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Synthesis of hydroxyapatite from limestone by using precipitation method

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Abstract. Hydroxyapatite from limestone was synthesized by precipitation method. During the synthesization, the temperature of a 200 mesh sample was increased to 600°C for 3 hours. It was transformed $CaCO_3$ into CaO powder. Then the CaO powder was dissolved with water to get $Ca(OH)_2$, then it dissolved with H_3PO_4 0.3M as a source of phosphate. The solution was mixed by using magnetic stirrer with a speed of 300 rpm for 1 hour. Then NH_4OH 1M solution was periodically dropped to that the solution until it became an alkaline with pH 10. The solution was stood for 24 hours and the precipitate was dried by using an oven in 120°C for 5 hours. Hydroxyapatite powder obtained was characterized by FTIR to see the major functional groups that are formed in hydroxyapatite limestone. The results obtained were 3 functional major groups that are phosphate (PO_4^{3-}), carbonate (CO_3^{2-}) and hydroxyl (OH^-) on hydroxyapatite limestone.
Key Words: Hydroxyapatite, Limestone, Precipitation Method, FTIR.

1. Introduction

Hydroxyapatite synthesis calcium is needed to quite high calcium as a biological source as its basic material. There are several ingredients that can be used to make hydroxyapatite such as beef bones [1], eggshells [2], limestones [3], shellfishes [4], etc. The greatest amount of calcium is limestone. Limestone is an inorganic mineral with the main constituent is calcium. The content of calcium carbonate ($CaCO_3$) in limestone is around 95% and the content of calcium carbonate in limestone can be purified to get calcium. That's why, limestone can be applied directly to various applications such as clinical, medical, for the development of biomaterials and it is very suitable to be applied to hydroxyapatite.

Nowadays, scientists conduct researches on limestone to be an alternative in medical as a substitute for human bones damaged, limestone contains a lot of calcium in the form of $CaCO_3$ (Calcium Carbonate), very close to the nature of human bones namely hydroxyapatite [5]. Known the compound composition of limestone minerals ($CaCO_3$) are Ca = 40.04%; C = 12.0%; O = 47.96% or CaO = 56.03%; CO_2 = 43.96.

There are various methods to make hydroxyapatite which can be clarified into a dry method, wet method, high-temperature process, biogenic and their combinations. From all of these methods, the chemical precipitation method is the most popular one. The chemical precipitation method is one part

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of the wet chemical method that is most widely used to make hydroxyapatite. Because synthesizing hydroxyapatite uses this method is saving costs than uses organic solvents in large quantities [6].

To produce hydroxyapatite through precipitation method can use various precursors containing calcium and phosphate, such as calcium hydroxide $Ca(OH)_2$ and phosphoric acid (H_3PO_4). The by-products produced by the reaction of $Ca(OH)_2$ and H_3PO_4 in hydroxyapatite synthesis are only water and the reaction does not involve foreign elements [7]. Hydroxyapatite is easier to make using the precipitation method because it directly uses 2 hydroxyapatite ion forming precursors, namely calcium and phosphate. The risk of failure to make hydroxyapatite is more terminalized. In addition, this method also uses a low temperature of < 60ºC to react to the solution and form crystals that are relatively soluble under normal conditions. Therefore, hydroxyapatite with this method can be used as a filler to make biocomposite.

The hydroxyapatite's structure consists of calcium ion, phosphorus, and hydroxyl ($Ca_{10}(PO_4)_6(OH)_2$) ions which are often applied as a substitute for bone and dental tissue minerals because their chemical structures have similarities so they can bind chemically with bones and teeth. Useful in biological usage because of its ability to allow perfect osteointegration, absence of local and systemic toxicity, and no genotoxic activity in the body's biological systems [8].

About 65% of the mineral fraction in human bones is composed of hydroxyapatite. Hydroxyapatite has been widely used to repair, replenish, add, and reconstruct bone damaged and tooth tissue and also in soft tissue [9]. The properties of calcium (Ca^{2+}) ions in hydroxyapatite can change toxic heavy metal ions and have sufficient ability to absorb organic chemical elements in the body and also have good biocompatibility and bioactivity [10].

Synthesized limestone-based hydroxyapatite using the hydrothermal method with variations in heating and pH [11]. The results obtained from the characterization of XRF were limestone containing 98.2% pure calcium. The XRD and XRF analyses were found that the highest score in making Hydroxyapatite was at pH 10. The best XRD analysis of hydroxyapatite was obtained with a smaller crystal size at 700ºC heating in 3 hours [3].

Meanwhile, synthesized eggshell-based hydroxyapatite using an alkaline precipitation method. In this method, only 2 precursors were needed to make hydroxyapatite, namely calcium precursor and phosphate precursor. The FTIR test results obtained that the functional groups of eggshell hydroxyapatite had the main functional group of -OH, $-(PO_4)_3^{2-}$, and $-CO_3^{2}-$ [2], [10], [12].

