the time of maturation on the chemical and structural composition of the grains of phosphocalcicapatites doped out of oxygen. In the method of making the phosphocalcicapatites, a solution of calcium hydroxide $Ca(OH)_2$ was neutralized with a solution of phosphoric acid H_3PO_4 in oxygenated-decarbonated medium at room temperature. The method could find future applications, for example, in the treatment of the infection of the bone. The apatitic fractions obtained present a well defined state of crystallinity and has an average specific surface (S_S= 170 m^2/g) relatively important compared with those of the phosphocalcic hydroxyapatite quoted in the literature. The adsorbed O_2 in the apatite structure influences considerably the specific surface of apatite. It reaches a maximum value of 183 m^2/g after 6 hours of maturation and the content of O_2 in the Oxygenated-Apatite (OA) reaches its maximum 1.7 % as in the first 10 minutes. The obtained results show the formation of an apatitic phase crystallized irregularly; once calcined with 900°C, the crystallinity of the phase becomes well organized. The thermal analyzes DTA and TGA show that the preparation phases undergo two losses of masses, a very weak one at 50°C, it corresponds to the water molecules adsorbed by apatite at the beginning and a second more important around 450°C and it corresponds to the loss of CO_2.

1. Introduction

Biomaterials of the osseous or dental filling containing the hydroxyapatite are well known because they are known to have excellent biocompatibility (very limited risk of the inflammatory reactions or rejections), a low solubility and a great quality of osteoinduction (tends to support an osseous rebuilding) [1]. These properties could be attributed to the chemical composition and the crystallographic structure of the hydroxyapatite. In spite of these properties; these biomaterials apatitic stay inactive againstpathogenic micro-organisms which can lead to in fabrics. Many studies were devoted to enhancing the characteristics ofbiomolecules like antibiotics, anti-cancer drug, and vitamins by associating them with a phosphocalcic apatite, so as to control and add additional properties[2, 3]. For this purpose, new biomaterials phosphocalcic which have an apatitic structure having on the species oxygenated with oxidation steps equal to or higher than -2 in the tunnels apatitic with a chemical formula $Ca_{10}(PO_4)_6(OH)_2O_2$ were synthesized,. The importance of the latter results owing to the fact that as the bone is

regenerated, oxygenated apatite reabsorbs by releasing a molecule of oxygen. Which behave as The oxygenis a disinfectant against the anaerobic bacteria by locally increasing the partial pressure of oxygen and on the other hand the ion O_2^{2-} peroxidizes destroys in situ the micro-organisms [4].Studies were carried out on the level of the tunnels, the latter apparently have a diameter growing when one passes from apatite coated with cadmium to apatites calcic, strontic and barytic. Thus, the rate of fixing of the oxygen molecules in these various apatites increases in parallel with the growth of the diameter, that can be explained by the adequacy between the average section of the tunnels and the section of the oxygen molecule.

The studies concerning the preparation of oxygenated phosphocalcic apatite are very limited. The latter was synthesized for the first time by Simpson and Miner in 1969, by treating calcium phosphate of β type with 110 volume ofhydrogen peroxide [5, 6]. In 1989, C. Ledardet al. patented an oxygenated phosphocalcic apatite synthesized from a mixing as solution of a $CaCl_2/H_2O_2$with a solution of $(NH_4)_2HPO_4/H_2O_2$[7]. In 2008, S.BELOUAFA et al. prepared phosphocalcic oxygenated apatites crystallized under the physiological conditions of 37°C and pH 7.4 by the reaction andprecipitation of phosphate and calcium solutions. In this case, the calcium solution was prepared by dissolution of a salt of calcium like ($CaCO_3$, $Ca(NO_3)_2$ or $CaCl_2$) in hydrogen peroxide 30%. The phosphate solution was prepared by adding phosphoric acid to a solution hydrogen peroxide 30% [8].

A simple method of making oxygenated apatite wascarried out by the acid-base reaction technique In this reactionphosphoric acid was reacted with calcium hydroxide in a hydrogen peroxide medium[9].

In 2013, Lamhamdi et al.[12] Prepared an oxygenated apatite by controlling hydrolysis of dicalcium phosphate dihydrate or brushite, with a solution of a hydrogen peroxide, this elaborate apatitic matrix is a nonstoechiometric apatite which has several advantages, such as the purity of the final stage, a nanometric structure and a well controlled and beforehand selected rheology [10].Also Yahyaoui et al. [11]synthesized oxygenated apatite from hydrolysis of cured brushite cement in aqueous medium, this apatite contain together molecular oxygen and peroxide ions. Which are removed by heating the final product at a temperature of about 300 °C[11].

