FUDMA Journal of Sciences (FJS)
ISSN online: 2616-1370
ISSN print: 2645 - 2944
Vol. 7 No. 3, June (Special Issue), 2023, pp 308 - 312
DOI: https://doi.org/10.33003/fjs-2023-0703-1885

PREPARATION AND CHARACTERIZATION OF HYDROXYAPATITE BY CHEMICAL TREATMENT

***[1]Oyewumi-Musa Rukayat Titilayo, [2]Bello M. O., [2]Abdus-Salam Nasiru and [1]Olabode Sururat Olaitan**

[1]Chemical and Geological Science Department, Al-Hikmah University, Ilorin, Nigeria.
[2]Department of Chemistry, University of Ilorin, P.M.B. 1515, Ilorin, Kwara State, Nigeria

*Corresponding authors' email: titilayomusa@gmail.com Phone: +2348038083240, +2347053768213

ABSTRACT

Hydroxyapatite powder (HA) was prepared using the chemical precipitation method using diammonium hydrogen phosphate and calcium nitrate tetrahydrate as the starting materials. The solution was kept stirring for 24hrs at room temperature, white precipitates were dried and calcined at 1000ºC and 1200ºC for 4hrs. The powder sample was characterized by scanning electron microscopy (SEM), Fourier infrared spectroscopy (FTIR), X-ray diffraction (XRD), Elemental dispersive X-ray (EDX). The results showed that obtained HA powders were greatly influenced by synthetic conditions. SEM shows the morphology of crystals structure, large pores sizes were observed at 50µm and 100µm. The FTIR shows the presence of CO_3^{2-} at 1390 cm^{-1} and 1384 cm^{-1} which may be due to the adsorption of atmospheric CO_2 on the surface of HA. PO_4^{2-} was observed at 1046 cm^{-1} and 1092 cm^{-1}. The EDX shows the presence of C, O, Na, Mg, Al, P, Ca. The histogram of EDX revealed oxygen carbon, phosphorus, and calcium as the major elements, sodium, magnesium, and aluminum were also present.

Keywords: Hydroxyapatite, chemical treatment, calcination temperature, characterization

INTRODUCTION

In this century, the production of materials with nanostructures has gained much attention for adsorption, catalysis, biomaterials, and optical applications. Hydroxyapatite (HA) is a hydrolyzed calcium phosphate material that has significant research applications, especially in the biomedical field. HA with the chemical formula $Ca_{10} (PO_4)_6 (OH)_2$ is the main component of bone and teeth. It is a synthetic ceramic material based on calcium phosphate (CaP) (Eslami *et al.*, 2010) Various methods employed for the preparation of HA are either through chemical synthesis or natural sources. In addition, these materials are also important in the study of adsorption due to the nature of the powders. The applications of HA are based on the establishment of a well-defined system for the characterization of the prepared HA, in which the composition, crystallinity, and nanostructure would have to be properly addressed. Detailed characterization indicates that an apatite layer is usually formed on the ceramic surface when implanted, this layer consists of a carbonate-ion-containing apatite, named "bone-like" apatite, forming a bond with human bone (Liu *et al.*, 2010). These properties will play a major role in investigating the surface properties which may develop potential bonding sites for heavy metals and impurities (Juang & Hon,1996) Bioactivity of CaP materials is dependent on many factors during the synthetic procedure, such as precursor reagents, pH and temperature.

Various methods have been reported to prepare HA including hydrothermal, spray-dry, and sol-gel techniques ((Neira *et al.*, 2009). Of these, the wet precipitation method is considered a relatively convenient method for the production of HA. The published HA wet precipitation methods generally include a titration step when mixing calcium and phosphorus chemical precursors (Castros *et al*, 2010). However, these approaches are associated with several disadvantages including lengthy and complex processes combined in some cases with the need for expensive equipment. Commercial production maybe even more complex, with patents describing sophisticated reactors for the manufacture of high-quality medical-grade HA (Prakash *et al.*, 2006) Despite this, the neutralization reaction between calcium hydroxide and phosphoric acid is advantageous due to the lack of noxious chemical by-products. The relationship between processing conditions and the morphology of the HA product has been reported for slow titration reactions. Specifically, for titration methods involving calcium hydroxide and phosphoric acid, an elevated temperature appeared to favor the preparation of particles with a low aspect ratio (Wilcock *et al.*, 2017).

