Synthesis of calcium hydroxyapatite powder from hen's eggshell

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Abstract

The interest in calcium phosphates arises from the fact that bones contain a high percentage of mineralized calcium phosphate . In this study, pure and biocompatible hydroxyapatite (HAP) powder was successfully synthesized using hen's egg shell as calcium source and phosphoric acid by precipitation method.The precipitate obtained was subjected to ripenning process for 24 hours, filtered, air dried, and calcined at temperatures of 400,800,900,and 1000 ºC. X-Ray diffraction(XRD) technique was used to investigate the formation of HAP powder, XRD results revealed the HAP formation and also indicate no occurrence of secondary phases. Fourier Transform Infrared(FT-IR) spectrum shows the characterstic peaks for phosphate and hydroxyl groups .The measured Ca/P ratio in HAP powder was 1.67 .

Key words

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تحضير مسحوق الهايدروكسي أبتايت من قشور بيض الدجاج

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الخلاصة:

تدخل مركبات الكالسيوم فسفور في تركيب العظام والأسنان بنسب مئوية عالية، وهي تعد من المواد ذات الفعالية المتميزة بايولوجيا،مما يجعل منها ملائمة للأستخدام كبدائل عظمية و في حقل الزوارع الجراحية . حضر في هذه الدراسة مسحوق الهايدروكسي أبتايت النقي بخلط معلق من هيدروكسيد الكالسيوم- المحضر أصلا من قشور بيض الدجاج- مع حامض الفسفوريك ،واخضع الراسب المتكون الى عمليات : انضاج لمدة ٢٤ساعة، وترشيح، وتجفيف، ومن ثم الى تلبيد بدرجات حرارية تراوحت من ٤٠٠ الى ١٠٠٠ درجة سلليزية .

للتحقق من تحضير هذا المسحوق ، استخدمت تقنية حيود الأشعة السينية ، وقد أكدت نتيجة الفحص تكون طور الهايدروكسي أبتايت الخالي من الأطوار الثانوية . من جانب آخر أظهرت نتائج الفحص بتقنية التحليل بالأشعة تحت الحمراء تواجد قمم مميزة لمجاميع الفوسفات والهيدروكسيل . اضافة الى ذلك فأن التحاليل الكيميائية التقليدية أظهرت ان نسبة الكالسيوم الى الفسفور في المسحوق المحضر هي ١،٦٧.

1-Introduction

The study of biomaterials shows a significant development in the last 30-35 years.Polymer materials are replacing organs, but they do not stimulate the growth of bone tissue. This function is done indeed by ceramic materials .These materials have biocompatibility, bioactivity and good mechanical properties. The main application of these materials is: prosthesis, as hip prosthesis, knee prosthesis and others [1].

It is generally acknowledged that calcium phosphate like hydroxyapatite (HAP) and tri-calcium phosphate (TCP) is good candidate to bone mineral. Additionally, bone substitutes should have degredation characterstics that allow

the organism to replace the foreign material by fully functional bone in a balanced time schedule [2].

HAP was used to coat metallic prosthesis, increasing the biocompatibility with bone tissue [3].

In 2002, Balamurugan et al produced a sol-gel coating of HAP produced from calcium phosphate precursor [4].

Several methods of chemical synthesis have been developed to prepare HAP powder using various types of calcium and phosphor sources [5-7].

The eggshell consists of about 94-97% of $CaCO_3$ and the other 3% is organic matter and egg pigment. It was found to be a waste material [8] .

Hence in this study the eggshell has been used as a calcium precursor to synthesize pure HAP with Ca/P ratio through wet chemical method .

2. Experimental

2.1 Synthesis of HAP

Uncrushed and washed eggshells were calcined in air atmosphere at 950 ºC for 1h. A stoichiometric amount of calcined eggshells were dispressed in well-degassed distilled water. Under rigorous stirring, the reagent grade orthophosphoric acid solution (0.3 M) was added in drops at controlled rate to the suspension at room temperature.

Initially , the PH of the solution was to be found 12 ,but at the end of addition of phosphoric acid, it decreased to 8.5 , the precipitate formed was subjected to ripenning (aging) treatment for 24 h followed by 1 h double distilled water and filtered again .After drying at 80 ºC for 2 h , the precipitate was calcined at various temperatures 400, 800 ,900, and 1000 ºC for 1h .

