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## Effect of pH Variation on Hydroxyapatite Synthesis through Sol-Gel method.

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### ABSTRACT

Nanoparticles of hydroxyapatite (HA) can be synthesized by low temperature through the sol-gel method. Limestone is used as a source of calcium for the formation of hydroxyapatite and diammonium hydrogen phosphate ((NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>) as a source of phosphate. Hydroxyapatite formation is done by variation of pH is 9, 10 and 11 were performed at 70°C. Products hydroxyapatite characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM) to determine the functional group, the type and size of the crystals and morphology . From the XRD data it can be seen that all products in each variation of pH is hydroxyapatite. In pH 9, size of the resulting crystals is smaller than pH 10 and 11. From the results of FT-IR, there is an OH group and PO<sub>4</sub> groups are detected as a function of the product group hydroxyapatite produced.

**Keywords:** hydroxyapatite, pH, sol-gel, limestone.

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## INTRODUCTION

Hydroxyapatite is known as a compound having good for body bioactivity and biocompatible properties. Hydroxyapatite can be used as a stationary phase in chromatography and also adsorbents for heavy metals. In the medical field, this material can be implanted into living systems and tissues as a function of damaged body tissues because it is non-toxic and has no side effects on the body [1].

Hydroxyapatite with molecular formula  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  contains a compound of calcium and phosphate. The comparison ratio of the Ca/P is 1.67 is one of the popular bioceramics materials because it resembles with inorganic chemistry composition in the human bones and teeth. Approximately 65% of human bone mineral fraction is composed of hydroxyapatite. Morphology, stoichiometric, crystallinity and crystal size distribution of hydroxyapatite is great for producing material for biomedical application, thus making many researches on hydroxyapatite today [2, 3].

Hydroxyapatite can be synthesized by various methods including hydrothermal [4], precipitation [5], microwave and ultrasonic irradiation [6]. But all of these methods have disadvantages that the low mechanical strength when coating, high temperature formation, less homogeneous microstructure and low crystallinity. [7] To overcome this problem, synthesis of hydroxyapatite can be done by sol-gel method. Sol-gel method has the advantage which the product will have a better homogeneous, low formation temperature and purity and high crystallinity [8-10].

In this study, the synthesis of hydroxyapatite carried out by sol-gel method with various pH of the formation of hydroxyapatite by added ammonia ( $\text{NH}_3$ ), limestone is used as raw material for a source of calcium because the largest component contained in limestone is calcium carbonate which is generally joined to form calcium carbonate ( $\text{CaCO}_3$ ) and diammonium hydrogen phosphate ( $(\text{NH}_4)_2\text{HPO}_4$ ) for a source of phosphate [11].

## MATERIALS AND METHODS

### Chemicals and Apparatus

Used reagent grade chemicals were limestone, nitric acid ( $\text{HNO}_3$ ), Ammonia ( $\text{NH}_3$ ), diammonium hydrogen phosphate ( $(\text{NH}_4)_2\text{HPO}_4$ ). Apparatus used in this study were thermometers, glassware, magnetic stirrer and hot plate, analytical balance, Whatman (42) filter paper, and pH meter.

### Sol-Gel Method

Sol-gel method is used to synthesize hydroxyapatite from limestone.

