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Preparation of Calcium Phosphate Via Precipitation Technique

Dr. Wafaa A. Hussain
Applied Sciences Department, University of Technology/Baghdad.
Email:wafaloay@yahoo.com
Luay H. Alwan
Applied Sciences Department, University of Technology/Baghdad.

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ABSTRACT:

Recently, there has been an increasing attention on the preparation of calcium phosphates CaP for the development, understanding and manufacturing of biomaterials. In this study, precipitation process was performed to prepare calcium phosphates powders by varying the Ca/P molar ratio as (1.54, 1.67 and 1.8). Calcium acetate was added to disodium hydrogen phosphate, the precipitate was left overnight and dried at 100^{o}C and then the powder was treated at 900^{o}C for 1 hour. The powder sample was evaluated using such as scanning electron microscope (SEM), X-ray diffraction (XRD), atomic force molecules (AFM) and Fourier Transform Infrared (FTIR). It can be concluded, it is possible to synthesis hydroxyapatite (HA) and biphasic calcium phosphate (BCP) powders with nano particle.

Keywords: calcium phosphates, Precipitation technique

تحضير فوسفات الكالسيوم بتقنية الترسيب

الخلاصة

ازداد الاهتمام في الوقت الحاضر في تحضير فوسفات الكالسيوم لتطوير و فهم وصناعة المواد الحيوية. في هذه الدراسة تم تنفيذ عملية الترسيب لتحضير مساحيق فوسفات الكالسيوم وذلك بتغيير النسبة المولارية للكالسيوم الى الفوسفات (1.54 و 1.67 و 1.8). تم إضافة اسيتات الكالسيوم إلى فوسفات هيدروجين ثنائي الصوديوم, ترك الراسب ليلة كاملة وجفف عند 100 ^{o}م وبعدها تم معاملة المسحوق عند 900 ^{o}م لمدة ساعة. قيمت عينة المسحوق باستخدام المجهر الالكتروني الماسح و حيود الأشعة السينية وجزيئات القوة الذرية و مطيافية الاشعة تحت الحمراء. يمكن الاستنتاج انه من الممكن تصنيع مساحيق هايدروكسيابتايت وفوسفات الكالسيوم ثنائي الطور بجسيمات نانويه.

INTRODUCTION:

Ceramics are thermal and chemical stability, high strength, wear resistance and durable, all these make ceramics good candidate materials for surgical implants. Ceramic materials that are specially developed for use as medical and dental implants are termed bioceramics. Bioceramics can have structural functions as joint or tissue replacements because they exhibit biological affinity and activity to surrounding host tissues, which can be used as coatings to improve the biocompatibility and corrosion resistance of metal implants, and can function as resorbable lattice, which provide temporary structures and a framework that is dissolved, replaced as the body rebuilds tissue [1,2].

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2412-0758/University of Technology-Iraq, Baghdad, Iraq

For many years, biodegradable implants have been thought to offer advantages over metal analogs. In orthopedic practice, metal implants can distort magnetic resonance imaging (MRI), and they release metal ions into the surrounding tissue. Further disadvantages include the need for a second surgical procedure for implant removal and complicated revision surgery resulting from the presence of the implant [3].

Bioceramics can fall into three biomaterial classification: inert, resorbable and active, meaning they can either remain unchanged, dissolve or actively take part in physiological processes [4].

Calcium phosphates CaP are broadly used in medicine and oral biology due to the apatite-like structure of enamel, dentin and bones, usually called “hard tissues” [5].

There are several calcium phosphates CaP ceramics that are most frequently used in the biomaterial field such as, hydroxyapatite (HA) $Ca_5(PO_4)_3(OH)$, tricalcium phosphate (TCP) $Ca_3(PO_4)_2$, dicalcium phosphate dihydrate (brushite) $CaHPO_4.2H_2O$, dicalcium phosphate (DCP) $CaHPO_4$, octacalcium phosphate (OCP) $Ca_8H_2(PO_4)_6.5H_2O$ and tetracalcium phosphate $Ca_4P_2O_9$ [6,7].

