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Synthesis of Hydroxyapatite from Halaban Limestone by Sol-Gel Method.

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ABSTRACT

A hydroxyapatit $\{Ca_{10}(PO_4)_6(OH)_2\}$ has been synthesized by sol-gel method from Halaban, Limestone ($CaCO_3$), $(NH_4)_2HPO_4$, and NH_4OH as source of calcium, phosphate, and hydroxyl, respectively. The variation of pH (7-11) in synthesize hydroxyapatite has significant effect for its morphology and percentation yield. The X-Ray Difraction (XRD) analysis showed a crystaline Hydroxyapatite formed without any impurity. The Fourier Transform Infra Red (FTIR) analysis showed spesific peaks for hydroxyapatite at wavenumber 3300 cm^{-1} for O-H streching and 900-1100 cm^{-1} for P-O streching. The Scanning Electron Microscopy (SEM) showed us that a needle hydroxyapatit has formed at pH 7, but the spherical and agglomerated hydroxyapatite formed at pH 10. The Incresing of pH increased the agglomeration of hydroxyapatite.

Keywords : Hydroxyapatite, pH, Limestone, Sol-gel.

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INTRODUCTION

Indonesia, especially West Sumatra, has some potential limestone areas with high purification of $CaCO_3$. In Halaban, Payakumbuh, West Sumatra has limestone deposite until 507.760.000 tons that it can use as source of calcium in synthesis Hydroxyapatite [1]. Hydroxyapatite is the inorganic phase that most similar to the biological apatite which is the principal constituent of bones and teeth [2].

This compound has great importance in materials chemistry because of its biocompability, bioactive, bioresorable, osteoconductivity, non-toxicity, and non inflammatory nature. [3]

Hydroxyapatite is manufactured in many forms and can be prepared as a dense ceramic[4], powder[5], ceramic coating or porous ceramic[6] as required for the particular application. Various techniques have been applied for the preparation of hydroxyapatite including hydrothermal [7,8], sol gel [9-12], coprecipitation [13], precipitation [14,15], and vapour diffusion [16].

As reported by researches, the sol gel method presents certain advantages such as homogeneous molecular mixing, low processing temperature and the ability to generate nanosized particles and nanocrystalline powders. There are report of several synthetic route within the sol gel method, studying different type of precursors, the influence of temperature and aging time, different drying and calcination temperature. All these reseaches present different Hydroxyapatite phase characteristic, according to chemical composition and process condition. [17,18].

Hydroxyapatite that synthesize used sol gel method but different pH resulted different properties of hydroxyapatite. Hydroxyapatite commonly synthesize using precipitation method in strong alkaline condition (pH 9 -11). If the pH lower than 9, Whitlockite {$Ca_3(PO_4)_2$} would be dominated. (HA strong alkali). [14]

Precursor also influence properties of hydroxyapatite [8]. Synthesis and natural precursor of calcium have different result. Synthesis precursor of calcium (ex: $Ca(NO_3)_2$) used ammonium hidrogen phospate $(NH_4)_2HPO_4$ as source of phosphate by sol gel method at pH 9, 10 and 12 resulted almost same properties for each pH (diffrent route adn cryst ha alkaline). Sol gel method used natural precursor (shell of garden snail) has better properties better than synthesis properties [8,10,12]

MATERIALS AND METHODS

Limestone from Halaban, Payakumbuh, Indonesia as source of calcium ($CaCO_3$) crushed, sieved and characterisation the composition used X-Ray Fluoresence . The limestone calcinated at 900 °C for 3 hours formed CaO and CO_2, HNO_3 pa (Merck), NH_4OH 21% (Bratachem), Diamonium Hidrogen Phosfat $(NH_4)_2HPO_4$ p.a (Merck), and Wheatman 42.

The limestone characterizated the compotition by X-Ray Fluoresence (XRF Arl 9800 xp, Simultaneous). Hydroxyapatite measured by Fourier Transform Infra Red (FTIR Perkin Elmer 1600 series) with KBr pellet, Scanning Electron Microscopy-Energy Dispersive X-Ray (SEM S-3400 N Hitachi, EDX Emax x-act720, Horiba), and X Ray Diffraction (Philips X'pert Powder).