In this investigation we report on the preparation of hydroxyapatite by chemical treatment technique was carried out. The motivation for the preparation of HA by chemical precipitation in an aqueous solution using different reagents was based on assessing the effect of varying temperatures. The CaP samples were characterized by Scanning Electron Microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), Elemental dispersive X-ray (EDX). HA preparation by wet chemical methods is known from earlier works. The present work aimed at preparing HA by chemical precipitation methods and, to compare the effect of varying temperature and powder characteristics.

MATERIALS AND METHODS

The starting materials for the preparation of hydroxyapatite were calcium nitrate tetrahydrate ($Ca (NO_3)_2. 4H_2O$) as a source of calcium ions and diammonium hydrogen phosphate ($(NH_4)_2 HPO_4$) as the source of phosphorus. The molar ratio of Ca/P was 1.67. The flow chart of the preparation is as shown in Fig. 1. An equimolar concentration of calcium nitrate tetrahydrate and diammonium hydrogen phosphate was prepared where 35.4 g of 250 ml of 0.6M $Ca (NO_3)_2. 4H_2O$ was dissolved in absolute ethanol and vigorously stirred at room temperature. A 19.88 g of 0.6 M $(NH_4)_2 HPO_4$ was dissolved in 250 ml distilled water and slowly added into $Ca(NO_3)_2.4H_2O$ to produce a milky solution. The pH of the solution was adjusted using a 2 M aqueous NaOH solution. The solution was stirred at room temperature for 24 hr to produce a thick milky gel and dried in an oven at 120^0C overnight. The dried gels were crushed and ground to fine powders, transferred into an alumina crucible, and then calcined at 1000 and 1200^0C for 4 hr using a heating and cooling rate of 5^0C/min. the above method was adopted from Sookesean *et al* (2010)

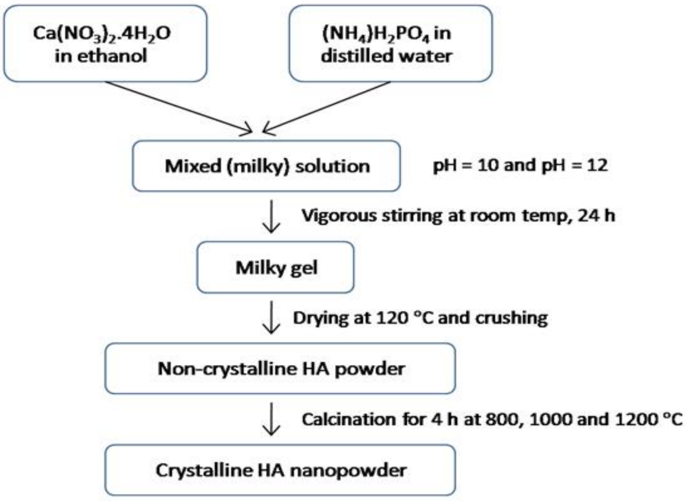


Figure 1: Flow chart of hydroxyapatite preparation.

Characterization

HA powder was analyzed by XRD (Siemens D2000) with CuKα radiation over a range of 10-70°. The particle morphology and pore size were evaluated by Scanning Electron Microscopy SEM, BIO-RAD (Microscience Division) coating system Au/Ar sputter coating at 50-60-mm. Then Infrared spectra of the materials were recorded by Perkin-Elmer spectrum BX FT-IR spectrometer.

RESULTS AND DISCUSSION

Figures 2a and 2b shows FTIR spectra of the powder prepared at 1000°C and 1200 °C indicating bands around 3286-3564cm^{-1}, which may correspond to the OH^- group from absorbed water molecule in the sample. The absorption peak between 819- 1390cm^{-1} can be assigned to some CO_3^{2-}. Band around1041-1046cm^{-1} corresponds to PO_4^{3-} in the apatitic environments. Bands at 1642.1-1642.5cm^{-1} can be assigned to lattice water molecules in HA powders present as a structured hydrated surface layer. The wavenumber 3134 cm^{-1} shows the presence of NH_4^+. The position of the bands present in this infrared spectra agrees well with those reported by several authors for pure hydroxyapatite powder (Ferraz *et al.*, 2004, Sanosh *et al.*, 2009).