Bioactive materials TCP and HA cause a positive reaction after implantation in terms of bony tissue formation, strengthening or interlocking which in turn promotes regeneration of the bone and its function. Bioactivity of CaP materials is dependent on many factors during the synthesis procedure, such as precursor reagents, impurity contents, crystal size and morphology, concentration and mixture order of reagents, pH and temperature. Also, the bioactivity response of Ca-P materials will depend on thermal treatment profile for drying and sintering. These conditions are controlled by synthesis preparation parameters and consequently for each application a specific route is selected [8].

Various processes for the preparation of HA powders have been developed over the past decades including wet synthesis, solid-state reaction [9], hydrothermal methods [10], sol-gel process [11] etc. The initial purpose of these processes is to produce HA powders which demonstrate desired characteristics, for example high specific surface area, fine grain size and size distribution including small in particle agglomeration. In particular, wet-chemical precipitation route is the most talented route owing to its ease in experiment operations, low working temperature, high percentages of pure products and inexpensive equipment requirement [5].

In order to gain insights into the complex structure found in biological mineral phases there would be required a well-defined characterization of the synthetic Ca-P, where the composition, crystallinity and nanostructure have to be properly addressed. These properties play a major role on the bioactivity of Ca-P based materials in terms of enhanced contact areas and degradation. In the present study, we aimed to synthesize calcium phosphate powders by wet precipitation technique in three different Ca:P molar ratio. The treated precipitation powder characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), atomic force molecules (AFM) and Fourier Transform Infrared Spectroscopy (FTIR).

Materials and methods:

Materials and synthesis

The starting materials include: Calcium acetate ($Ca(AC)_2$) (BDH Limited poole England) and disodium hydrogen phosphate (Na_2HPO_4) (BDH Limited poole England). Distilled water was used in all synthesis steps.

A solution of disodium hydrogen phosphate (Na_2HPO_4) of 0.015 M was dissolved in distilled water (150) ml, and a solution of calcium acetate ($Ca(AC)_2$) of 0.023, 0.025 and 0.027 M was also dissolved in distilled water (250) ml in Ca:P molar ratio (1.54 MR_1, 1.67 MR_2 and 1.8 MR_3). A solution of calcium acetate added drop by drop to the boiling disodium hydrogen phosphate solution [12]. The obtained precipitations can be described by Equations [13].

$$10Ca^{2+} + 6HPO_4^{-} + 2OH^{-} \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 6H^{+} \quad \text{......(1)}$$

$$10Ca^{2+} + 6H_2PO_4^{-} + 2OH^{-} \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 12H^{+} \quad \text{......(2)}$$

$$3Ca^{2+} + 2HPO_4^{-} \rightarrow Ca_3(PO_4)_2 + 2H^{+} \quad \text{......(3)}$$

$$3Ca^{2+} + 2H_2PO_4^{-} \rightarrow Ca_3(PO_4)_2 + 4H^{+} \quad \text{......(4)}$$

The precipitate was aged overnight at room temperature, washed with distilled water, filtered by using filter paper and dried at 100 ^{o}C. The dried powder was crushed by using mortar and pestle then calcined in alumina crucible at 900^{o}C for one hour in air atmosphere at the rate of 5^{o}C/min.

Characterization

Scanning electron microscopy was performed to determine microstructure of the resulting powders after heat treatment. CaP powders were analyzed by X-ray diffraction (XRD) with Siemens-Brucker D5000 diffractometer. This instrument works with voltage and current settings of 40 KV and 30 mA, respectively, and uses Cu-Kα radiation (1.54060 Å). Scanning speed 5 deg/min, scan mode: continuous scan. The particle size analysis of CaP was done by atomic force microscopy (AFM). Scanning probe microscope (CSPM-5000) as instrument was used for this analysis. Fourier transform infra red (FTIR) spectrum of synthesized CaP powder was obtained over the wave numbers 400-4000 cm^{-1}. The powder was dispersed into pellets of KBr (mixed in 1:4 ratios).