In current work, we were interested to evaluatethe influence of the process of maturation in one hand on the chemical and structural composition of the formed phosphocalcic apatite grains and on the other hand on the quantity adsorbed of molecular oxygen in the tunnels apatitic.

2. Materials and methods

2.1. Preparation of an apatite doped by molecular oxygen

Initially, a 10% solution of hydrogen peroxide (100 mL) was prepared bydilution from a stock solution with 30%concentration. To it was addedcalcium oxide (4.12 g)was added to the soil. The mixture was left under continuous agitation at room temperature for 4 hours. Phosphoric acid (stoichiometric amount as given by the equation illustrated in the Figure 1) was dissolved in a 50 mL solution 10% H_2O_2.

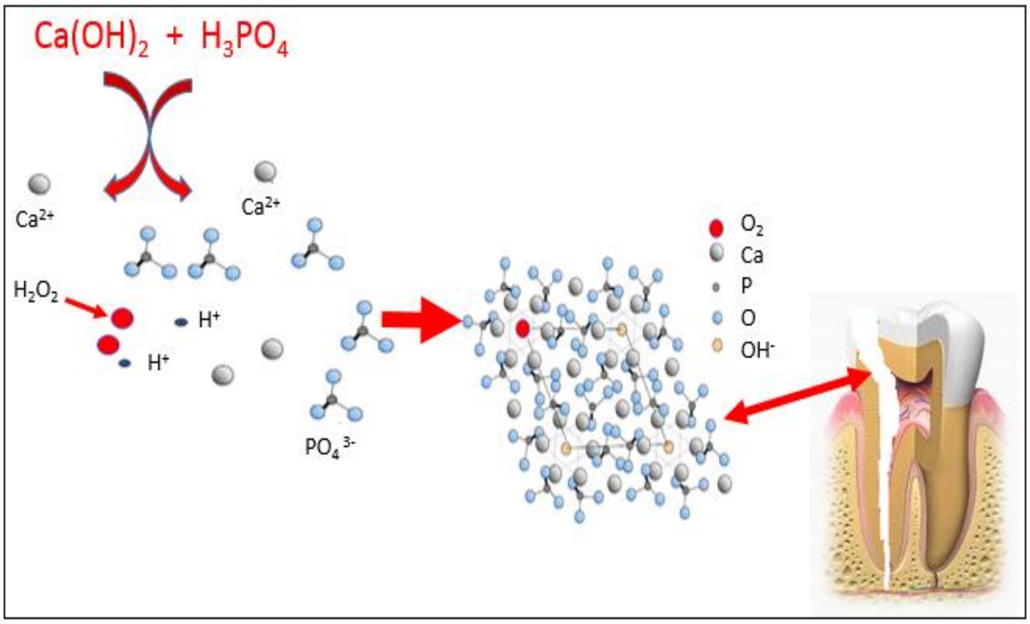

Figure 1: General synthetic scheme of oxygenated apatite [12].

The solution was an added dropwise to the calcium oxide solution. The reaction mixture was maintained under a strong agitation for two hours. The produced solution was left at room temperature for three days. A known volumes of solution were taken during the three days after 10 minutes, 6 hours, 1 day and 3 days of maturation.The withdrawn samples were filtered (vacuum filtration) and dried in an oven to produce yellow clear thick residue. The residue was then heated in an oven at 300 °C. The calcination is expected to cause a change of the ions peroxides inside the network, and molecular oxygen should retain in the network apatitic.The pH of the reaction medium was followed according to the time of maturation;after 2 hours of strong agitation, the pH reaches the value of 9.2.After about 6.0 hours of maturation, the pH of the medium decreases to 7.8.Maturation longer than 6 hours is causing an increase in the pH to about 8.2 per(one to three days).
A representation scheme for the synthesis of the oxygenated apatite is shown in Fig.1.
Oxygenated apatite has an antiseptic Role: limit the proliferation of anaerobic microorganisms in the site of implantation**.**Oxygenated apatite in fact contains molecular oxygen in the tunnels of its apatite structure. Experiments have shown that these molecules are released into the environment or by the gradual dissolution of the material, either by chemical exchange with the environment. [12].

