

Fabrication And Characterization Of Hydroxyapatite Nanopowder From Geloina Coaxans

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Abstract

Fabrication and characterization of hydroxyapatite from Geloina coaxans and H_3PO_4 as precursors have been done. The main of chemical composition from Geloina coaxans shell was $CaCO_3$, this material can be used as calcium source on fabrication of hydroxyapatite. Calcium oxide was obtained by calcination $CaCO_3$ at $900^\circ C$ for 12 hour. Synthesis of HAp was done with molar ratio of precursor 1,67 and pH of solution was adjusted at 11 with different stirring times (4 and 6) hours. Hydroxyapatite synthesized was characterized using XRD instrument, and the result proved that HAp nanopowder can be obtained successfully with stirring time for 4 hour with specific peak at $2\theta = 31.7$. Using Scherrer equation, particle size of HAp powder was 26.42 nm. FTIR analysis was also done to determine functional group of HAp. The FTIR spectra of HAp powder obtained show there were characteristics band exhibited in sample spectra. Thermal analysis and particle size analysis were also investigated with TG-DTA and PSA instruments respectively. Analysis morphology by SEM revealed nearly uniform spherical morphology

Key Words: *Geloina coaxans shell, H_3PO_4 , HAp*

1. INTRODUCTION

Calcium phosphate ceramic or hydroxyapatite (HA) is a potensial material, because its have many applications. The structure and morphology are crucial parameters on HAp synthesized, such as HAp with porous structure can be employed for tissue infiltration that improves bone attachment with the same characteristics as implanted tissues [1,2]. Porous HAp has been developed and is widely used as an implant material. HAp are also used as sensor gas, catalyst etc. The biocompatibility, bioactive and non toxic are specific properties of HAp that cause this material was prepared. There are several methods have been developed on synthesis HAp material such as co-precipitation [3], sol-gel [4], microwave irradiation [5], and hydrothermal reaction [6,7].

Hydroxyapatit or $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ can be prepared by several of calcium and phosphate sources. The bovine bone [8], sheel of garden snail [9], and aboandon shell [10] have been used as calcium sources whereas H_3PO_4 and $[\text{NH}_4]_2\text{HPO}$ as phosphate sources respectively. Geloina coaxans shell was one of mollusca shell that have high carbonate composition, that can be decomposed by calcination to produce calcium oxide as precursor Ca on synthesis HAp. The usage of Geloina coaxans shell as precursor from natural sources is inexpensive and uncomplicated.

This article is focused on nanosized HAp that was synthesized by wet method. The stirring time was used as parameter reaction to identification the calcium phosphate salts obtained, because stirring time is a one of important factor on synthesis calcium phosphate salts. Geloina coaxans shell (GCS) and H_3PO_4 were used as calcium and phosphate sources respectively. Synthesis of HAp will be done with molar ratio of precursor 1,67 and pH of solution was adjusted at 11 with different stirring times (4 and 6) hours.

2. EXPERIMENT

Preparation of Geloina coaxans as precursor Ca

Geloina coaxans shell (sample) was collected and washed for removing its inner membrane. After that, sample was dried out and mashed. The particle size of sample was adjust 200 mesh. The Geloina coaxans shell was decomposed by calcination using furnace to remove organic matter and decompose calcium carbonate into calcium oxide at 900°C for 12 hours.

Synthesis of Hydroxyapatite (HAp)

Hydroxyapatite was synthesized by precipitation method with molar ratio of precursor $(\text{Ca}/\text{P})=1,67$. 5,7045 mass of CaO was diluted with 100 ml of double-distilled water. The $\text{Ca}(\text{OH})_2$ solution was vigorously stirred in 250 ml beaker glass at room temperature and 100 ml of H_3PO_4 was added drop-wise, and then stirring at 300 rpm for 4 and 6 hours. The pH of system was maintained at 11 throughout the stirring process by using 0,1 M NH_4OH solution. The solution was overnight, then a white precipitate was formed. This product was vacum dried and calcinated at 900°C for 2 hours. The synthesized powder was used for further characterization.

Characterization

The prepared HAp were characterized by X-Ray Diffractrometer (XRD), Particle Size Analyzer (PSA) Fourier Transform Infra Red (FT-IR), Scanning Electron Microscope (SEM) and Themal Gravimetry and Thermal Diffential Analysis (TG-DTA)

3. RESULTS AND DISCUSSION

The powder of HAP synthesized using precipitation method was analyzed by XRD instrument. The XRD analysis was done to determinate mineral phase and crystallinity of prepared HAp. The result of hydroxyapatite synthesized are shown in **Figure 1**

