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Hydroxyapatite Material: Synthesis by Using Precipitation Method from Limestone

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ABSTRACT

Limestone is made of calcium carbonate. An Attempt is made to convert calcium carbonate to calcium oxide for precursor of calcium in hydroxyapatite synthesis. Phosphate was from hydrogen phosphate [H_3PO_4]. Diammonium hydrogen phosphate [(NH4)2HPO4] were used as precursors and ammonia was used as the agent for pH adjustment. The synthesized samples was characterized by Fourier Transform Infra Red (FTIR), X-ray Difraction (XRD), Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS). Result show that hydroxyapatite with calcium oxide 1 M was give fine produce. Analysis of BET, result show Intercept of 1.174e+01 and slope of 250.030, total pore volume obtained from hydroxyapatite 3.881e-02 cc/g and average pore radius of 5.83490e+01 Å.

Keywords: limestone, hydroxyapatite, calcium carbonate, calcium oxide, hydrogen phosphate

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INTRODUCTION

Limestone is having chemical compound calcium carbonate. It can convert to calcium oxide with calcinated at 900^{o}C. Calcium oxide can be used for precursor of calcium in synthesis of hydroxyapatite [1-3]. Other calcium source is like from snail [4], coral [5], animals bone [6], and eggshell [7]. Hydroxyapatite is a naturally existing in the inorganic component of human bone, tooth enamel, and dentin, usually called “hard tissues” [8]. The crystal size of hydroxyapatite in natural human bone is in nano range and primarily calcium and phosphorus. Hydroxyapatite is with a stoichiometric Ca/P ratio of 1.67 [9]. Nanocrystalline hydroxyapatite can successfully be produsedby precipitation technique from raw materials. Hydroxyapatite grain gradually increased in size when temperature increased from 100 to 1200^{o}C, and the hydroxyapatite hexagonal-bypyramidal phase was not trasformed to the calcium phosphates phases up to 1200^{o}C [10]. The recent trend method for synthesis of hydroxyapatite is precipitation, sol-gel, hydrothermal, emulsi, etc [11-16].

In this investigation, the precipitation method has been adapted to synthesize nanocrystaline hydroxyapatite powder from limestone. Powder characterization including phase composition, morphology and distribution of grain size has been performed. It was characterized by Fourier Transform Infra Red (FTIR), X-ray Difraction (XRD), Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS).

MATERIALS AND METHODS

In the present work, hydroxyapatite compounds were prepared by solution-precipitation method using $Ca(OH)_2$ and H_3PO_4. Calcium hydroxide was from calcinating limestone convert to calcium oxide. It was occured after calcinated at 900^{o}C. After that, 5.6 g CaO dissolved in 1000 ml H_2O (aquades). The filtrate is taken, then added a solution of

100 ml 0.06 M hydrogen phosphated, H_3PO_4, slowly while stirring for 1 hour at 25°C (room temperature) at pH, 11. The addition of ammonium hydroxide (NH_4OH) to pH adjustment.

$$10Ca(OH)_2 + 6\ H_3PO_4 \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 18H_2O$$

The solution formed was precipitated for 1 day or +15 hours until a precipitate is formed. The precipitate that formed was filtered and dried at a temperature of + 110^{o}C aiming to eliminate solvents that still contained. The precipitate which has been dried and then ground into powder, then calcinated at 900^{o}C for 2 hours. Nanopowder formed then characterized with FTIR, XRD and SEM.

RESULTS AND DISCUSSION

analysis of FTIR

Infrared characteristic was carried out on two samples to study the spectra characteristics indivicates of the chemical bonding in the synthesized hyroxyapatite. The spectrum can be dividedinto some regions with peaks having wave numbers around 3437, 3448, and 3571 cm^{-1} are due prensence of –OH bond. The peaks observed around at 1042, 1034, 1089 and 962 cm^{-1} are due to the precence of P-O bonds in phosphate groups. Thus, the presence of PO_4^{3-} group in hydroxyapatite is almost confirmed from IR studies [1,2,15].

