

## EFFECT OF TEMPERATURE ON SYNTHESIS OF HYDROXYAPATITE FROM LIMESTONE

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### ABSTRACT

Hydroxyapatite (HAP) powder has been synthesized from the limestone by precipitation method and effect temperature mixing when added di-ammonium hydrogen phosphate solution. As precursor, used calcium nitrate tetrahydrate ( $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ) and di-ammonium hydrogen phosphate ( $(\text{NH}_4)_2\text{HPO}_4$ ). Diammonium hydrogen phosphate [ $(\text{NH}_4)_2\text{HPO}_4$ ] were used as precursors and ammonia was used as the agent for pH adjustment. The optimum temperature was found to be  $90^\circ\text{C}$ . Below this temperature, the hydroxyapatite powder formed tricalcium phosphate. The crystalline size of hydroxyapatite powder found to be in range of 22,5-68,5 nm. The synthesized samples was characterized by Fourier Transform Infra Red (FTIR), X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS).

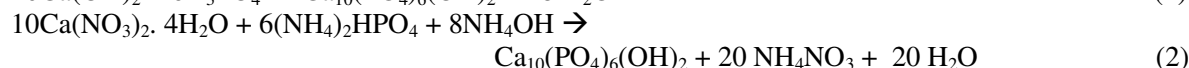
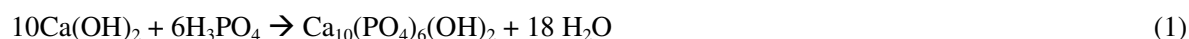
**Keywords:** Hydroxyapatite, Temperature, Precipitation method, Limestone

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### INTRODUCTION

Nanoparticle be interesting study to be discussed in the field materials. On the nanometer scale ( $1 \text{ nm} = 10^9 \text{ m}$ ) has properties that are not found in large particle size, thus providing more opportunities useful in the application. The use of nanomaterials has many advantages and provide added value to a material to achieve technological advancement that is efficient, economical and environmentally friendly<sup>1</sup>.

Hydroxyapatite is a highly developed material compound usefulness at this time. Hydroxyapatite used in various fields such as medical, biotechnology, as well as in the field of wastewater treatment. Utilization in the field of environmental chemistry one of which is the ability of hydroxyapatite on the adsorption of heavy metals. Hydroxyapatite able to adsorb heavy metals such as Ni toxic contained in the waste<sup>2</sup>. The usefulness of hydroxyapatite also was developed in the biomedical field as antibacterial, because hydroxyapatite [ $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ] is the main mineral elements in human bones<sup>3</sup>. For the manufacture of hydroxyapatite, required a high source of calcium as a precursor, such as calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ) or calcium nitrate tetrahydrate<sup>4</sup> ( $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ). Sources of calcium can also be obtained from animal bones<sup>5</sup>, snail shell<sup>6</sup>, and limestone<sup>7</sup>. As for the source of phosphate may be obtained from orthophosphoric acid<sup>8</sup> ( $\text{H}_3\text{PO}_4$ ) or diammonium phosphate<sup>9</sup> ( $(\text{NH}_4)_2\text{HPO}_4$ ).



Techniques are often known and very popular used in the synthesis of HAP is a precipitation technique. This technique is also called the wet precipitation or precipitation aquaous or chemical precipitation. HAP can be produced in relatively large quantities and the absence of the use of organic solvents at a reasonable cost, so this technique into something that is widely in demand<sup>10</sup>.

In this study, limestone used to synthesize hydroxyapatite (HAP) with precipitation method. Mixing temperature variations will be observed to determine the best temperature conditions that can form hydroxyapatite nanoparticles. The results of the synthesis of hydroxyapatite characterized using Fourier

## EXPERIMENTAL

In the synthesis of hydroxyapatite by precipitation method, limestone is calcinated for 5 hours at 900°C, to change the phase of calcium carbonate ( $\text{CaCO}_3$ ) into calcium oxide ( $\text{CaO}$ ). Then 5.6 g of  $\text{CaO}$  dissolved in 100 ml of 2 M  $\text{HNO}_3$ . The filtrate is taken, then added a solution of 100 ml 0.6 M ( $(\text{NH}_4)_2\text{HPO}_4$ ) slowly while stirring for 1 hour at 60, 70, 80 and 90°C at pH, 11. The addition of ammonium hydroxide ( $\text{NH}_4\text{OH}$ ) to pH adjustment. The solution formed was precipitated for 1 day or  $\pm 15$  hours until a precipitate is formed. The precipitate that formed was filtered and dried at a temperature of  $\pm 110^\circ\text{C}$  aiming to eliminate solvents that still contained. The precipitate which has been dried and then ground into powder, then calcinated at 800°C for 2 hours. Nanopowder formed then characterized.