From these descriptions, in this study, the manufacture of nano-hydroxyapatite with limestone-based material is done. Limestone is obtained from the Sidikalang area, North Sumatera. Synthesis of limestone hydroxyapatite is done by alkaline precipitation method, then the nano-hydroxyapatite powder is characterized by the FTIR test to see hydroxyapatite absorption peaks.

2. Experimental Method

The material used to make hydroxyapatite powder is 200 mesh limestone, 0.3M H_3PO_4, 1M NH_4OH, and distilled water. Limestone ($CaCO_3$) is obtained from Sidikalang and processed by PT. Agro Niaga Globalindo Medan. Tools for making hydroxyapatite powder are analytical balance sheets for weighing materials, mortar and filter paper for smoothing materials, furnaces for heating materials, magnetic stirrers for mixing materials and heating solutions, glassware, and thermometers. The synthesized hydroxyapatite powder was characterized by FTIR.

The first step for making hydroxyapatite is calcified the $CaCO_3$ limestone using a furnace with a temperature of 600ºC within 4 hours to become CaO powder.

Figure 1. Limestone $CaCO_3$ size 200 mesh.

CaO powder was weighed using a scale with a mass of 11.84 grams. Then dissolved with 200 ml of distilled water, CaO suspension stirred for 15 minutes so CaO could react in water and became Calcium hydroxide or Ca $(OH)_2$. 0.3 M H_3PO_4 solution is added to Ca $(OH)_2$ solution as a source of 200 ml phosphate with a rate of addition 5 ml/minute. Mixing was done by using a magnetic stirrer for 1 hour at a speed of 300 rpm.

Then, the mixed solution warmed using a hotplate at 90ºC. While warming up, 1 M NH_4OH solution was added periodically to transform the solution to alkaline with a pH of 10. The effect of adding NH4OH 1 M solution is changing in color, turned from turbid into milky white.

The warmed solution stood for 24 hours at room temperature. Then the solution filtered with filter paper to obtain the sediment yield. The precipitate was dried using an oven at 120ºC for 5 hours. The dried powder characterized by FTIR test to determine FTIR characterization of powder composition and powder functional groups.

3. Result and Discussion

Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) was synthesized from a calcium source derived from calcium oxide (CaO). Calcium oxide (CaO) could be obtained from the calcination of $CaCO_3$ contained in natural materials such as limestone. CaO powder dissolved with water to transform it into Calcium hydroxide $Ca(OH)_2$. $Ca(OH)_2$ solution mixed with a phosphoric acid solution to obtain a phosphate source as the main ion hydroxyapatite forming.

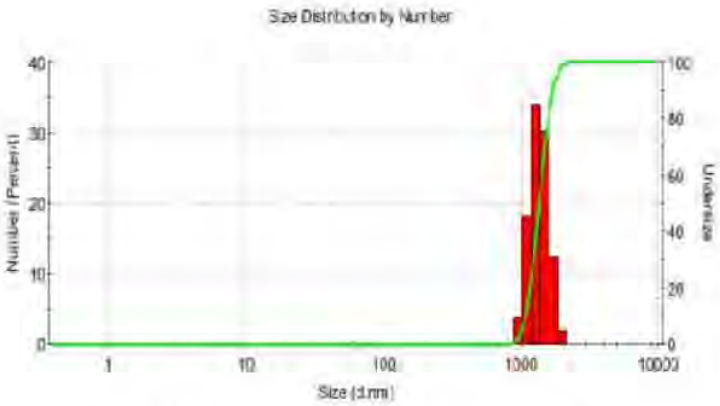

Figure 2. Result Particle Surface Analysis (PSA).

Fig. 2 Show that the particle size is around 1000 nm, it is still very large because it is only crushed and ground, then sieved with 200 mesh. To get a smaller size (the size of the nanoparticles) must be ball mill [13]. The preparation of hydroxyapatite powder (Fig. 3) in this study was carried out using the wet precipitation method. The wet method uses chemical reactions to precipitate solids from the solution. In this method $Ca(OH)_2$ and phosphate precursors such as H_3PO_4 are reacted at low temperatures with the following equation [14]:

$$10\ Ca(OH)_2 + 6\ H_3(PO)_4 \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 18\ H_2O$$

Then the precipitate obtained from the precipitation method was dried to get hydroxyapatite powder using an oven with a temperature of 120°C for 5 hours. The oven drying process aimed to remove excess water vapor and OH- ions in deposit.

Figure 3. Limestone Hydroxyapatite Powder.

Analysis of the FTIR spectrum on hydroxyapatite was done to determine the functional groups found in the synthesized compounds. The functional group on Hydroxyapatite was characterized by the appearance of absorption at a wavenumber 500-4000 cm^{-1}. The infrared spectrum of the hydroxyapatite synthesized by the alkaline precipitation method is presented in Fig. 3 and an analysis of the absorption peaks are presented in Table 1.