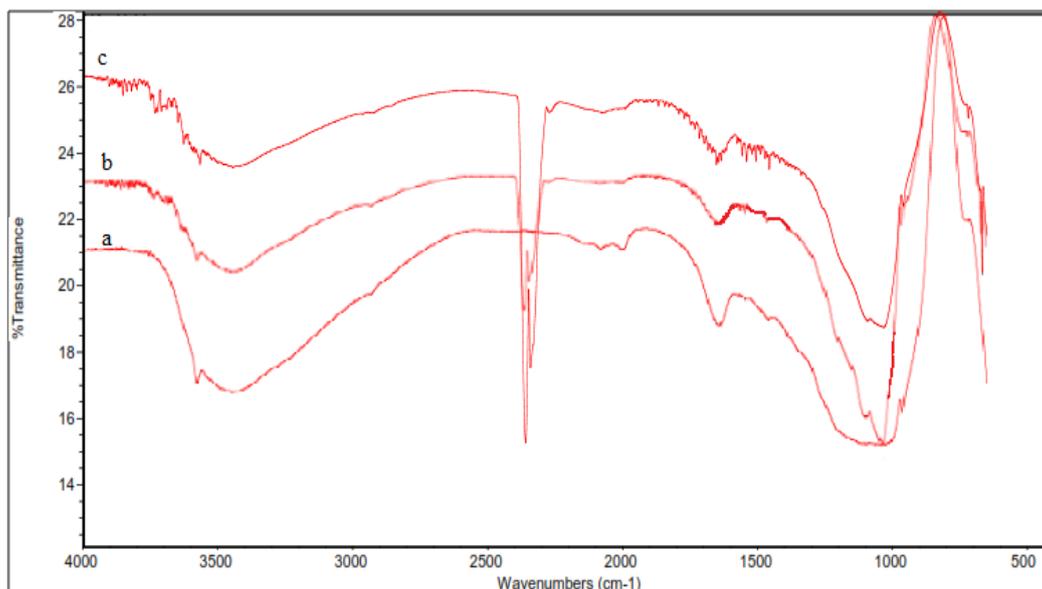
### Experimental

To synthesize hydroxyapatite powders via sol-gel processing, 5.6 grams of CaO were added to 100 ml of  $\text{HNO}_3$  1 M and stirred (600 rpm, 1 hour,  $65^\circ\text{C}$ ). Then, they were filtered and resulted  $\text{Ca}(\text{NO}_3)_2$ . Stoichiometric amounts of calcium nitrate ( $\text{Ca}(\text{NO}_3)_2$ ) and diammonium hydrogen phosphate were dissolved in two separate aqueous solutions at room temperature. The pH of mixture was adjusted to 9, 10 and 11 in ammonia solution then stirred with temperature  $70^\circ\text{C}$  for 5 hours. The formed sol was aging for 1 day to obtain a gel. Then filtered and dried at  $105^\circ\text{C}$  for 3 hours and calcined at  $600^\circ\text{C}$  for 5 hours. Products were characterized using XRD (Philips X'pert powder) to identify phase composition and crystallinity and SEM for surface morphology and particle size estimation and FT-IR to determine the functional groups.

## RESULTS AND DISCUSSION

### Fourier Transform Infrared Spectroscopy (FT-IR)

FT-IR analysis was conducted to determine the functional groups on produced hydroxyapatite crystals. Figure 1 shows the FT-IR spectra of hydroxyapatite at pH variation 9, 10 and 11.



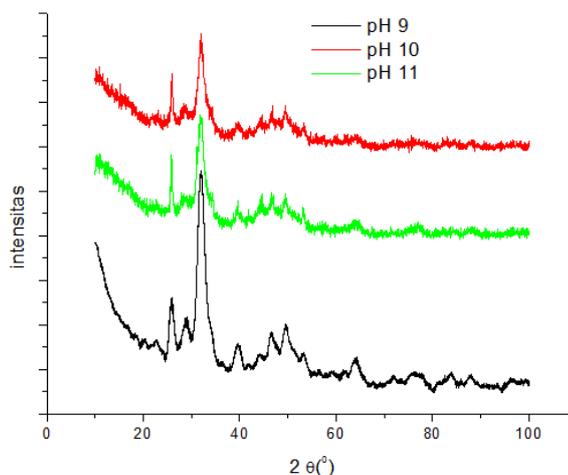
**Figure 1: FT-IR spectrum of hydroxyapatite at pH a.9, b.10 and c. 11.**

At pH 9, the absorption area  $3570.14\text{ cm}^{-1}$  and  $3441.90\text{ cm}^{-1}$  are functional groups of OH stretching, while the OH bending contained in the  $1635\text{ cm}^{-1}$  region. For  $(\text{PO}_4)^{3-}$  functional groups generated at  $1041.49\text{ cm}^{-1}$  region. Likewise, at pH 10 and 11, for the OH functional groups generated in the area stretching  $3448.12$  and  $3445.69\text{ cm}^{-1}$ .  $(-\text{PO}_4)^{3-}$  functional groups at  $1031.72$  and  $1031.33\text{ cm}^{-1}$  areas.

However, there are  $\text{CO}_2$  functional groups in  $2359.75\text{ cm}^{-1}$  and  $2659.94\text{ cm}^{-1}$  absorption area for pH 10 and 11. This is might because during the process of making KBr salt not done in a vacuum room, so that  $\text{CO}_2$  in environment around the tool participate in KBr and read by infrared absorption.

**X-ray diffraction (XRD)**

XRD analysis was conducted to determine whether the hydroxyapatite crystals that are formed were amorphous, crystalline or polycrystalline. Analysis with XRD was depicted in Figure 2 showing for hydroxyapatite synthesized at variation pH.