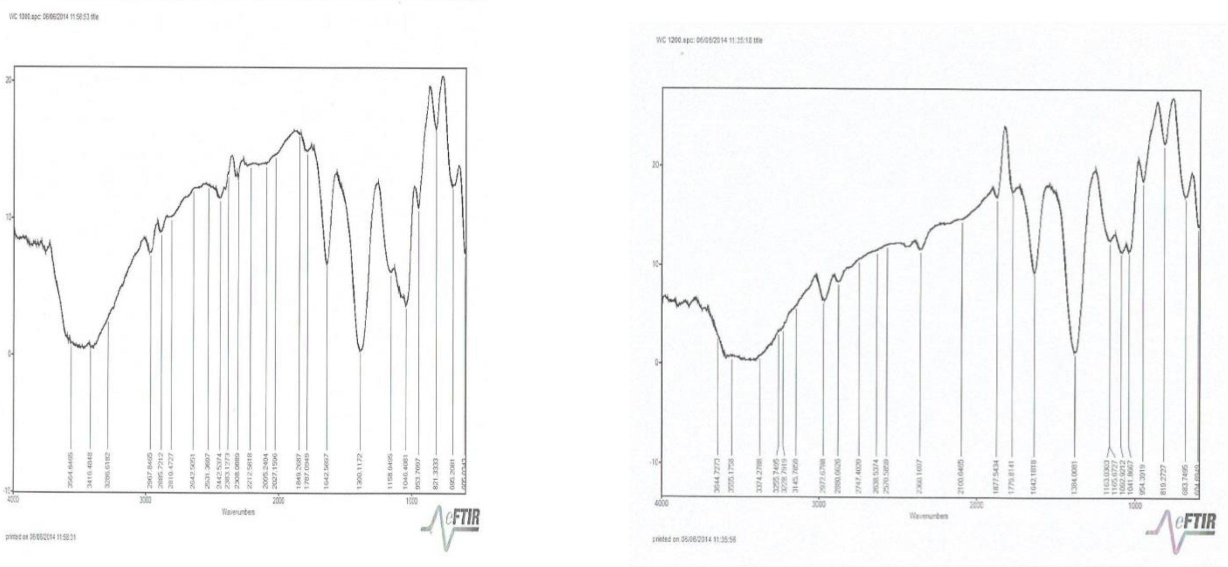


Figure. 2a and 2b: FTIR spectra of powders from precursors calcium nitrate with diammonium hydrogen phosphate after aging for 24hrs and calcined at (a) 1000^{0}C (b) 1200^{0}C

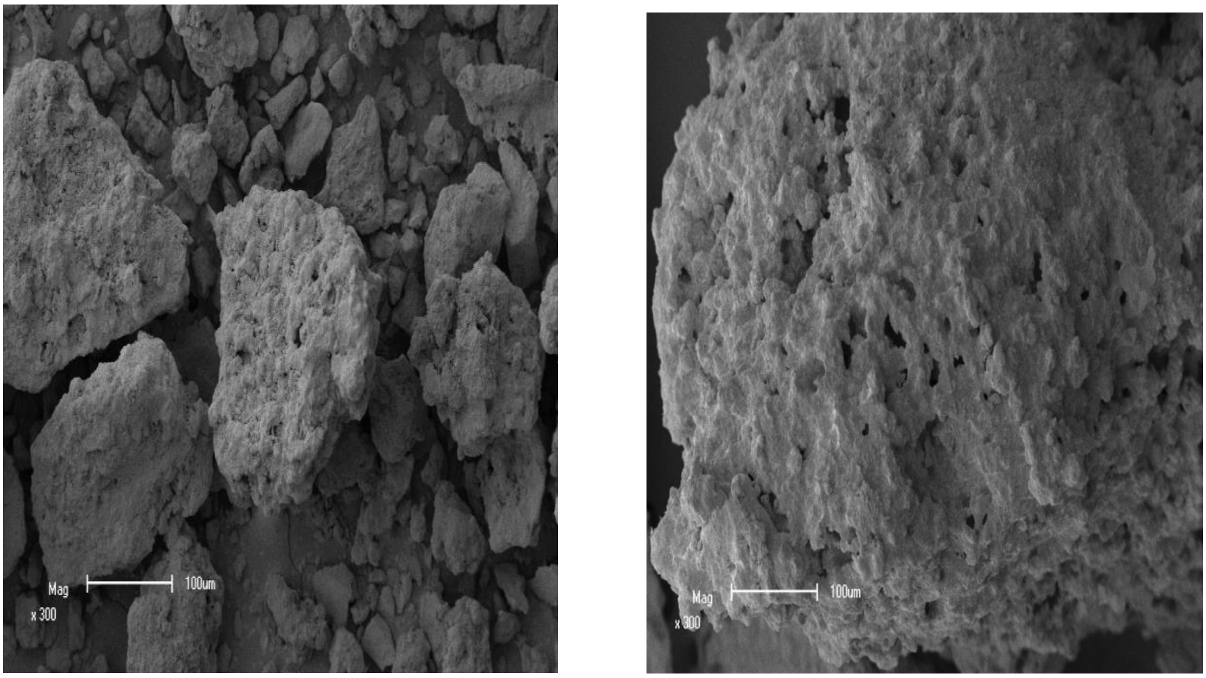
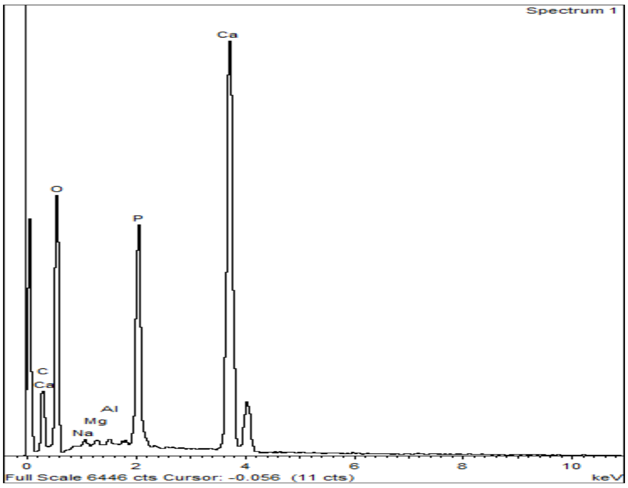