Results and discussion:

SEM analysis

SEM micrograph of the CaP powder obtained from MR_3 after heat-treatment is shown in Figure (1). The figures show the precipitation powder with different magnification, form the figures it can be found a homogeneous microstructure with ellipsoidal grains with 93 nm average diameter.

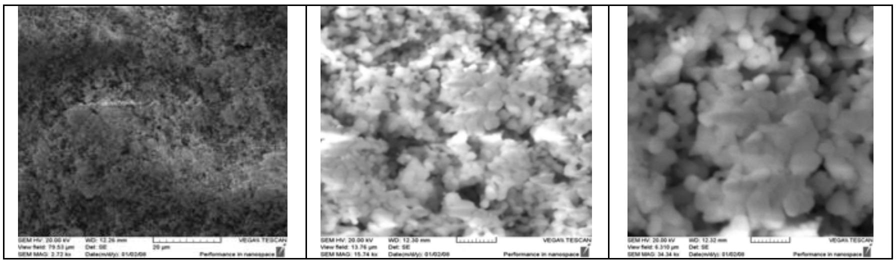

Figure (1) SEM images of the powder obtained from MR_3

XRD analysis

Characterization of the obtained powder after heat treatment was done with XRD. The straight base line and the sharp peaks of the diffractogram in Figures (2,3 and 4) confirmed that the product was well crystallized.

If the Ca/P molar ratio is lower than 1.67 (MR_1), then beta tricalcium phosphate $Ca_3(PO_4)_2$ present as a main phase and traces of HA were also detected at the XRD patterns as shown in Fig.(2). Mixtures of HA and TCP, known as biphasic calcium phosphate (BCP), have been investigated as bone substitutes.

The stoichiometric ratio (1.67) MR_2 expected a pure HA phase as shown in Fig. (3).

When the Ca/P molar ratio is 1.8 (MR_3), the XRD patterns indicated that hydroxyapatite HA was formed in this sample as a main phase and traces of CaO was also detected as shown in Fig.(4).

These extraneous phases may adversely affect the biological response to the implant in vivo. In certain circumstances it might be desirable for an implant to assist in bone repair and then be slowly resorbed and replaced by natural tissue. However, it is necessary to match the rate of resorbtion with that of the expected bone tissue regeneration. When the solubility of a calcium phosphate is higher than the rate of tissue regeneration, it will only be limited use in bone cavity and defect filling [14].

