THE EFFECT OF pH ON SYNTHESIS OF HYDROXYAPATITE FROM GELOINA COAXANS SHELL

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ABSTRACT

The effect of pH on synthesis of hydroxyapatite from Geloina coaxans shell has been done by precipitation method. Geloina coaxans shells and several phosphate sources (NH₄)₂ HPO₄ and H₃PO₄ were used as precursors on synthesis of HAp. Synthesis of HAp was done with molar ratio of precursors 1,67 and pH of solution were varied at 10, 12, 13, and 14. The result proved that nano-HAp can be obtained successfully and shown that pH value was a significant parameter variable on synthesis HAp that can influence crystalinity and purity of HAp. Using Schererr equation, particle size of HAp powder of (NH₄)₂HPO₄ was 26.69 while H₃PO₄ was 40 nm respectively.

Keywords: Geloina coaxans, HAp, (NH₄)₂HPO₄ and H₃PO₄

I. INTRODUCTION

Hydroxyapatite Ca₁₀(PO₄)₆(OH)₂ or HAp is the main mineral constituent of teeth and vertebrate bones. It has been well proved and documented that HAp nanoparticles can significantly increase the biocompatibility and bioactivity of biomaterials. There are many type of Ca/P salts, such as single, polycrystaline and composite. The phases used depend on the properties and function required. Several factors such as parameter reaction, source or type of precursors and method of preparation have been developed to synthesis HAp.

HAp have many applications that caused many reasons to synthesis this material. By synthesis of HAp the mechanical properties, particle or crystal size and morphology of HAp can be controlled. HAp can be used as a aborbent of dyes [1] and heavy metals [2], catalyst for chemical reactions such as the Michael-type addition and methane oxidation [3], [4] and biosensor [5]. The several research also has been done to fabrication of HAp such as hydrothermal [6], microwave [7] and precipitation [8].
Source and type of precursors of Ca/P also influence HAp synthesized. Geloina coxans shell was a potential material that can be used as calcium (Ca) source because have high carbonate composition. This carbonate can be decomposed by calcination to produce calcium oxide as precursor Ca on synthesis HAp. The usage of Geloina coxans shell as precursor from natural sources is inexpensive and uncomplicated. The previous research revealed HAp can be produced by using Mussel shell [7] and Oyster shell [8]. This article is focused to learn the effect of pH on synthesis of hydroxyapatite from Geloina coxans shell that was synthesized by wet method. pH is important factor that can influence HAp synthesized. This parameter was done to analyze the influence condition of solution on synthesis HAp. The analysis of product was done by XRD instrument to identification the calcium phosphate salts obtained. Synthesis of HAp will be done with molar ratio of precursor 1,67 and pH of solution was varied at 10,12,13 and 14.

II. EXPERIMENTAL SECTION

2.1 Materials

The materials, which were used in this research, Geloina coxans shell (Rokan Hilir-Riau Province), diammonium hydrophosphate (NH₄)₂ HPO₄ (merck), H₃PO₄(merck), NH₄OH 0,1 M and aquabidest.

2.2 Instrumentation

The equipments which were used: glass equipments, blender (Philips), furnace (vulcan™ seri A 130), digital pH, oven (Gallen kemp), hotplate (Rexim RSH-1DR as One), analytical balance (Mettler AE 200) sieve-200 mesh, crucible, (W.S Tyler Incorporated U.S.A), vacuum, whatman 42, aluminum foil, X-Ray Fluorecence (S2 Ranger Burker), X-Ray Diffraction (Gbc Emm).

2.3 PROCEDURE

Preparation of Geloina coxans as precursor Ca

Geloina coxans 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 adjusted 200 mesh. The powder obtained was analyzed by X-Ray Fluorescence technique to determinate the chemical composition of Geloina coxans shell. The Geloina coxans shell was decomposed by calcination using furnace to remove organic composition 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 (Ca/P)=1,67. CaO was diluted with aquabidest. The Ca(OH)₂ solution was vigorously stirred in 250 ml beaker glass at room temperature and 100 ml of diammonium hydrogenphosphate was added drop-wise, and then stirring at 300 rpm. The pH of system was varied at 10,12, 13 and 14 throughout the stirring process by using 0,1 M NH₄OH solution. The solution was overnight, then a white precipitate was formed. This product was vacuum dried and calcinated at 900°C for 2 hours. The synthesized powder was used for further characterization.

2.4 Characterization

The prepared HAp were characterized by X-Ray Fluoresence and X-Ray Diffractrometer (XRD) techniques.