Figure 3: SEM micrographs of HA prepared and calcined at (a) 1000ºC and (b) 1200^0C

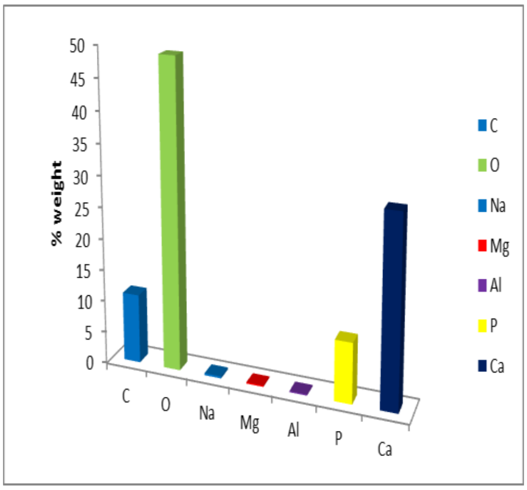
Figures 3a and 3b show SEM images of samples at 1000^0C and 1200^0C. The powders are highly agglomerated with large pore sizes. The image revealed that the pore sizes became more distinct as the calcination temperature increases. Calcination temperature brings a direct impact to changes in grain growth, where a higher calcination temperature yields an increase in grain size. This grain growth may be associated with the absorption of heat energy by the particles (Murugan *et al.*, 2003).

The quantitative results of EDX on HA chemical composition for the two samples can be observed in Figures 4a and b below. As expected, the major elemental components were phosphorus (P) and calcium (Ca) that formed the HA prepared and other trace elements. These trace elements have not interfered in the synthesis reaction and most likely they would not have reacted during the synthesis, staying in the amorphous phase (Santos *et al.*, 2004).