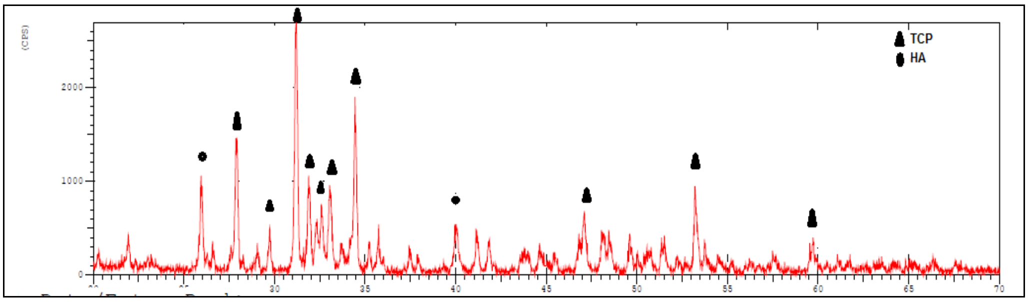

Figure (2) X-ray pattern of sample MR_1

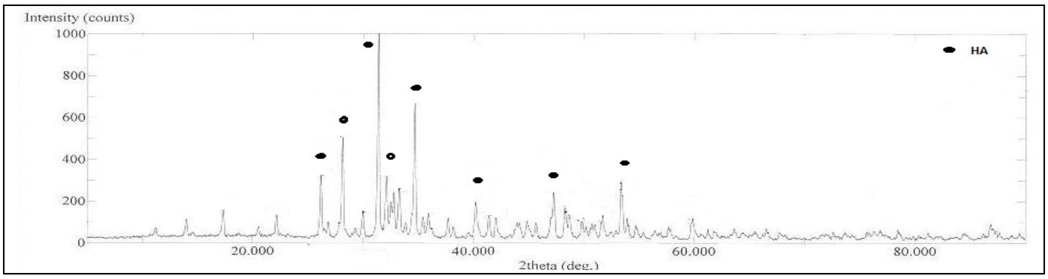

Figure (3) X-ray pattern of sample MR_2

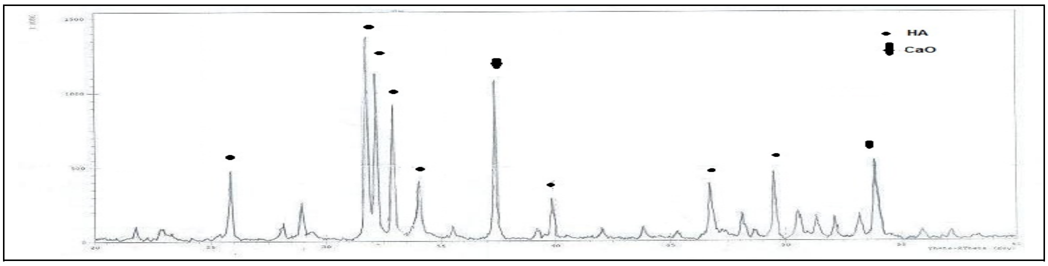

Figure (4) X-ray pattern of sample MR_3

Atomic Force Microscopy (AFM)

AFM provides nanometer-scale information about surface structure. The AFM images of the surface topography of CaP particles are shown in Figure (5, 6 and 7) for samples prepared in the three different Ca:P molar ratios . The size of the particles was determined from the AFM images. The nanoparticles were anisotropic with ellipsoidal geometry this can be seen from 3-D images on the right. While average diameter of the three powders are 90.59 nm, 111.22 nm, and 93.42 nm for MR_1 , MR_2 and MR_3 samples respectively were determined from particle distribution images on the left.

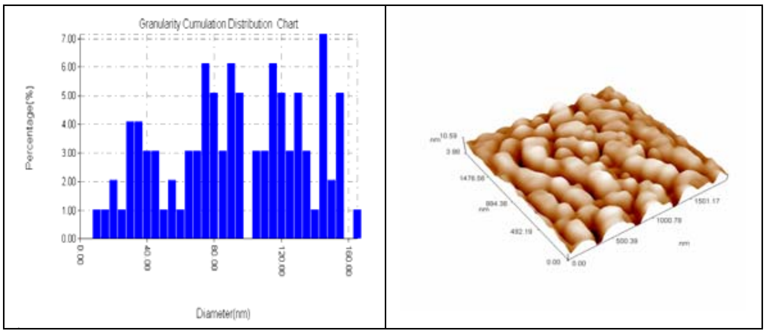

Figure (5) AFM images of sample MR_1.

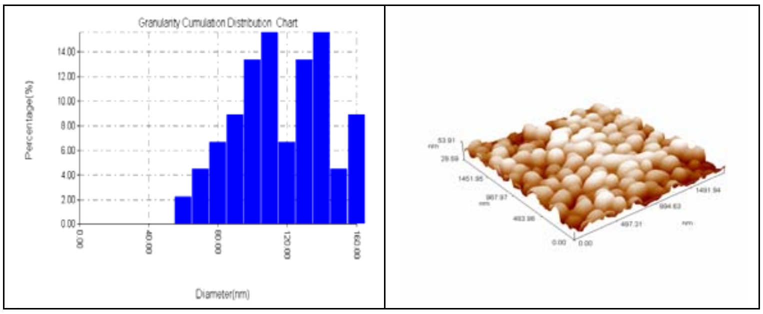

Figure (6) AFM images of sample MR_2.