EXPERIMENTAL

Synthesis of Hydroxyapatite from Limestone

CaO formed by calcinated Limestone ($CaCO_3$) 4,2 g (0,075 mol) dissolved with 70 mL HNO_3 2 M and strirrer at 85°C for 15 menits and filtered. The Filtrate ($Ca(NO_3)_2$) added NH_4OH until pH 7 – 11 and formed sol $Ca(OH)_2$. The sol of $Ca(OH)_2$ added $(NH_4)_2HPO_4$ 0,18 M , 250 mL (0,045 mol) dropwise and stirred 450 rpm. The white sol agged overnight and filtered. The white filtrate heated 110°C for 5 hours to remove water and calcinated at 600°C for 2 hours. Hydroxyapatite characteristed by FTIR, SEM-EDX, dan XRD.

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RESULTS AND DISCUSSION

The Composition of Halaban Limestone showed in Table 1.Based on the XRF (X-Ray Flouresence) data, the value of CaO was more than 50%. That means the limestone qualify as source of calcium [1].

The limestone calcinated to burn the organic compound and to form CaO. The reaction of CaO and HNO_3 resulted $Ca(NO_3)_2$ (clear solution) and brown precipitated at bottom beaker as known as slilica. [4] Filtration separated silica and $Ca(NO_3)_2$. The filtrate reacted with NH_4OH as source of hydroxyl ion and pH controller. This reaction formed white solution of $Ca(OH)_2$. The complete reaction of synthesize hydroxyapatite is :

1. $CaCO_3 \xrightarrow{T = 900°C\ t = 3\ hours} CaO + CO_2$...
2. $CaO + 2\ HNO \longrightarrow Ca(NO_3)_2 + H_2O$
3. $Ca(NO_3)_2 + 2\ NH_4OH \rightleftharpoons$ ($_2$ + $2\ NH_4NO_3$
4. $10\ Ca(OH)_2 + 6\ (NH_4)_2HPO_4 \longrightarrow Ca_{10}(PO_4)_6(OH)_2 + 6\ H_2O + 12\ NH_4OH$ +

The Effect of pH to percent of Hydroxyapatite yield was showed inTable 2. The higher of hydroxyapatite yield was at pH 7 and 8, and at pH 9 up to 11, the percent of hydroxyapatite yield decreased. It caused the isoelectric point of hydroxyapatite was between pH 7-8 (7,3 – 7,5) [18]. Isoelectric point is the pH which a particular molecul has no net electrical charge and the precipitation will be maximum. The incerasing of pH do not increase the percent of hydroxyapatite yield.[14,16,18]

X-Ray Difraction Analysis showed in Fig.1. Hydroxyapatite based on ICDD (Intenational has spesific peak at 2θ = 25,9 (002), 31,8 (211), 34,0 (202) ; 39,8 (310) ; dan 49,5 (213). The difractogram showed that pure hydroxyapatited formed at pH 7 – 11 without any impurities. The impurities of hydroxyapatite such as $Ca_3(PO_4)_2$ not detected because there was no spesific peak at 2θ = 25,80° ; 27,8° ; 31,0° ; dan 34,0°. Another impuruties, CaO not detected at spesific peak, 2θ = 37,5°. The another impurities also not detected such as $CaHPO_4$, $CaHPO_4.2H_2O$ [3,5,6]

Fourier Transfor Infra Red Analysis showed in Fig.2. The spectra of hydroxyapatite at every pH was very similar. Based on FTIR spectrum of hydroxyapatit at pH 7 up to 11, at least 3 peaks identified as the spesific peak of hydroxyapatite. The peaks at wavenumber 3300 – 3500 cm^{-1} , 900 – 1100 cm^{-1}, and 1600 cm^{-1}.