Infrared spectra of HAP (Fig.-1) informed the hydroxyl (OH<sup>-</sup>) functional group by absorption band at 60, 70, 80 and 90°C, respectively at around 3429, 3417, 3571 and 3571 cm<sup>-1</sup>. The absorption bands of (PO<sub>4</sub><sup>3-</sup>) functional groups presence at around 1046, 943, 1043, and 1107 cm<sup>-1</sup>.<sup>11</sup>

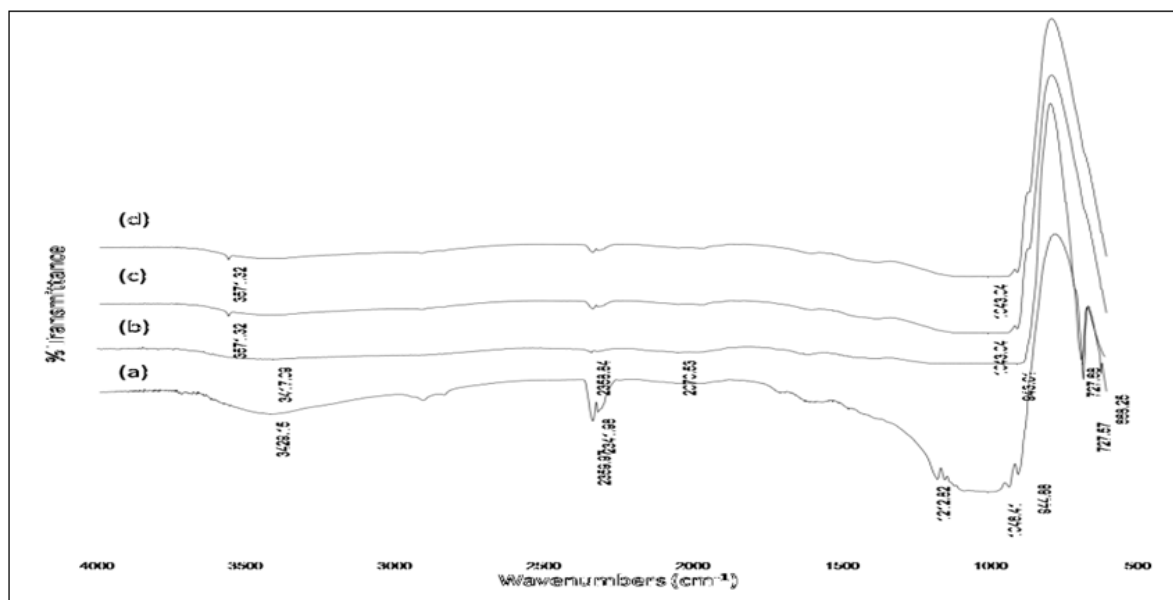


Figure- 2 shows the X-ray diffraction pattern of hydroxyapatite with mixing temperature variations during the mixing of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  with  $(\text{NH}_4)_2\text{HPO}_4$ . From Fig.-2 it can be seen that the spectrum on the other

mixing temperatures of 60, 70, and 80 has a shape that is almost similar, where many established Tri Calcium phosphate (TCP). While at 90°C has many forms of hydroxyapatite. It can be seen from the results of XRD suitability standard temperature 90°C with ICSD 16742 (Fig.-3). The presence of noise contained in the spectrum indicates the presence of amorphous hydroxyapatite, while the sharp spectrum indicates the formation of hydroxyapatite crystals. From the XRD data can also be seen the size of the crystals formed using the Scherrer equation, where a large crystal size is indicated by a sharp peak with a narrow peak width, while the small crystal size indicated by the peak width. By entering the value of FWHM (Full Width at Maximum) Scherrer equation to the known size of hydroxyapatite crystals<sup>12,13</sup>.

$$t = \frac{(0,9)\lambda}{\beta \cos \theta} \quad (3)$$

Where  $t$  is the particle size,  $\lambda$  is the wavelength used,  $B$  is the value of FWHM and  $\theta$  is the Bragg diffraction angle. As for determining the specific surface area used the following formula:

$$S = \frac{(6 \times 10^3)}{d\rho} \quad (4)$$

Where  $S$  is the specific surface area ( $\text{m}^2/\text{g}$ ),  $t$  is the size of the crystal and  $d$  is the theoretical density of hydroxyapatite ( $3,16 \text{ g/cm}^3$ )<sup>12</sup>. This equation can be determined based on the crystal size and specific surface area is formed at the mixing temperature variations, can be seen in the following Table-1.