III. RESULTS AND DISCUSSION

3.1. The chemical composition analysis of Geloina coxans.

The chemical composition of Geloina coxans was analyzed by X-Ray Fluoresence (XRF) technique. The obtained results show that the main composition of Geloina coxans was CaO and several oxides such as Na₂O; MgO; SiO₂; Al₂O₃; SO₃ and K₂O of trivial amount. Chemical composition of Geloina coxans can be seen on Table 1 below.
Table 1 The chemical composition analysis of Geloina coaxans by XRF technique

<table>
<thead>
<tr>
<th>Chemical composition</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>86.01</td>
</tr>
<tr>
<td>Na₂O</td>
<td>8.19</td>
</tr>
<tr>
<td>MgO</td>
<td>1.73</td>
</tr>
<tr>
<td>SiO₂</td>
<td>0.73</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.60</td>
</tr>
<tr>
<td>SO₃</td>
<td>0.58</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.57</td>
</tr>
</tbody>
</table>

3.2. The phase minerals analysis of Geloina coaxans calcinated at 900°C for 12 hours.

Calcination were done to learn the decomposition calcium carbonate to calcium oxides. Analysis was used by X-Ray Diffraction (XRD) to determine the minerals phase and crystalinity of Geloina coaxans after calcination at 900°C for 12 hours. In Figure 1, the result of phase mineral analysis is shown.

3.3. Analysis of HAp synthesized by X-Ray Diffraction

The powder of HAp synthesized using precipitation method was analyzed by XRD instrument. XRD analysis was done to determinate mineral phase and crystalinity of prepared HAp nano-crystalline. In Figure 2 and Figure 3, the result of hydroxyapatite is shown.
Figure 2 XRD Patterns of HAp powder synthesized at different pH (A=10; B=12; C=13; dan D=14) using (NH₄)₂HPO₄ as precursor

Figure 3 XRD Patterns of HAp powder synthesized at different pH at (A=10; B=12; C=13; dan D=14) using H₃PO₄ as precursor

CaO + H₂O → Ca(OH)₂ [1]
10 Ca(OH)₂ + 6(NH₄)₂HPO₄ → Ca₁₀(PO₄)₆(OH)₂ + 12NH₃ + 18H₂O [2]

Analysis was done by X-Ray Diffraction (XRD) to determine the minerals phase and crystallinity of HAp at different pH. The several parameters have been done to learn crystallinity and purity of HAp obtained. pH is important factor that can influence HAp synthesized. This parameter was done to analyze the influence condition of solution on synthesis HAp.

A specific peak of HAp or hydroxyapatite was observed in the synthesized sample. In the Figure 2, the specific peak of HAp appeared at several pH but pH was 13 show HAp synthesized has good crystallinity than others, this result indicate that a better crystallization has been formed. The peaks of HAp can be seen at θ=31,7° and θ=25,9° (JCPDS No 09-0432. However pH can influence crystallinity and purity of HAp obtained and types of calcium salts produced. The crystallite size of HAp nanoparticles was determined using the Scherrer equation.
Where $D$ is the average of crystallite size, $\beta$ the corrected full width of the peak at half of the maximum intensity, FWHM (in radians), $\lambda$ = the wave length of X-Ray radiation (0.154060 nm) and $K = $ constant related to crystallite shape.

Crystal size of HAp synthesized at pH was 14 examined with Scherrer equation above, and obtained crystal size of HAp was 26,69 nm while Guo et al (2013) using (NH$_4$)$_2$ HPO and calcium nitrate produced particle size of HAp were 11, 49 and 249 nm for calcination time 450$^\circ$, 750$^\circ$ and 900$^\circ$C respectively. Whereas in Figure 3 by using H$_3$PO$_4$ as precursor pH was 10 showed the better crystallinity than other pH, and crystal size of HAp synthesized was 40 nm. the peaks of Hap appeared at $2\theta=31.7^\circ$ and $2\theta=46.8^\circ$. Abidi et al (2013) using H$_3$PO$_4$ produced crystal size of HAp about 8.47-24.47 nm.

The previous research explained that variation of pH at 5,6,9, and 11 proved that at pH 11 was stable condition to synthesis Hap if compared with other pH [10] while other research learned that suitable pH was a crucial factor on synthesis HAp [11], also revealed that nano-crystalline of HAp can be produced if pH of solution was more than 9, and pH also be able to influence the morphology of Hap synthesized [12].

**CONCLUSION**

The effect of pH on synthesis of hydroxyapatite from Geloina coaxans shell has been done by precipitation method. Geloina coaxans shells and several phosphate sources (NH$_4$)$_2$ HPO$_4$ and H$_3$PO$_4$ were used as precursors on synthesis of HAp. The result proved that nano-HAp can be obtained successfully and shown that pH value was a significant parameter variable on synthesis HAp that can influence crystalinity and purity of HAp. Using Scherrer equation, particle size of HAp powder of (NH$_4$)$_2$HPO$_4$ was 26,69 while H$_3$PO$_4$ was 40 nm respectively.

**REFERENCES**