2.2 Characterization of powder

2.2.a X-ray diffraction analysis

The development crystalline phases of the synthesized powder was identified by using x-ray diffractometer system (XRD 6000-Schimadzu) with Cukα (λ=0.154nm). The measurement were made with a scanning speed of 5 deg/min and sampling interval of 0.05 deg,over a range of 25-55 (deg) at room temperature.The full width at half maximum of the 300 reflection is taken as a measure of crystalline phase development.

2.2.b FT-IR spectral analysis

The formation of the HAP phase was tested by FT-IR spectral analysis. FT-IR Transmittance spectrum of the powder which calcined at 1000 ºC sample was obtained in the 4000-400 cm region on infrared spectrometer (Schimadzu model 8000 series).

The sample was prepared in the form of disk by compression a mixture of HAP and KBr powders (1 to 25 ratios).

2.2.c Chemical analysis

The chemical composition of the HAP powder prepared was analyzed for its stoichiometry Ca/P ratio of 1.67 using atomic absorption spectroscopy (AAS 670 Schimadzu , JAPAN) .

2.2.d Density

The theoretical density of HAP powder is already known (=3.16 g/cm^3), so its bulk density was measured by the method of pycnometry . 5 ml pycnometer (Weight=9.2581g) and ethanol (density=0.77898 g/cm^3) were used for this purpose.

3. Results and Discussion

3.1 X-ray diffraction studies

The raw eggshell showed CaCO3 phase as shown in Fig.1, and CaO was detected in the calcined eggshell Fig.2. The $CaCO_3$ was completely decomposed to CaO at about 800 ºC. The calcined powder was white colored, soft and porous.

The XRD patterns of HAP powder synthesized are shown in Fig.3. The

samples heated at 400 ºC show broad peaks indicating the formation of micro-Crystallite phases, which increase with heating temperature. The crystalline sizes were calculated using Scherrers relationship

$$d=k\lambda/(FWHM)\cos\theta$$

where d is the average diameter in nm , k is the shape factor , and (FWHM) the full width half maximum .
The Bragg reflection at the (300) plane was considered to calculate the crystallite size . The sizes of crystallites for this plane are summarized in Table1.

Table1. HAP crystalline size as a function of heating temperature

Heating Temp. (ºC)	FWHM (deg)	Crystallite Size (nm)
800	0.25	33.1
900	0.2	39.7
1000	0.18	44.9

The XRD patterns also indicate no occurrence of other secondary phases.

3.2 FT-IR spectral study

Fig .4 shows FT-IR spectrum of hydroxyapatite heated at 1000 ºC. The characterstic frequencies derived from PO4 modes are seen at around 569, 603, 964, 1045 cm^{-1}.
The broad band observed around 1631 and 3425 cm^{-1} indicate adsorbed H_2O in sample. The band at around 3425 cm^{-1}, which is due to adsorbed water overlaps with the weak band at around 3570cm^{-1}, which is due to structural OH. The band (bending) due to the structural OH in HAP also occurs at 632.6 cm^{-1}.
The infrared band position and their assignments are summarized in Table 2.

Table 2: Assignment of the observed vibrational frequencies of HAP powder heated at 1000 ºC

Assignments	Observed vibrational frequencies(cm^{-1})
PO4 bend ν4	569
PO4 bend ν4	603.7
Structural OH	632.6
PO4 strech ν1	964.3
PO4 bend ν2	1045.3
CO3 group (ν3)	1427
H2O adsorbed(ν2)	1631.7
H2O adsorbed	3425
Structural OH	3570
OH strech	3749

3.3 Chemical analysis

The phase constitution and chemical homogeneity were examined by quantitative Chemical analysis via AAS. The Ca/P molar ratio was found to be 1.67.

3.4 Density

The measured density of the prepared HAP powder was found to be 3.003 g/cm^3 which are equal to 95% of the theoretical density.

Conclusions

Stoichiometric, pure HAP powder was synthesized using eggshell and phosphoric acid by precipitation method. XRD and FT-IR analysis indicate the phase purity of HAP powder. The present study suggests that eggshells are a possible material for recycling technology for future waste management. Also, eggshell-originated HAP is a potential bioceramic, and mass product could be useful as an inexpensive ceramic.