Analysis of XRD

Fig.2 shows the XRD pattern of hyroxyapatite 0.1 M and 1 M. It can be seen from the results of XRD two patterns was different (Fig.2). Hyroxyapatite 0,1 M suitability with hydroxyapatite ICSD 26205 standart (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.

Analysis of SEM-EDX

SEM observation was performed at State University of Malang (UNM). The images was observed to be almost like spherical in agglomerate particles. The uniform grain size with narrow size distribution corresponding to the cristallinity improvement of HA 0.1 M powders.

The result of measurement of elemental composition (Ca and P content) and Ca/P molar ratio are summarized in Table 1. The Ca/P stoichiometry of 0.1 M was analysed by EDX. It shows that HA powder with Ca/P ratio is below ratio 1.67, indicate other compound in sample [2,7].

Analysis of BET

Analysis of the surface area of the hydroxyapatite synthesized from limestone, carried out using equipment Surface Area Analyzer (SAA). Obtained hydroxyapatite surface area of 13.304. From the analysis of BET, to use nitrogen gas adsorption isotherms, adsorption isotherms obtained chart below.

Table 1. Ca and P content in th synthesized hydroxyapatite powder and Ca/P ratio

Element	Measured content (*Wt%)*	*Ca/P* ratio
PK	22.90	1.51
CaK	44.65	

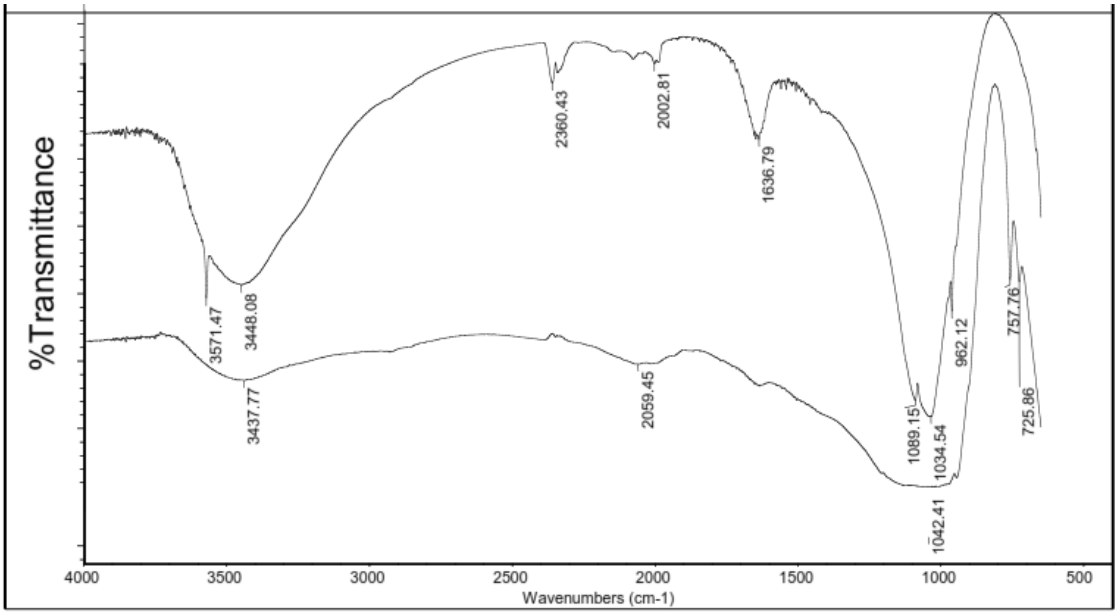

Fig. 1 FTIR spectrum of hyroxyapatite powders at (a) 0.1 M and (b) 1M

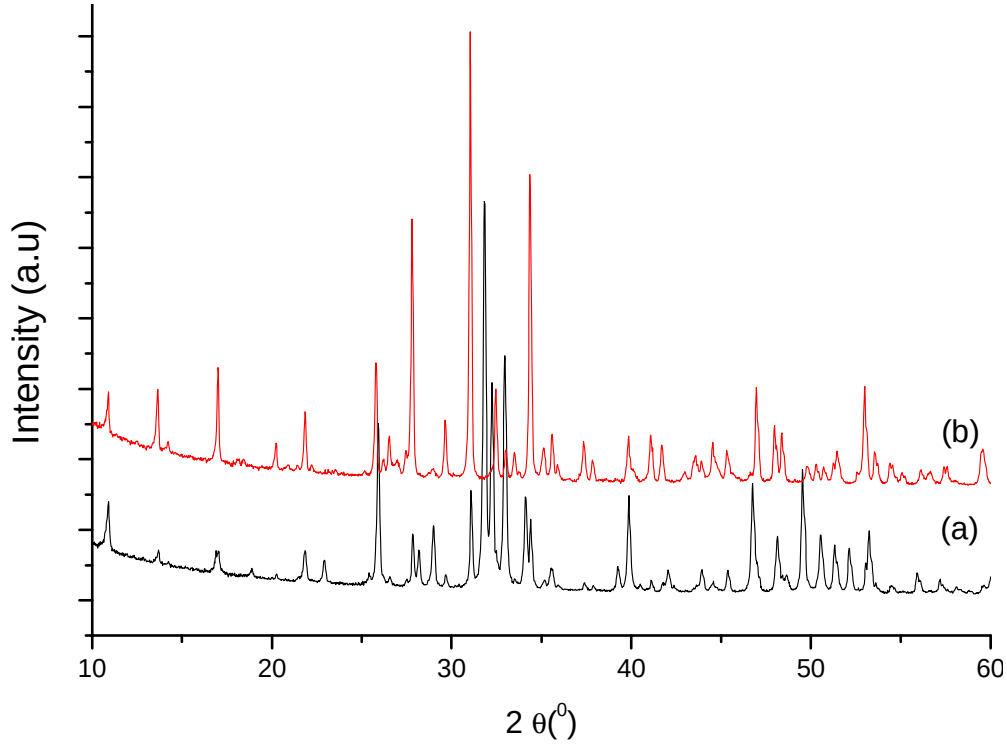

Fig. 2. XRD patterns of HA powders at (a) 0.1 M and (b) 1M

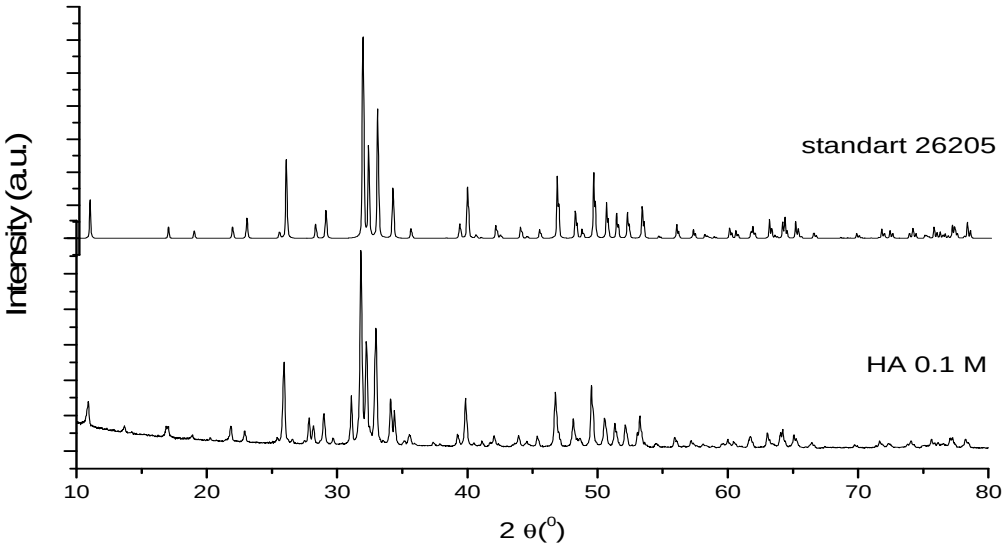

Fig. 3. XRD pattern of HA powders synthesized with HA standart ICDS 26205

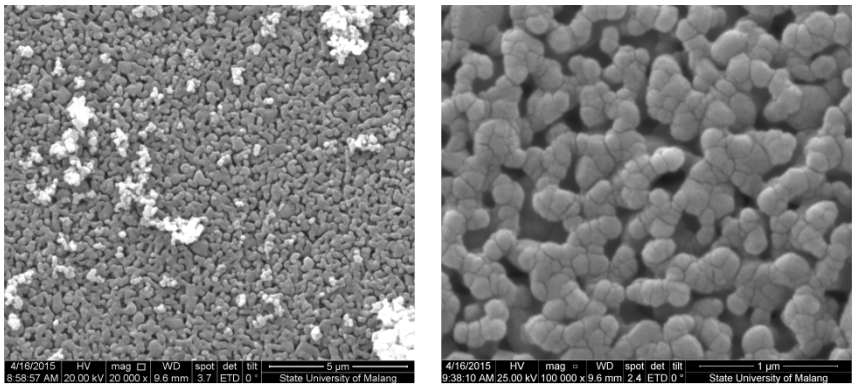

Fig. 4. SEM images of HA powder at 0,1 M

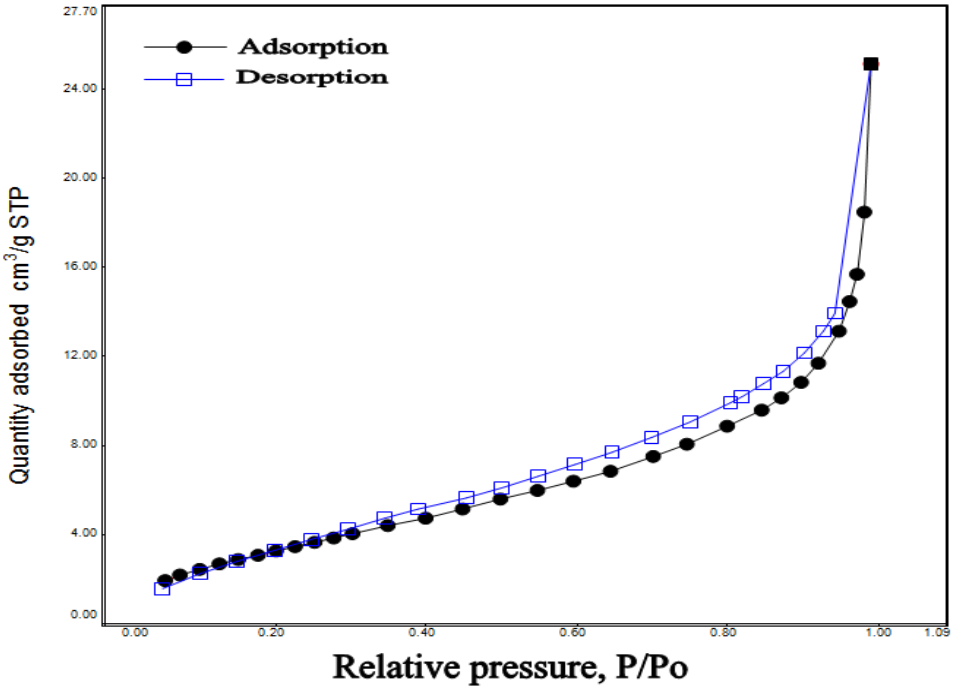

Fig. 5. Isoterm Adsorption-Desorption nitrogen gas of the hidroxyapatite
Intercept of 1.174e+01 and slope of 250.030, total pore volume obtained from hydroxyapatite 3.881e-02 cc/g and average pore radius of 5.83490e+0

CONCLUSION

Precipitation method was used in the present hydroxyapatite to its simplicity as well as aconomical benefit it offers on industrial scale. The precursor calcium from calcinating limestone convert to calcium oxide dissolved H_2O (aquades) can result hydroxyapatite. Hyroxyapatite 0,1 M was better than hydroxyapatite 1 M. It Ca/P ratio is below ratio 1.67, indicate other compound in sample Analysis of the surface area from BET, Intercept of 1.174e+01 and slope of 250.030, total pore volume obtained from hydroxyapatite 3.881e-02 cc/g and average pore radius of 5.83490e+01 Å.

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