2.2. Characterization of synthesized apatite

The prepared samples of oxygenated apatite were characterized by Fourier transform infrared spectroscopy (FTIR) using a Schimadzu FT-IR8400S series instrument(ShimadzuScientific Instruments). Spectra were acquired over the region 400-4000 cm^{-1}for samples in pellet form containing 1 mg sample in powder form mixed with 200 mg KBr (spectroscopic grade). The structure of the samples was also evaluated by X-ray diffraction (XRD) using a Shimadzu XRD Shimadzu 6000 diffractometer with Cu-Kα radiation (1.5418A˚). Diffraction peak at 25.9◦ was selected for determining the crystallite size ofScherrer's formula since it is the cheapest and isolated from other peaks. The peak allocates is (002) Miller's plane family and shows the crystal growth along the axis of HAp crystalline structure.The thermogravimetric analysis was carried out by Shimadzu DTG-60 simultaneous DTA- TG, heating rate was10 ° C/min and the temperature domain ranging from 25 to 1000 °C.The proportioning of the molar ratio Ca/P is carried out by ICP–AES method, the liquid sample is nebulized then dried into solid aerosols under an argon flow, which then transported directly to the heart of the plasma torch sample will be atomized. The calibration into concentration was performed with reference solutions prepared with a background salt.
Specific surface and the distribution of the pores were determined by BET (Brunaur, Emmett, Teller) and BJH (Barret, Joyner, Halenda) methods, respectively using an Autosorb 1 instrument. The samples treated with water that was deduced under secondary vacuum for20 hours at 250 °C. The gas that used in this study is the nitrogen with a molecular mass of 28.013g, the cross section of the order of 16.200 A^2 and the liquid density equal to 0.808 g/cc. The measurements were performed at 77 °C. Prior to measurements, was deduced to obtain a clean surface.

3. Results and discussion

3.1. Characterization by infra-red spectroscopy of absorption with transformed fourrier

Figure 2 shows the FT-IR spectra of the products of reaction that has a Ca/P ratio = 1.67, calcined at 300°C and taken at various times of maturation: (a): after 10 minutes, (b): 1 day and (c): 3 days.
The spectra show one observes the slightly carbonated apatite of the one hour maturation sample, the one day sample became more carbonated, and the IR show complete carbonated apatite after 3-days of maturation.. The wide and intense band in the range 3000-3400 cm^{-1} confirms the presence of the water molecules adsorbed on the surface of the crystals apathetic [13]. The bands in the range 1000-1150 cm^{-1} and 550-650 cm^{-1} correspond respectively to the elongations and antisymmetric deformations of the phosphates groups (PO_4^{3-}) located in sites apatitic [14, 15]. The band at 961 cm^{-1}is assigned to the symmetrical elongation of groups (PO_4^{3-}) [14, 15]. The apatitic carbonates appear in the waveumber range 1350-1500 cm^{-1} are characteristic of the ions carbonates adsorbed on the surface [14, 15]. The second spectral area (850-900 cm^{-1}) revealed still a band at 875 cm^{-1} corresponds to the phosphate ions HPO_4^{2-} and/or CO_3^{2-} [16].

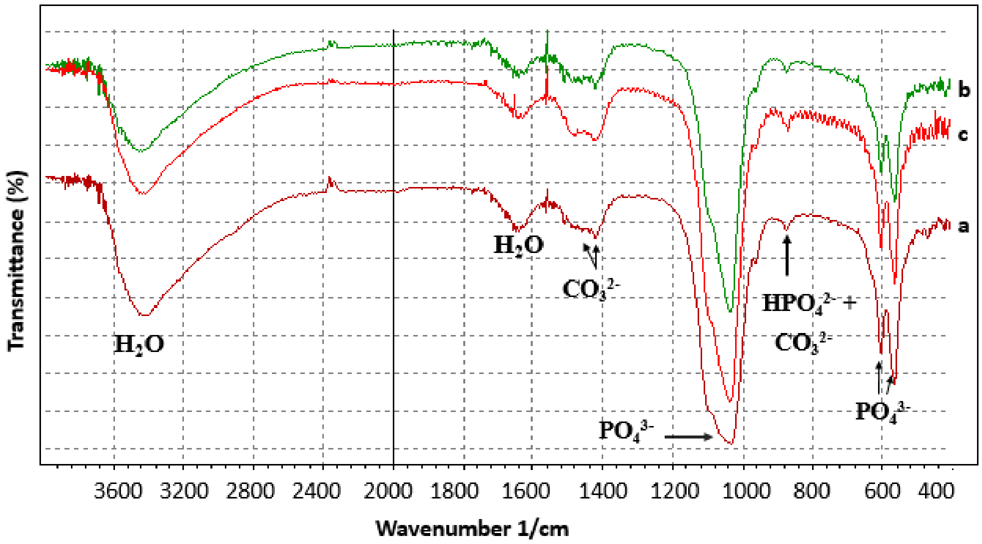

Figure 2:adsorption spectrum (FTIR) of the AO of the ratio Ca / P = 1.67 calcined at 300 ° C (a): 10 minutes, (b) 1 day and (c): 3 days.