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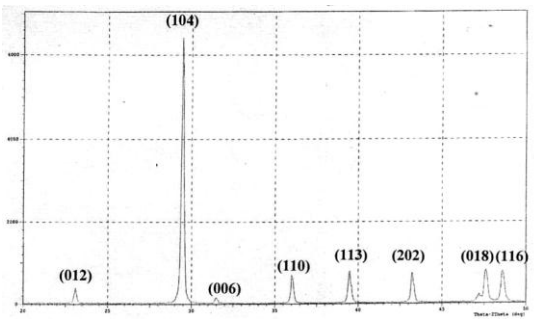

Fig.1 XRD Pattern of raw Egg- shell powder (calcite)

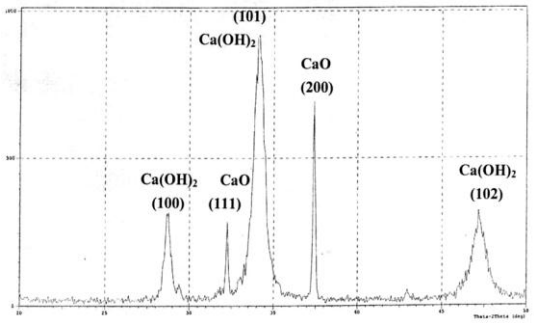

Fig.2. XRD Pattern of calcined Egg - shell powder

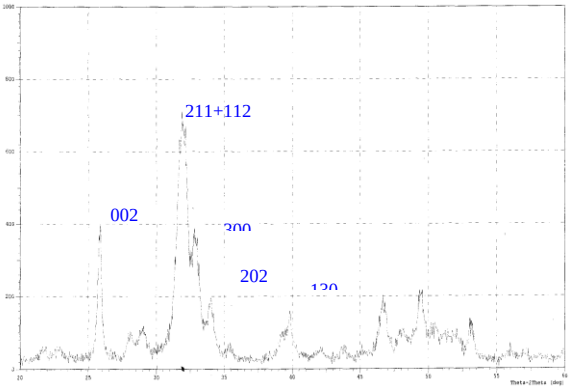

Fig.3 a. XRD Pattern of Synthesized HAP powder calcined at 400 °C

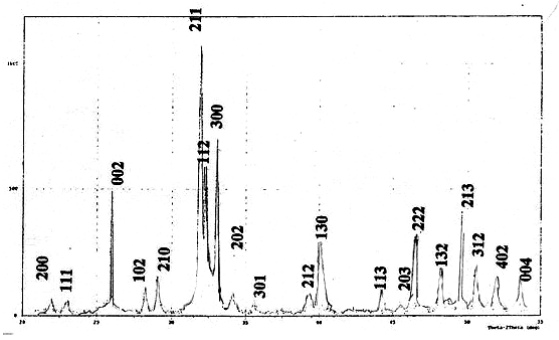

Fig.3.b XRD Pattern of Synthesized HAP powder calcined at 800 °C

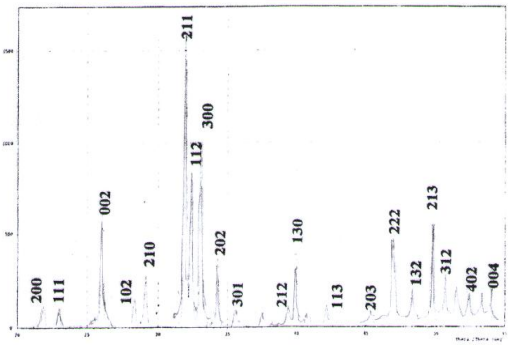

Fig.3 c. XRD Pattern of Synthesized HAP powder calcined at 900 ^{o}C

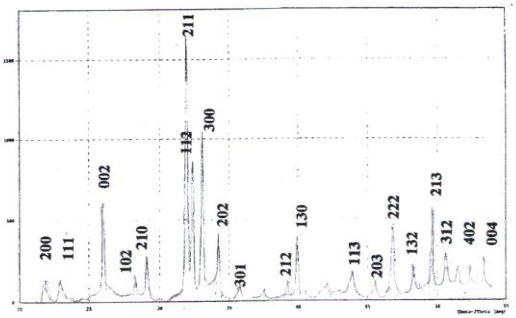

Fig.3 d. XRD Pattern of Synthesized HAP powder calcined at 1000 ^{o}C

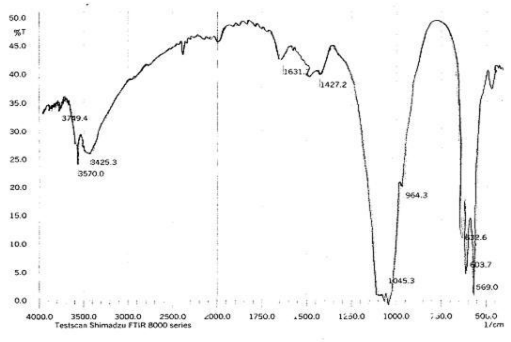

Fig.4 FT-IR spectrum of Synthesized HAP powder calcined at 1000 °C