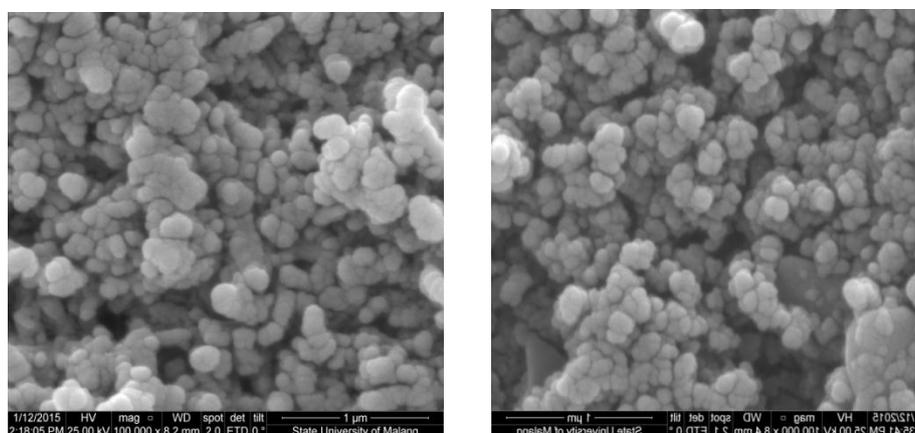
**Figure 2: X-ray pattern of hydroxyapatite were performed at pH 9, 10 and 11**

From Figure 2 it can be seen that the sharp peaks with high intensity are at angle  $2\theta = 25.8728^\circ$  and  $32.2243^\circ$  in accordance with the standards of the ICSD no.26205 at pH 9 which indicates that the compound formed is hydroxyapatite with Miller index hkl values (211) and (002), as well as at pH 10 and 11. From the XRD data shows that at pH 9, 10 and 11 formed compound is hydroxyapatite and has an amorphous phase.

From the XRD data can also be known size of the crystals that are formed by using the Scherrer equation, where a sharp peak with a narrow peak width indicates that the large crystal size, while the broad peak indicates small crystal size. By measuring the FWHM (Full Width at Half Maximum) and insert the Scherrer equation it can be seen the size of the crystals of hydroxyapatite. The size of the crystals produced at pH 9 were in the range of 8-11 nm, for pH 10 it size is 11-26 nm and at pH 11 of 10-45 nm. So it can be concluded that at pH 9 hydroxyapatite produced has smallest crystal size.

### Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) analysis is done to see the surface morphology of the sample by shooting sample surface with electrons. SEM analysis was performed on hydroxyapatite pH 9 and pH 11.



(a)

(b)

**Figure 3: SEM image of hydroxyapatite at (a) pH 9 and (b) pH 11**

From Figure 3 it can be seen that the formation of hydroxyapatite at pH 9 and pH 11 to form spherical. Hydroxyapatite formed at pH 9 and at pH 11 gives almost the same results where the particle size spread is uniform and homogeneous.

### CONCLUSIONS

The research that has been done can be concluded that the hydroxyapatite can synthesized from limestone by using sol-gel method. Synthesis of hydroxyapatite at pH 9 gives better results than the synthesis of hydroxyapatite at pH 10 and pH 11 with a smaller crystal size and distributed particles spread.

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### REFERENCES

- [1] Sooksaen P, Jumpanol N. Science J 2010; 1: 20-27.
- [2] N Montazeri, R Jahandideh, Esmaeil Biazar. Ceramic-silikaty 2011; 55: 123-126.
- [3] Ziani, Salima. Meski, Samira. Khiredine, Hafit. Int J App Ceram Technol 2014; 11: 83-91.
- [4] Gomes JFG, et al. International Journal of Chemical Reactor Engineerin, 2008.



- [5] Shirley JM Duarte, Congresso Iationo americano de orgaos artificiais e biomaterials, 2012.
- [6] Onur Rauf Bingol, Caner Durucan. American J Biomed Sci 2011;4: 50-59
- [7] SN Danilchenko, et al. J Biol Phys Chem 2009; 9 : 119-126.
- [8] Samar J Kalita, Saurabh Verma. Mater Sci Eng C 2010; 30: 295-303.
- [9] Palanivelu RA. Rubankumar. Int J ChemTech Res 2013; 5: 2965-2969.
- [10] Sari TP, Jamarun N, Syukri, Azharman Z, Asregi A. Orient J Chem 2014; 30: 1799-1804.
- [11] Jamarun N, Yuwan S, Juita R. Rahayuningsih J. J App Chem 2015; 2: 1-8.