The phosphate group $(PO_4)^{3-}$, exhibit a strong, complex band in the range corresponding to the asymetrical streching vibration of P-O with a shoulder at 1085 cm^{-1} and a medium intensity band at 960 cm^{-1} with a shoulder (945 cm^{-1}) due to symetric streching vibration. The asymetrical bending vibration is characterized by bands located at 560 – 610 cm^{-1}.[5]

Table 1;The Composition of Halaban Limestone

Compound	% Composition
SiO_2	0,68
Al_2O_3	0,07
Fe_2O_3	0,06
CaO	52,23
MgO	0,59
LOI*	41,7

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Table 2; The Effect of pH for % yield of Hydroxyapatite

pH	Mass of HA	% Yield
7	6,061 gram	80,78
8	5,878 gram	78,34
9	5,244 gram	69,89
10	5,081 gram	67,72
11	5,366 gram	71,52

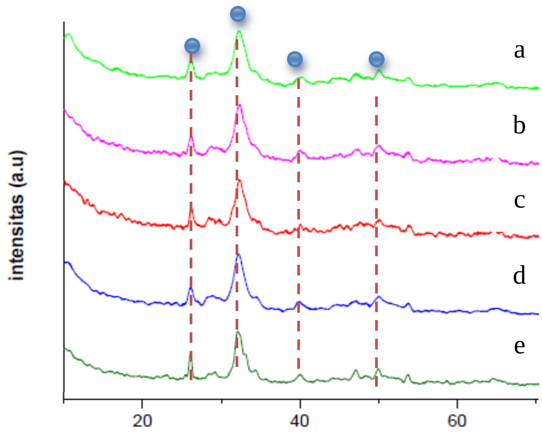

Fig. 1 : The Difractogram of hydroxyapatite at pH ((a = pH 7; b = pH 8, c= pH 9; d = pH 10, - e = pH 11)

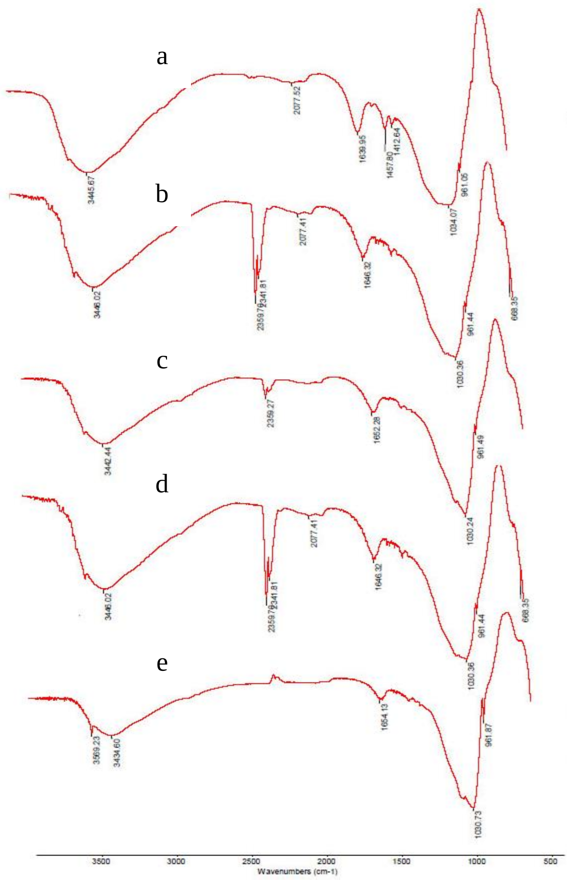

Fig 2 : FTIR spectra of hydroxyapatite from pH 7-11 (a = pH 7; b = pH 8, c= pH 9; d = pH 10, - e = pH 11)