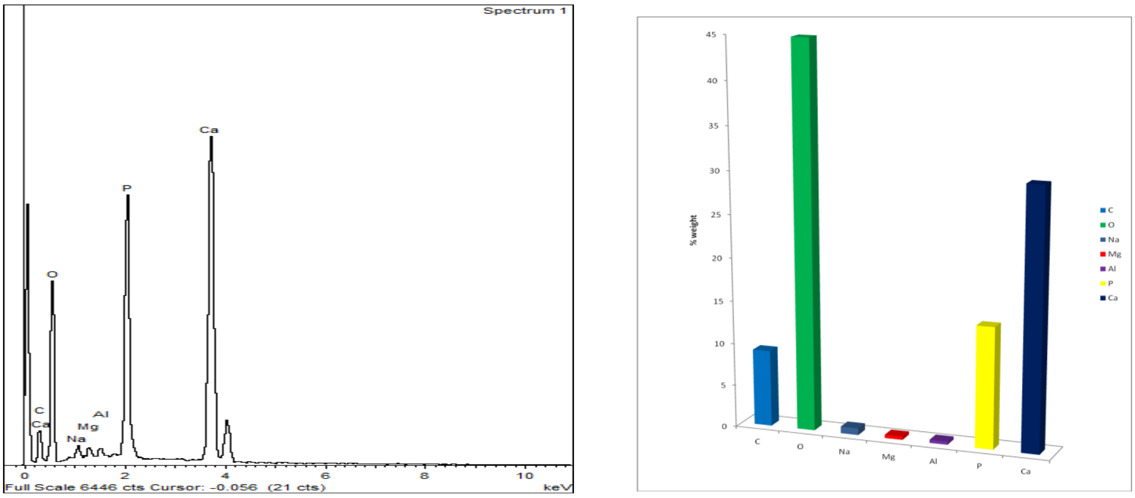
The EDX spectrum shows the elements present with their respective weight composition. They include Carbon, Oxygen, Sodium, Magnesium, Aluminum, Phosphorus, and Calcium. The elements follow the order of increased weight: O<Ca< C<P, in which all these are basic components of hydroxyapatite.



a) EDX Spectrum for 1000ºC



Histogram of EDX Analysis for 1000ºC



b) EDX Spectrum for 1200ºC Histogram of EDX Analysis for 1200ºC

Figure 4: EDX Spectra at (a) 1000ºC and (b) 1200ºC

The XRD pattern of hydroxyapatite showed sharp peaks which indicate good crystallinity. It can be seen that, as the calcination temperature increases, the crystallite size also increases and several of the HA lines becomes more distinct at a higher temperature which suggests an increase in the degree of crystallinity degree. This conforms to studies that HA calcined at higher temperatures exhibit good crystallinity (Takashi *et al.*, 1995, Weng,1998, Kimura, 2007).

The XRD pattern shows that hydroxyapatite obtained at 1000˚C and 1200˚C in Figures 4 & 5 contains mineral compounds like Nitratine, Apatite, Calcite, and Nontronite.

Apatite is a result of phosphate mineral, usually referring to hydroxyapatite, fluorapatite, chlorapite with high concentrations of OH^- present in the crystal. Calcite is a carbonate mineral with its suitable form as $CaCO_3$, a common constituent of sedimentary rocks and limestone. Nitratine or nitratite is a mineral, naturally occurring from sodium nitrate $NaNO_3$. It is so isostructural with calcite. It has the highest percentage in the XRD interpretation due to its presence in the precursor. Nontrinite, a member of the Smectite group, appeared to be present in both samples but minimal amount.

Table 1: Different variations in the percentage of the compounds present in both samples.

	Apatite (%)	**Calcite (%)**	**Nitratine (%)**	**Nontronite (%)**
WC (1000˚C)	21	16	48	15
WC (1200˚C)	19	14	43	24

All compounds present decrease as temperature increases, except for nontronite which increases as calcination temperature increases to 1200˚C.

Hsieh *et al.* (2001) mentioned that the reactions that simultaneously occur during calcination could be the gel decomposed into HA and the remaining $Ca(NO_3)_2$ decomposed to CaO. A study of thermal decomposition occurs in the temperature range 500-650˚C. In this study powders calcined at 1000˚C and 1200˚C also formed CaO.