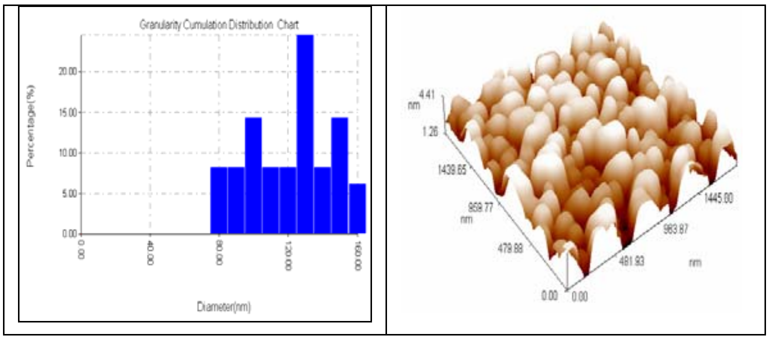

Figure (7) AFM images of sample MR_3.

FTIR analysis

Infrared characterization was carried out for the sample to study the spectral characteristics indicative of the chemical bonding in the synthesized CaP powder. The most characteristic chemical groups in the FTIR spectrum of synthesized HA are PO_4^{3-}, OH^-, and CO_3^{2-} in the three molar ratio MR_1, MR_2 and MR_3 as shown in the figures (8, 9, and 10) respectively. PO_4^{3-} group forms intensive IR transmission bands at 561 and 601 cm^{-1} (characteristic to TCP) for MR_1, 543 and 605 cm^{-1} for MR_2, and 570 and 603 cm^{-1} for MR_3 and at 1000 – 1100 cm^{-1} for the three ratios. OH^- group is relatively wide, from 3600 to 2600 cm^{-1}, a weak peak is formed at 632 cm^{-1} for MR_3 and additional OH^- peak appears at 3644 cm^{-1}, which means that there is a CaO in the powder. CaO content is proven by presence intensive peak of CO_3^{2-} group as shown in figure 10 [15]. CO_3^{2-} group forms weak and intensive peaks as shown in Figures (8, 9, and 10). Transmission bands of chemical bonds of the synthesized CaP spectrum are summarized in Table 1.

Table 1: Transmission bands of synthesized CaP chemical groups (cm^{-1})

	MR_1	MR_2	MR_3
PO_4^{3-}	561,601, 1028	543,605,1008,1020,1030,1037,1085, 1068,1072,1084,1093,1116	472, 570, 603, 960,1030,1050,1091
OH^-	3429	3435, 3595	632, 3572, 3674
CO_3^{2-}	869,1653	1647,2368	873, 1413, 1460, 1990