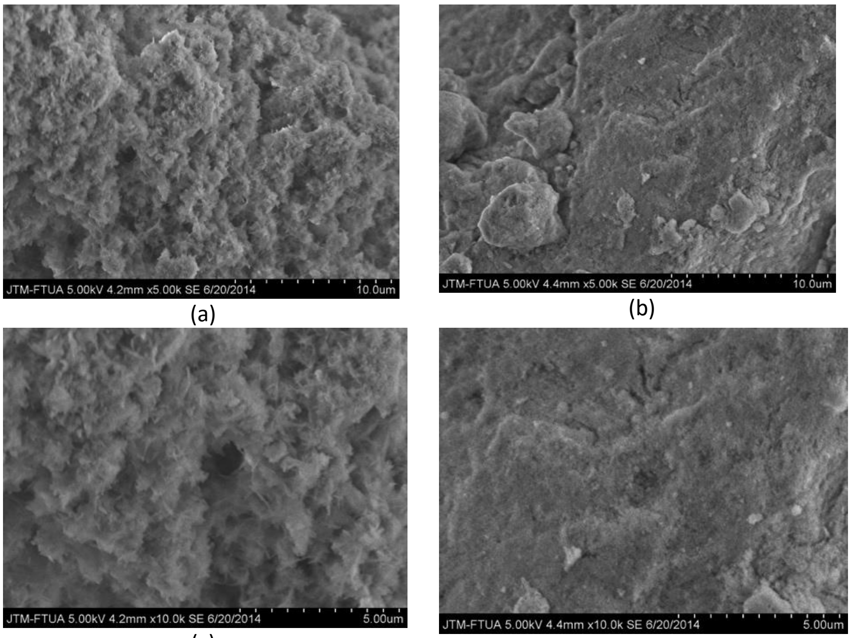

Fig 3 : (a) SEM result for hydroxyapatite at pH 7, 5000x (b) SEM result for hydroxyapatite at pH 10, 5000x (c)SEM result for hydroxyapatite at pH 7, 10.000x (d) SEM result for hydroxyapatite atpH 10, 10.000x

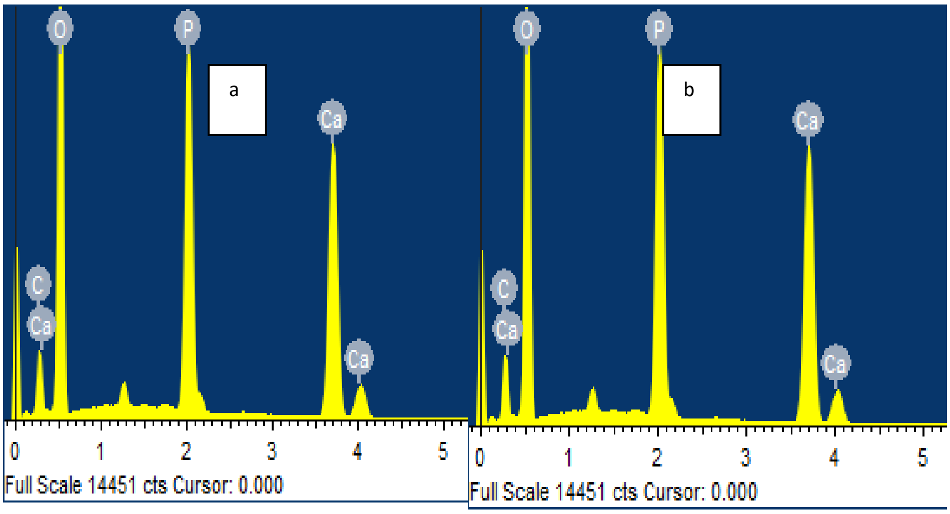

Fig. 4 EDX spectra of Hydroxyapatite at pH 7(a) and pH 10 (b)

The board band at wavenumber 3300 – 3500 cm^{-1} with medium intensity corresponding to streching of hydroxyl group (-OH). The hydroxyl bending appear at 1600 cm^{-1} [8]. Another peak at 2000 – 2100 cm^{-1} is streching of $CO_2$from the air.

The result of SEM (Scanning Electron Microscopy) showed in Fig. 4. The pH has significant effect for the morphology of hydroxyapatite. In alkaline solution, hydroxyapatite like spherical and agglomerated, the porosity is very low, very dense and tight. In neural condition (pH 7), hydroxyapatite like needle and the porosity is higher than pH 10. The Increasing of pH increases agglomeration of hydroxyapatite**.**

CONCLUSION

Synthesis of hydroxyapatite has been successfully carried out by sol-gel method with a variation of pH 7 -11. Based on the results of XRD, FT-IR and SEM-EDX, hydroxyapatite produced has a high purity. The Scanning Electron Microscopy (SEM) showed us that a needle hydroxyapatit has formed at pH 7, the spherical and agglomerated Hydroxyapatite formed at pH 10. The Incresing of pH increased the agglomeration of

Hydroxyapatite. The pH also influence the percent of hydroxyapatite yield. The best of the percent of hydroxyapatite yield was at pH 7 and 8 (more less 80%), because the pH was very near with isoelectric point of hydroxyapaite, but at higher pH (9 – 11) , the percent of hydroxyapatite yield decrease (more less70%).

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