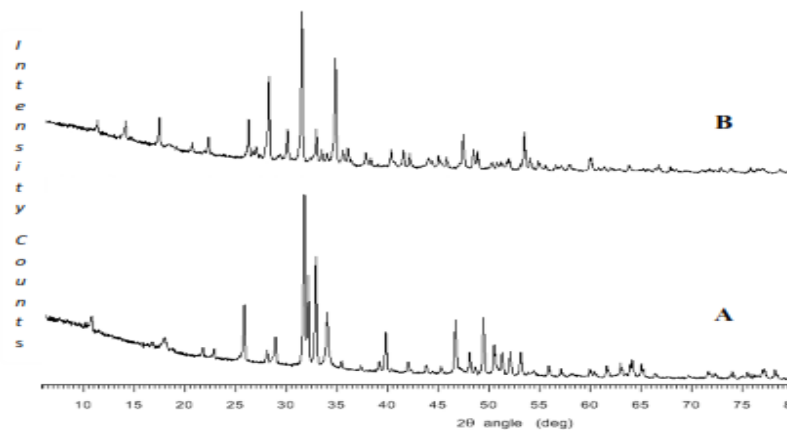
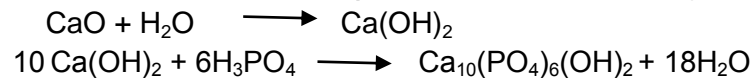


Figure 1. XRD Patterns of HAp powder synthesized at different stirring time

(A= 4 hour dan B= 6 hour)



A specific peak of hydroxyapatite or HAp was observed in the sample. In the **Figure 1.a** the highest intensity appeared at $2\theta = 31.7435$ which indicate a specific peak of HAp; and others peak of HAp at $2\theta = 32.9368$; 49.4730 ; 34.0540 ; 39.8334 and 50.5249 . The sample synthesized also have other peak at $2\theta = 25.8313$, that show β -TCP mineral, it well resembles with the standard JCPDS file No 09-0432 and No 09-0169 respectively. Whereas the stirring time for 6 hours (**Fig 1.b**) showed other of calcium phosphate salts such β -TCP appeared at $2\theta = 31.0725$; 47.0002 and 53.0397 . The other mineral α -TCP also appeared at $2\theta = 34.3603$; 27.7915 ; 25.7816 and 29.6260 it compared with the standard JCPDS file No 09-0169 and No 29-0359. However, the stirring time influenced crystallinity and purity of HAp obtained and types of calcium salts produced. The HAp obtained at stirring time for 4 hour have crystallinity and purity about 86%, this result indicate that a better crystallization has been formed.

The crystallite size of HAp nanoparticles can be determined using the Scherrer equation

$$I_c = \frac{K\lambda}{\beta \cos \theta}$$

Where l_c is the average of crystallite size, β = full width of the peak at half of the maximum intensity, FWHM (in radians), λ = the wave length of X-Ray radiation (0,154060 nm) and K = contant related to crystallite shape

Crystal size of HAp synthesized for 4 hours examined with Scherrer equation above, and crystal size obtained of HAp was 26.419 nm. HAp was also produced using H_3PO_4 as phosphate source and crystal size of HAp obtained about 8.47-24.47 nm [11], whereas using $(NH_4)_2 HPO_4$ and calcium nitrate as precursors obtained crystal size of HAp were 11, 49 and 249 nm for calcination time at 450° , $750^\circ C$ and $900^\circ C$ respectively.[12] Particle size of HAp synthesized was also analyzed with particle size analyzer by malvern instrument. The result on **Figure 2** revealed that particle size of HAp was 1456 nm. The previous research, with calcination temperature at $600^\circ C$, the crystal and particle size were 43 and 1510 nm and calcination temperature at $850^\circ C$ crystal and particle size were 57 and 928 nm respectively.[11] The **Figure 3** show the TGA combined with DTA for HAp syntesized. The powder synthesized has a peak at $400-500^\circ C$ show a endothermic process of hydroxyapatite