3.2. Characterization by diffraction of the X-ray

Figure 3 represents the X-ray diffraction of the reaction products of the mixture with a ratio Ca/P = 1.67 initially introduced and calcined at 300°C with (a): 10 minutes, (b): 6 hours, (c): 1 day and (d): 3 days of maturation. From the spectra it can be concluded that all the prepared products evolved to an identical phase apatitic, as from the IR spctra, . All the phases are crystalline (broad peaks).To better understand the productthecalcination of products was carried out at900°C. Figure 4 shown the X- ray diffraction of the products of the reactionof the mixing of Ca/P ratio = 1.67 calcined at 900°C with (a): 10 minutes, (b): 6 hours, (c) 1 day and (d): 3 days of maturation.The analysis of X-ray diffraction spectra shows good crystallinity of the products.

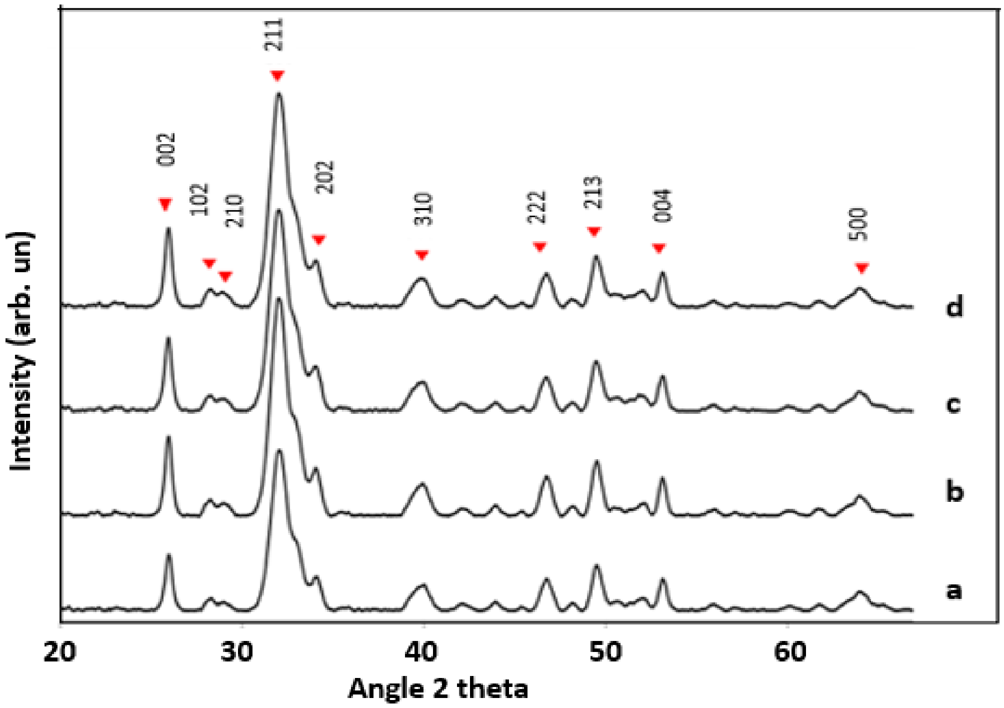

Figure 3:spectrum X-ray diffraction of the AO of the ratio Ca / P = 1.67 calcined at 300 ° C (a): 10 minutes, (b): 6 hours, (c): 1 day and (d): 3 days.