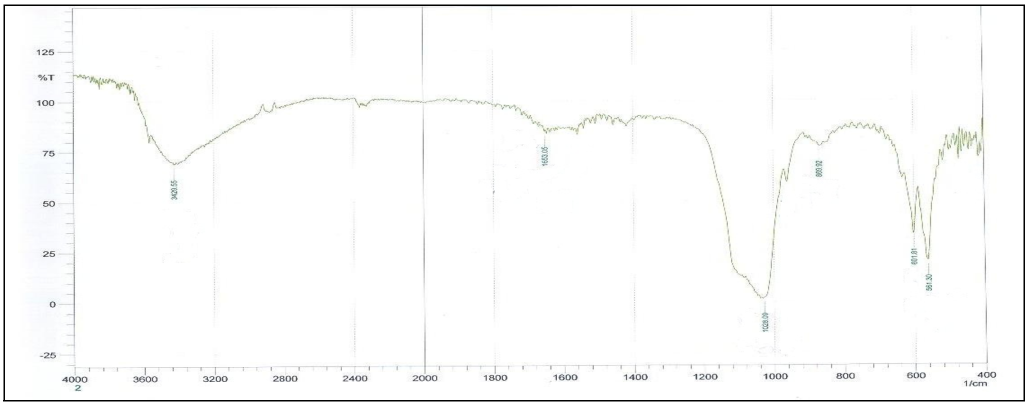

Figure (8) The FT-IR spectra of sample MR_1.

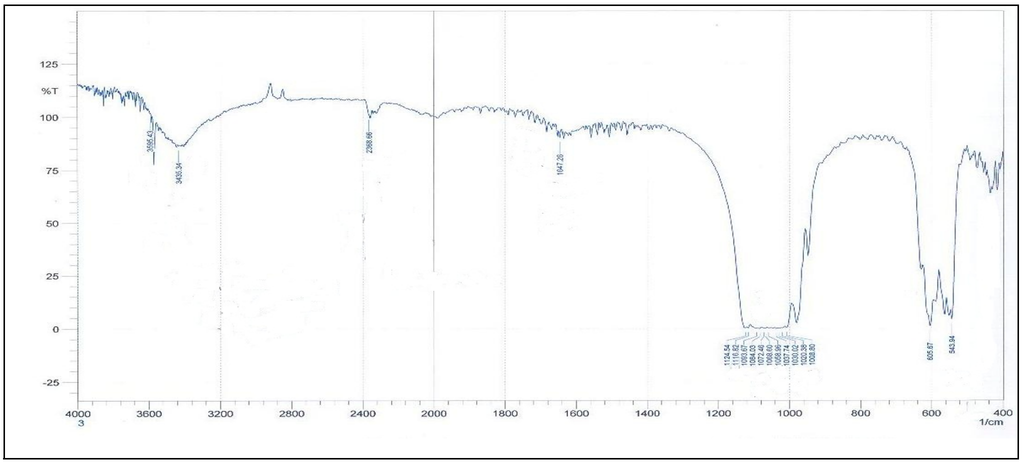

Figure (9) The FT-IR spectra of sample MR_2.

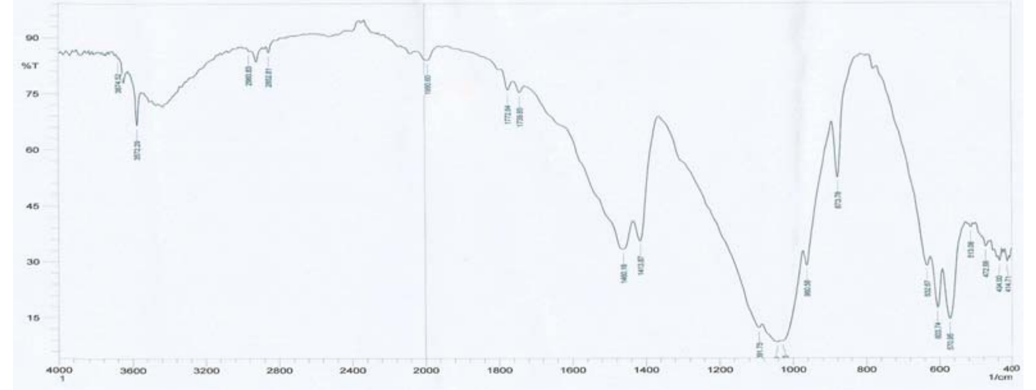

Figure (10) The FT-IR spectra of sample MR_3.

CONCLUSION:

For this study the wet-chemical precipitation could be the optimized process to induce the formation of hydroxyapatite rather than biphasic calcium phosphate, a nano grain size can be achieved by using this route.

Some secondary phases are formed during calcium phosphate process depend on original Ca/P ratio.

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