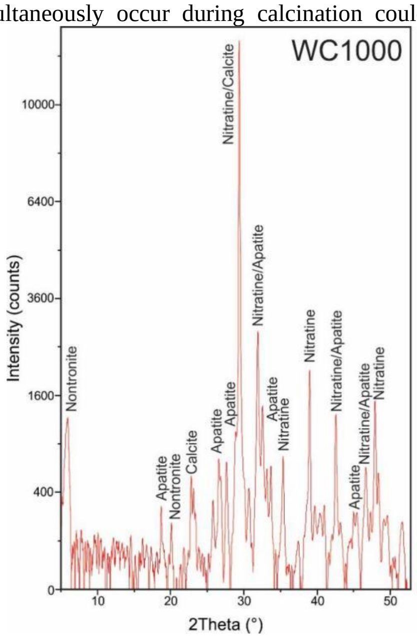


Figure 4: XRD patterns of HA prepared at 1000^{0}C

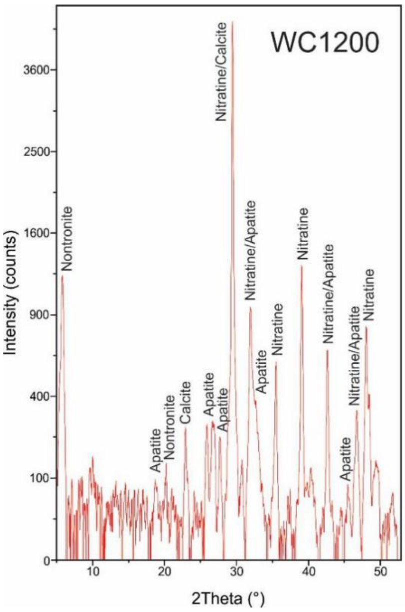


Figure 5: XRD patterns of HA prepared at 1200^{0}C

CONCLUSION

Hydroxyapatite was successfully synthesized using more readily available materials. The experimental conditions used were easy to maintain and no extreme environmental condition was essential. The XRD pattern with reference to JCPDS number 09-432 shows the presence of different minerals, with apatite having dominant peaks in the materials. Through the FTIR analysis, the presence of the following ions (OH^-, PO_4^{3-}, CO_3^{2-}) confirmed the material to be a Hydroxyapatite compound. The SEM micrograph depicts the presence of agglomerates with pores, which became more intense as the temperature was increased to 1200˚C; the presence of these pores may suggest the material to be a good candidate for the adsorption process. Thus, by these various characterizations conducted it can be concluded that hydroxyapatite exists in the samples prepared. Therefore, both hydroxyapatite powder synthesized at temperatures 1000˚C and 1200˚C is good samples when compared to previous works.

REFERENCES

Eslami H., Solati H., Tahriri M., Bakhshi F., (2010). Synthesis and characterization of nanocrystalline hydroxyapatite obtained by wet chemical technique, *Material Science* Poland 28, 342-347.

Ferraz M.P., Monteiro F.J., Manuel C.M., (2004). Hydroxyapatite nanoparticles. A review of preparation methodologies. *Journal of Applied Biomaterial Biomechanics* 21, S74-80.

Hsieh M., Perng L., Chin T., Perng H., (2001). The phase purity of sol-gel derived hydroxyapatite ceramic. *Biomaterials*, 22 (19)., 2601-2607.

Juang H.Y. and Hon M.H., (1996). Effect of calcination on sintering of hydroxyapatite *Journal of Biomaterials*, 17, 2059-2064.

Kim, M., Lin Lewis N., and Cohen Y., (2010). Surface nano-structuring of reverse osmosis membranes via atmospheric pressure plasma-include graft polymerization from the reduction of mineral scaling propensity, *Journal Membrane Science*, 354, 142 – 149.

Kimura I., (2007). Synthesis of Hydroxyapatite by Interfacial Reaction in a Multiple Emulsion. *Research Letter Science,* Article ID 71284: 1-4.

Liu D.M., Yang Q., Troczynski T., Tseng W.J., (2002). Structural evolution of sol-gel derived hydroxyapatite. *Journal of Biomaterials* 23, 1679-87

Liu. D.M., Troczynski, T., and Tseng. W.J., (2001). Water-based sol-gel synthesis of hydroxyapatite. *Process development Biomaterials* 22, 1721-30.

Murugan *et al* (2003). Microwave synthesis of Bioresorbable carbonated hydroxyapatite using Goniopora. Bioceramics. 240-242, 51-52.

Sanosh K.P., Min-Cheol C., Balakrishnan A., Kim T.N., and Seong-Jai C., (2009). Preparation and Characterization of Nano-hydroxyapatite powder using a sol-gel technique, *Bulletin Material Science,* 32, 465-470.

Sooksaen P., Jumpanoi N., Suttiphan P., Kimchaiyoung E., (2010). Crystallization of Nano-sized Hydroxyapatite via Wet Chemical Process under Strong Alkaline Conditions. *Science Journal of UBU* 1, 20-27.

Takashi H., Yashima M., Kakihana M., Yoshimura M.,(1995). Synthesis of stoichiometric hydroxyapatite by a gel route from the aqueous solution of citric and phosphonoacetic acid. *European Journal of Solid State Inorganic Chemistry* 32-835.

Weng, W.J., (1998). Evaluation of hydroxyapatite using a hydrothermal technique, *Journal of Biomaterials* 19, 125.