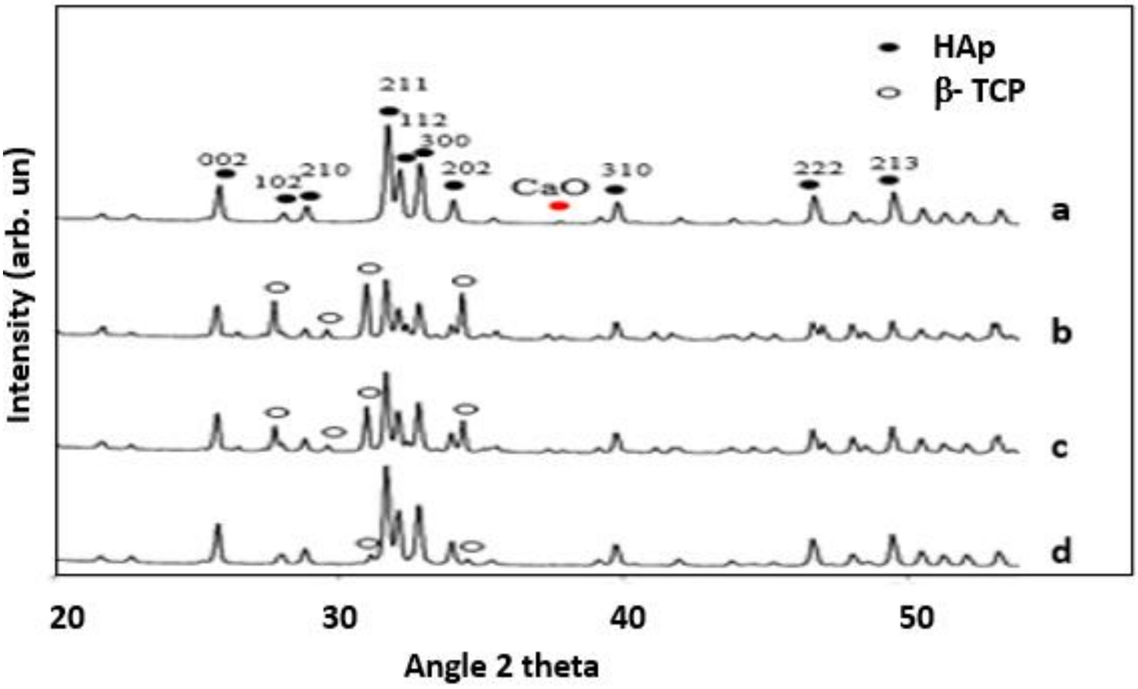

Figure4:spectrum X-ray diffraction of the AO of the ratio Ca / P = 1.67 calcined at 900 ° C (a): 10 minutes, (b): 6 hours, (c): 1 day and (d): 3 days

For low values of the maturation time (10 min), the X-ray analysis result shows the presence of a small amount of calcium oxide that has not reacted,the results are in agreement with the elemental chemical analysis performed by ICP-AES. Indeed the latter present a value little high of Ca/P ratio of the order 1.71. So far, all the analysis results confirm that the reaction product is composed of a two-phase mixture between the oxygenated apatite and oxide calcium. The β-TCP phase disappears in a continuous way during the maturation time. From the intensity of the peaks of each phase [17], the ratio of the binary system HAp/β-TCP are dependent on the maturation as shown in Table 1.

Table1. Evolution of the ratio HAP / β-TCP depending on the maturing time

Maturation time	HAP/ β-TCP ratio
10 min	100/0
6 hours	55/45
1 day	64/36
3days	95/5

Previous work has shown that the powders of apatites of Ca/P ratio strictly between 3/2 and 10/6 have an apatitic structure deficient in calcium $Ca_{10-x}\square_x(HPO_4)_x(PO_4)_{6-x}(OH)_{2-2x}\square_{2x}$ with 0 <x<1. The latter evolving towards a biphasic system composed of the hydroxyapatite and tricalcium phosphate according to the published work [15]:

$$Ca_{10-x}\square_x(HPO_4)_x(PO_4)_{6-x}(OH)_{2-2x}\square_{2x}\ (1-x) \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 3x\ Ca_3(PO_4)_2 + x\ H_2O$$

3.3.Chemical analysis

The chemical analysis results are summarized in Table 2 for the reaction products with Ca/P ratioof 1.67 initially introduced at different maturation time.

Table 2. Ca (mg / L), P (mg / L) and Ca / P ratio measured of the OA at different times of maturation

Maturation time	Ca (mg/L)	P (mg/L)	Ca/P
10 minutes	330,25	149,28	1,71
6 hours	322,14	154,66	1,61
1 day	327,45	155,3	1,63
3days	324	152	1,64

The sample with a 10 minutes of maturation time, showed an atomic ratio Ca/P to be 1.71.We followed by TGA and DTA the loss of mass This ratio takes low values in the domain (≥ 6:00). This decrease is may be due to transferring of the reaction mixtureto other more stable apatitic phases under these conditions. The entire of these results confirm the formation of apatite lacunar deficit in calcium at room temperature [18].

3.4. Characterization by thermogravimetric and differential analysis coupled

We followed by TGA and DTA the loss of mass and the thermal variations, respectively of the oxygenated apatite prepared of the room temperature up to 1000°C under nitrogen current, with a speed of the rise in temperature of 10°C/min.The curve TGA (Figure 5a) shows two very weak losses of mass at the beginning of the thermogram and 600°C. The first loss of mass is due to the desorption of surface water. Whereas the second loss, it corresponds to the elimination of residual carbonates of type A detected by infra-red spectroscopy around 1450 cm^{-1}.The possibility of substitution of the ions hydroxyls OH- (hydroxyapatite of the A) type and/or the phosphates groups PO_4^{3-} (hydroxyapatite of the B) type by the ions carbonates CO_3^{2-} were described in literature.As regards the curve DTA relating to oxygenated porous apatite (Figure 5b), it shows the presence of two exothermic effects which appear at temperatures respectively close to 50°C and beyond 450°C and which corresponds successively to the elimination of the water molecules adsorbed on the surface of this material and the elimination of the ions carbonates.