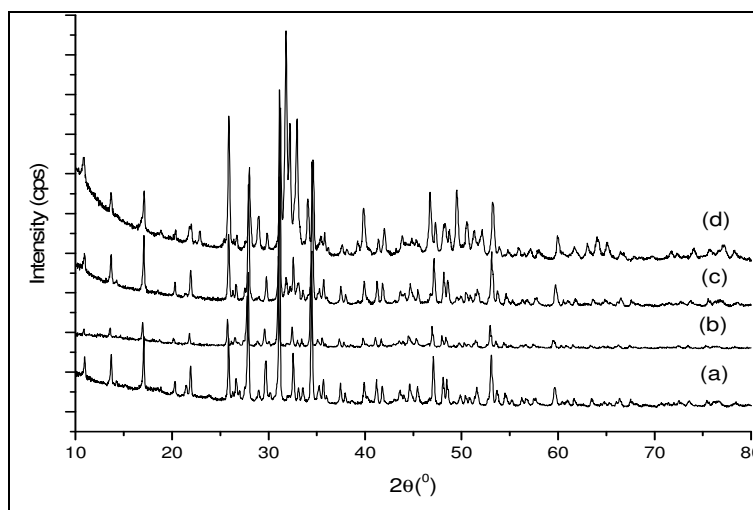


Fig.-2: X-ray diffraction patterns of hydroxyapatite synthesized at (a) 60, (b) 70, (c) 80, and (d) 90°C

### Analysis of SEM

Fig.-4 shows the SEM images of the synthesis of hydroxyapatite in the form of powder with a treatment at a temperature of 90°C while mixing. Magnification showed formed spherical of nano-sized grains.

Table-1: Crystal size and Specific Surface Area Based on results of Mixing Temperature Variations

| Temperature (°C) | Crystal size (nm) | Specific Surface Area ( $\text{m}^2/\text{g}$ ) |
|------------------|-------------------|-------------------------------------------------|
| 60               | 23.6 – 112        | 16.9 – 80                                       |
| 70               | 10 – 115.6        | 16 – 183.6                                      |
| 80               | 16.8 – 111.6      | 17 – 113                                        |
| 90               | 22.5 – 68.5       | 27.7 – 84.3                                     |

### Analysis of EDS

EDS analysis results indicate that the ratio of Ca/P on hydroxyapatite powder at a temperature of 90°C which is more than 1.67. It indicates the presence of other compounds such as CaO contained in the hydroxyapatite powder has been synthesized<sup>8</sup>.

### CONCLUSION

The results of this study presents an alternative method in the synthesis of hydroxyapatite through precipitation technique can be synthesized from limestone. By using a temperature of 90°C on mixing calcium phosphate, the sizes of the nano-sized crystals formed and provide a large surface area. SEM results showed spherical formed nano-sized grains. The ratio of the results of EDS analysis is greater than 1.67 indicates the presence of other compounds are formed.

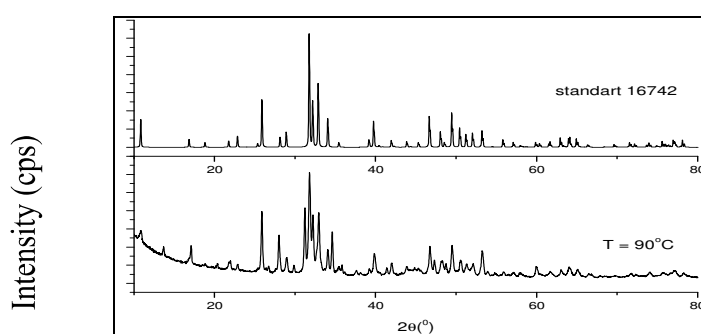


Fig.-3: X-ray diffraction patterns of hydroxyapatite synthesized at 90°C with standart 16742

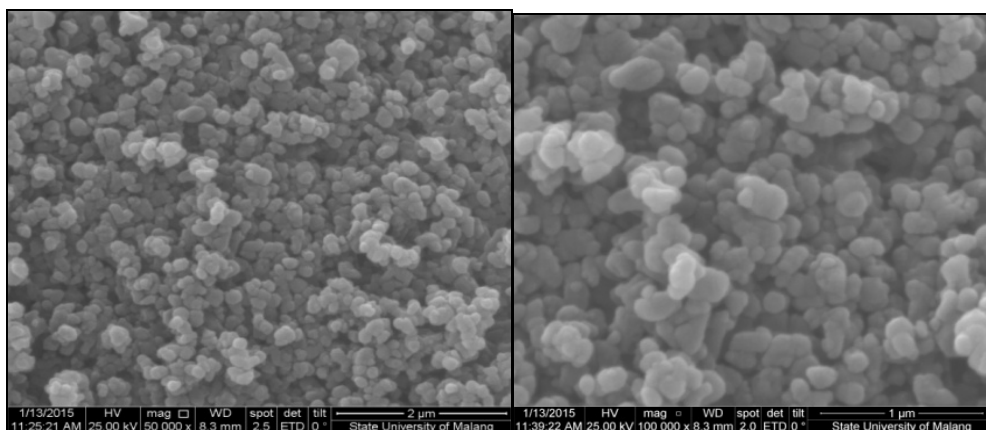


Fig.-4: SEM images of hydroxyapatite powders mixing temperature at 90°C (a) 50.000X, and (b) 100.000X

### ACKNOWLEDGEMENTS

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