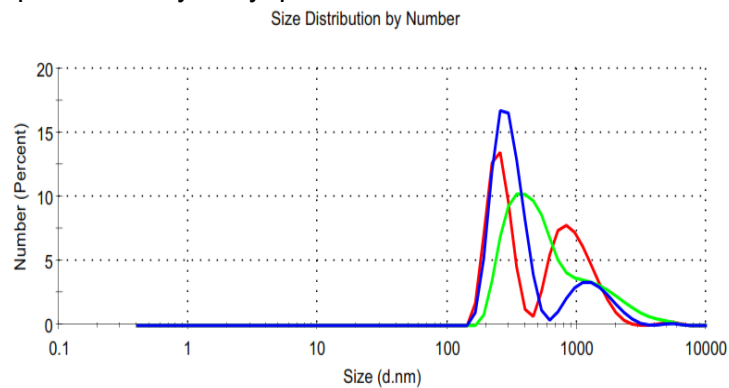


Figure 2. Particle Size of HAp

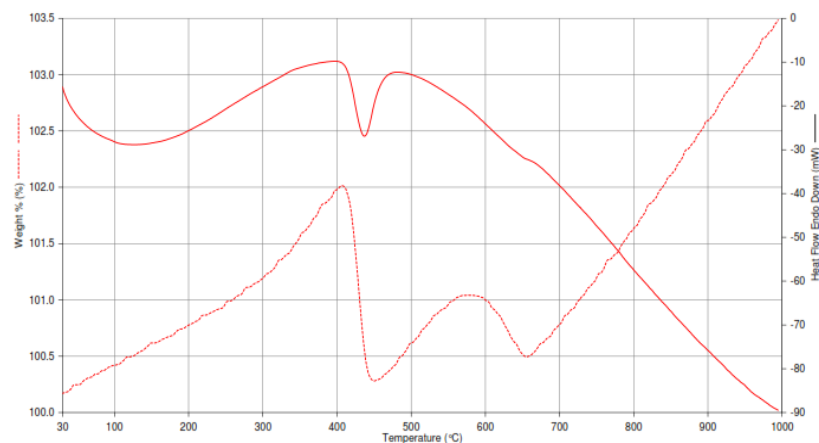


Figure 3. Pattern of TG-DTA of hydroxyapatite

The functional group analysis of prepared HAp was investigated using Fourier Transform Infra Red (FT-IR) instrument. The FT-IR spectra of obtained HAp show specific characteristic band exhibited in sample spectra.

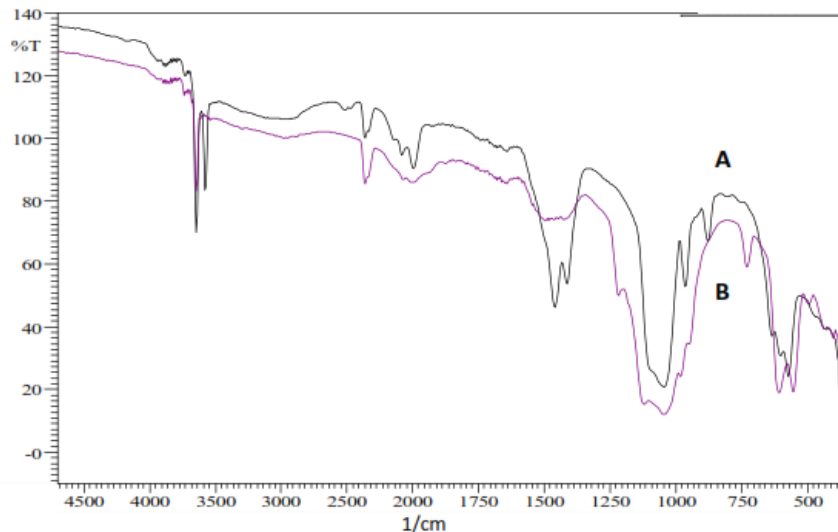


Figure 4. FT-IR Spectra of stirring time for 4 and 6 hours at 900°C
[[A= 4 hour; B= 6 hour]

FTIR Analysis was conducted (**Fig-4a**), the band at 3572 cm^{-1} represent hydroxyl group (OH) that assigned to the stretching vibration of OH, which was clearly indicated that HAp particle absorbed water molecule. The band at 3570 cm^{-1} and 630 cm^{-1} were the stretching and liberating of O-H respectively. [11] The characteristic vibration of PO_4^{3-} groups were detected 569 cm^{-1} , $600,6\text{ cm}^{-1}$, 961 cm^{-1} and $1042,04\text{ cm}^{-1}$. The band at 950-1110 indicated stretching $\nu(\text{P-O})$ for phosphate whereas 374-603 represent stretching of phosphate.[13] Additionally, vibration peak at 1410 cm^{-1} and 1458 cm^{-1} represent of carbonate (CO_3^{2-}) that was caused by CO_2 adsorbed on synthesis HAp. Whereas (**Fig-4b**), The band appeared at 3640, 1445, 1110, 1042, 946, 601 dan 551 cm^{-1} .

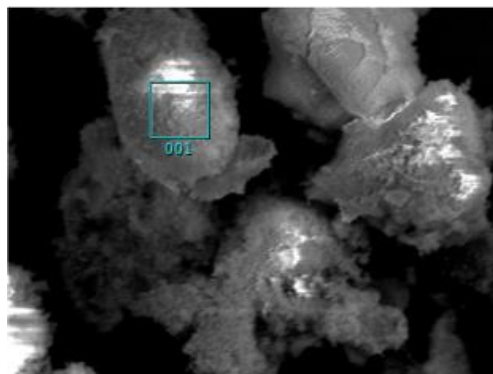


Figure 5. SEM of HAp

The micrograph showed nearly uniform spherical cotton of HAp. Morphology of HAp synthesized using abalone shells as calcium source revealed nanorod of HAp.[10] whereas with different calcination temperature at 750, 850 and 900°C also produced uniform structure and explained that morphology of HAp was also influenced by calcination temperature.[11]

4. CONCLUSIONS

In this study, the usage of *Geloina coaxans* shell as calcium source on fabrication hydroxyapatite has been done. The effect of stirring time on synthesis HAp was done to examine phase mineral and crystallinity of prepared hydroxyapatite. XRD analysis revealed nanopowder of hydroxyapatite can be obtained at stirring time 4 hour with pH of solution was maintained at 11. Analysis by FT-IR technique showed that hydroxyapatite synthesized have a specific characteristic band on sample spectra. Identification of morphology obtained HAp using scanning electron microscopy show spherical cotton morphology.

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