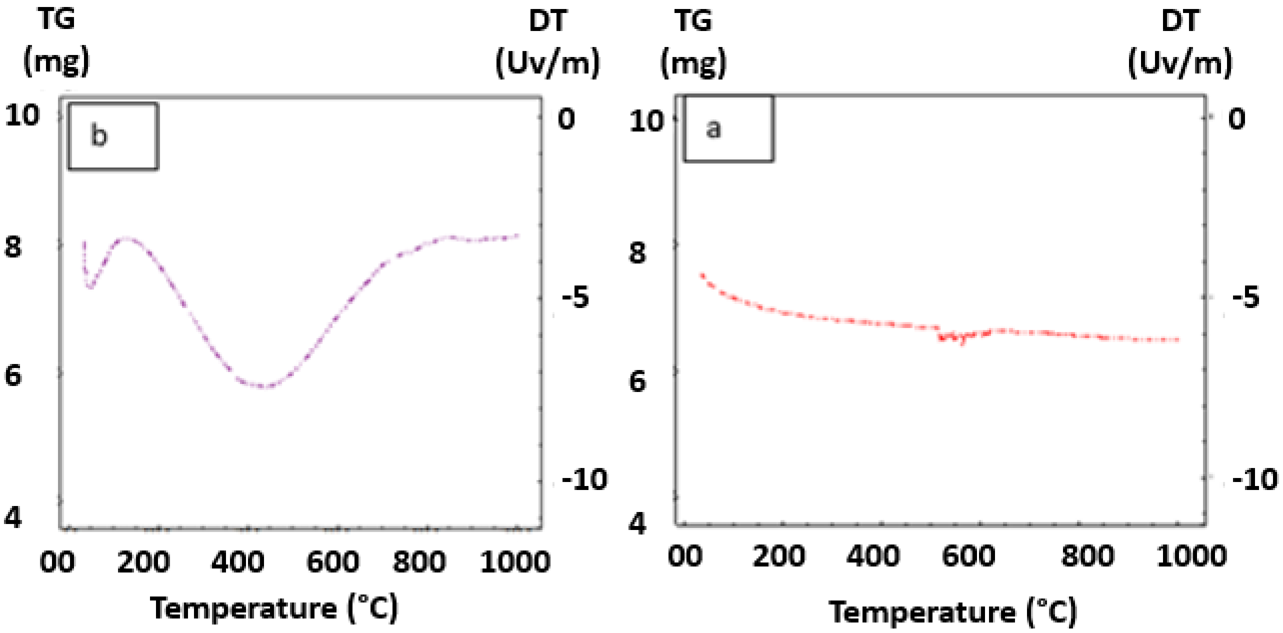

Figure 5:Thermogravimetric (a) and Differential thermal analysis (b) of OA

3.5. Description of the isotherms of adsorption

The isotherms of N_2 adsorption-desorption on the surface of prepared oxygenated apatite at 25°C for various times of maturation are represented respectively in Figure 6. The isotherms obtained are characterized by a progressive increase in the quantity adsorbed according to the relative pressure of balance for values of P/P_0 higher than 0.6. At low pressures, the isotherm is characterized by a stage of saturation, characteristic of the mésoporeux adsorbents in which there is a capillary condensation.The process of desorption in this case is not reversible, it is characterized by a hysteresis of desorption compared to adsorption. The isotherm thus observed is of type IV according to the classification of IUPAC, characteristic of an adsorption in the mesopores. At low pressure, adsorption is stronger in the micropores because of the strong gas-solid interaction.According to the curves of adsorption of nitrogen with the durations of treatment, the adsorbed volume of nitrogen increases with the treatment time due to an increase in the total specific surface with the duration of the treatment.

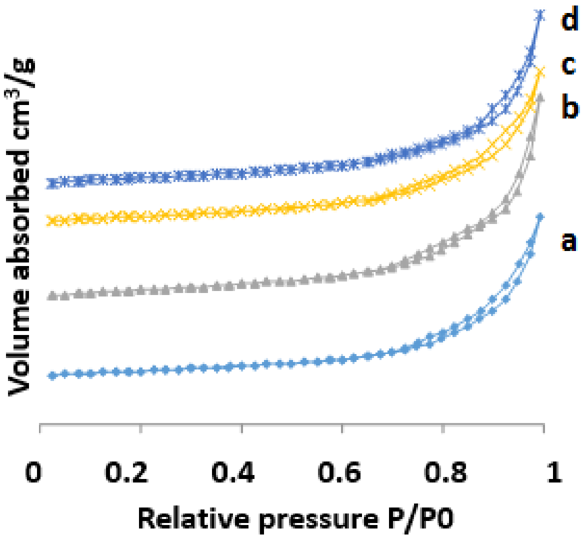

Figure 6: Isothermal of adsorption-desorption of N_2 on the OA of the ratio Ca / P = 1.67 calcined at 300 °C. (a): After 10 minutes of maturation, (b): 6 hours, (c): 1 day, and (d): 3 days

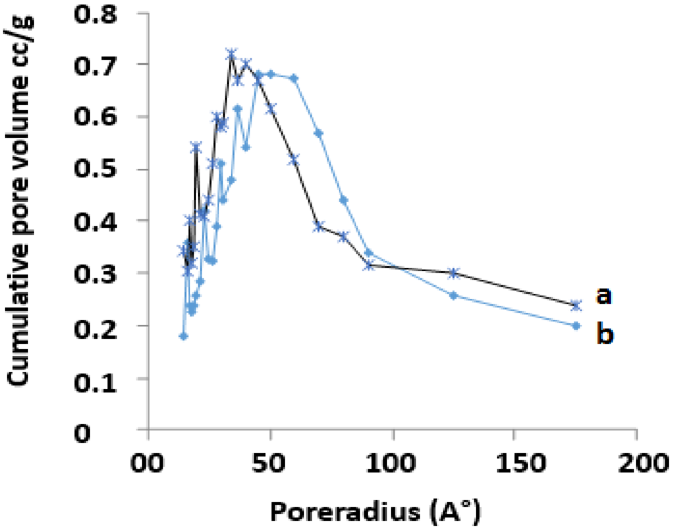

Figure7:volumic distribution of the pore sizes of the oxygenated apatites to different maturation time.(a): After 10 minutes of maturation, (b): 3 days.

The pace of the isotherms of adsorption-desorption don’t change with the duration of the treatment, which indicates that, the nature of the pores didn’t change, with mesopores of size averages between 40-50 A°. The results of measurements of specific surface, porous volume and the average diameter of the pore of the oxygenated apatites prepared at various times of maturation are summarized in Table 3. The data analysis shown in the table, reveals us that the apatite treated with hydrogen peroxide is characterized by an increase in the specific surface compared with that of the apatite of reference (HAp) which is about 86 m^2/g. Moreover, it is clearly appears that the measurement of the specific surface of oxygenated apatite at various times of maturation gives different values that cover the range from 183.4 to 141.6 m^2/g. For the six hours time period, total specific surface is about 183.4 m^2/g higher, that is characterized by an increase in the size of the pores with a volume of about 0.851 cm^3/g and an average size of pore of 56.65 A°.

The results of measurements of specific surface obtained reveal the influence of the molecular oxygen inserted in the tunnels apatitic and the ions peroxides on the specific surface of the oxygenated apatite particles.We determined the distribution of porous volume by means of the method of BJH based on the relation of Kelvin, which does not take account of the pores whose diameter exceeds 200 nm [19].

Table 3. Volumetric analysis of the oxygenated apatites -effect of maturation-

Sample	Specific surface (m^2/g)	pore volume (cc/g)	Rays of the pores (A)
Ca/P = 1.67 (10 min)	141.6	0.686	50.20
Ca/P = 1.67 (6 hours)	183.4	0.851	56.65
Ca/P = 1.67 (1 day)	158.8	0.651	44.86
Ca/P = 1.67 (3 days)	162	0.69	40

The model of the pores considered is that with walls cylindrical and whose ray varies from 2 to 40 nm. By way of an example, the curves of voluminal distribution of the size of the pores of the A.O - 10 min and the A.O - 3 days are illustrated by Figure 7.

The curve of voluminal distribution of the size of the pores of the oxygenated apatite at different time of maturation (10 min, 6 houres, 1 day, 3 days) presents a broad distribution of pores and the appearance of several populations compared to the hydroxyapatite reference whose diameter of pores varies from 3 to 40 nm with a maximum of 10 nm, 11.3 nm, 8.2 nm and 8.9 nm, respectively at various times of maturation: 10 min, 6 houres, 1 day and 3 days. Results are shown in Table 4. It also presents a reduction in the macroporosity according to the duration of treatment. These results show that, the effect of oxygenated species inserted in the tunnels apatitic on the distribution of the size of the pores.

Table 4. Determination of pore volume distribution as a function of pore diameter of the oxygenated apatites -effect of maturation-

OA-10min-		OA -6H-		OA-1d-		OA -3d-	
Dp (A°)	V_P (cc/g)	Dp (A°)	V_P (cc/g)	Dp (A°)	V_P (cc/g)	Dp (A°)	V_P (cc/g)
32.1	0.36	43.2	0.46	34	0.405	36	0.35
46.4	0.42	54	0.55	40	0.54	48	0.44
56.8	0.508	68	0.68	68	0.72	58	0.52
75	0.618	113.2	0.84	82	0.695	74	0.63
100.4	0.68	…….	…......	………	………	89.66	0.65

3.6. The effect maturation time on the molecular oxygen content

Table 5 shows the time of maturation, the molecular oxygen content and the chemical formula of the phosphocalcic oxygenated apatite as a function of time. From thisFigure 5,it can be noted that, the molecular oxygen content in phosphocalcic oxygenated apatite varies between 1.4% and 1.7%.

Table 5.n (O2) n (CO2) and chemical formula of the AO of ratio Ca / P = 1.67 for different maturation times.

Maturation time	$n(O_2)$ – mole-	$n(CO_2)$ –mole-	Chemical formula
10 min	$2,7\ 10^{-4}$	$6,5\ 10^{-6}$	$Ca_{10}(PO_4)_6(OH)_{1,98}(O_2)_{0,53}(CO_3)_{0,01}$
6 hours	$2,2\ 10^{-4}$	$6,2\ 10^{-6}$	$Ca_{10}(PO_4)_6(OH)_{1,98}(O_2)_{0,44}(CO_3)_{0,01}$
1 day	$1,9\ 10^{-4}$	$6,5\ 10^{-6}$	$Ca_{10}(PO_4)_6(OH)_{1,98}(O_2)_{0,37}(CO_3)_{0,01}$
3 days	$2,2\ 10^{-4}$	$6,3\ 10^{-6}$	$Ca_{10}(PO_4)_6(OH)_{1,98}(O_2)_{0,44}(CO_3)_{0,01}$

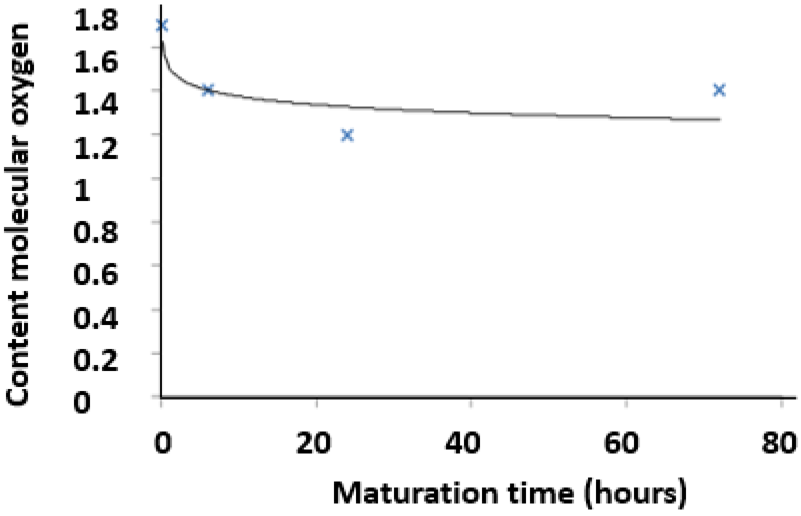

Figure 8: Variation of the molecular oxygen content as a function of maturation time.

The variation of the molecular oxygen content versus maturation time is shown in Figure 8.From this figure 8, it can be noted that the molecular quantity of inserted oxygen does not vary considerably with time, and there remains practically constant up to 80 hr of maturation. A change in quantity of oxygen appaera in the first 10 minutes of maturation.

Conclusion

Oxygenated phosphocalcicapatites are increasingly essential in the field of the orthopedic and dental surgery, their interest lies in the presence of the molecular oxygen inserted in the tunnels of apatite. This study aims at the evaluation of the effect of the maturation time on the chemical and structural composition of synthesized apatitic materials. The method of synthesis used is the neutralization of the calcium hydroxide ($Ca(OH)_2$ + X% [H_2O_2]) coldly prepared and free from $CO_2$with a diluted phosphoric acid solution (H_3PO_4 + X % [H_2O_2]). The obtained results confirm the formation of overdrawn lacunar calcium apatites with the ambient one. The insertion of O_2in the apatite structure influences considerably the specific surface of apatite, it reaches a maximum value of 183 m^2/g after 6 hours of maturation and the content of O_2 in the AO reaches its maximum 1.7% as in the first 10 minutes. The obtained results show the formation of an apatitic phase crystallized irregularly; once calcined with 900°C, the crystallinity of the phase becomes better; however, it was intended the formation of β-TCP in mixture with apatite, the formation of β-TCP decreases according to the duration of treatment.The thermal analyzes DTA and TGA show that the preparation phases undergo two losses of masses, a very weak one at 50°C, it corresponds to the water molecules adsorbed by apatite at the beginning and a second more important around 450°C and it corresponds to the loss of CO_2.

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