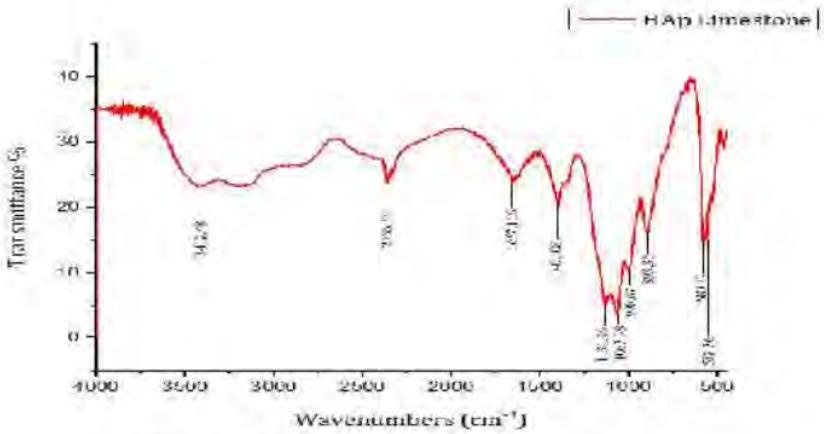

Figure 4. The Spectrum of Limestone Hydroxyapatite.

Table 1. Data of groups of FTIR result from hydroxyapatite limestone.

Groups	Wave Number (cm^{-1})
Phosphate (PO_4^{3-})	532.76; 580.32; 893.35; 998.67; 1067.98; 1131.96
Calcium oxide (CaO)	1657.106
Carbonate (CO_3^{2-})	1400.08
Carbon dioxide (CO_2)	2366.33
Hydroxyl (OH^-)	3412.48

The results of the FTIR (Fig. 4), showed that the presence of phosphate and hydroxyl groups on limestone hydroxyapatite, indicated that the hydroxyapatite phase had formed quite well. The phosphate group (PO_4^{3-}) has the highest intensity bond, namely at wave number 532.76; 580.32; 893.35; 998.67; 1067.98; 1131.96 cm^{-1}. The hydroxyl group (OH-) is shown by the appearance of the absorption peak wave number around 3412.48 cm^{-1}. The CaO phase in limestone hydroxyapatite is shown at wave number 1657.106 cm^{-1}. The formation of these groups on limestone hydroxyapatite is in accordance with the chemical structure of hydroxyapatite in Figure 3.

The phosphate group (PO_4^{3-}) bond is the strongest with vibration structuring found at wave interval numbers from 1000 to 1150 cm^{-1} [15]. The OH^- group bond is present at wave number 3400 and 630 cm^{-1}. The CaO function group on hydroxyapatite is found at wave vibrations from 1400 to 1700 cm^{-1}. The CaO phase found in hydroxyapatite can bind CO_2 in the air. This causes in the FTIR analysis, found carbon dioxide (CO_2) bonds with fairly high intensity on limestone hydroxyapatite, which is at wavenumbers between 2366.33 cm^{-1} [15].

The carbonate (CO_3^{2-}) function group also appeared at the wave number 1400.08 cm^{-1}. The presence of CO_3^{2-} groups is from the reaction of hydroxyapatite with CO_2 contained in the atmosphere during synthesis and heat treatment [16]. Cluster CO_3^{2-} also exists in human bones which is the substance of the PO_4^{3-} group. CO_3^{2-} categorized as impurities that existed before the synthesis process or impurities present in the hydroxyapatite base material.

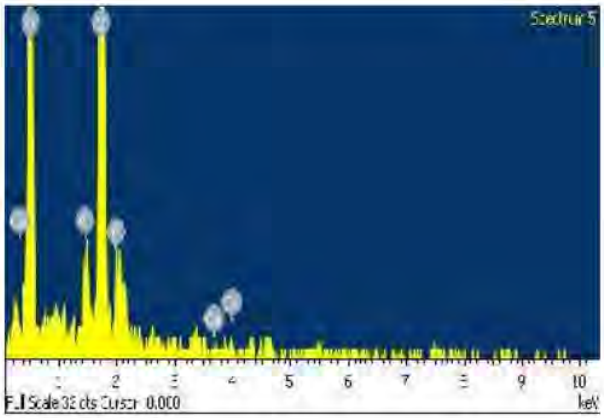

Figure 5. The Spectrum of EDX Limestone Hydroxyapatite.

From Fig. 5 the spectrum above can be seen that the elements contained in limestone are elements O, Al, Si, P and Ca. The percentage of Energy Dispersive X-ray (EDX) results from the spectrum representing the sampling can be seen in Table 2:

Table 2. The result EDX of limestone hydroxyapatite

Element	Mass (% wt)	Atomic (% wt)
O	66.08	77.48
Al	3.19	2.22
Si	27.82	18.58
P	2.65	1.60
Ca	0.26	0.12
Total	100	100

EDX testing at a point in the sample produces output in the form of a percentage of elements only. The order of elements from the most dominant in hydroxyapatite are elements O, Si, Al, P and Ca with an average of 66.08%; 27.82%; 3.19%; 2.65%; 0.26%. Then the elements above are in accordance with the formation of hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) while the Al and Si elements are impurities with compositions of 3.19% and 27.82% which are caused by several factors, namely the purification of limestone to poor hydroxyapatite, equipment which can oxidize and several other factors.

4. Conclusion

The results of FTIR characterization of limestone hydroxyapatite powder made by the alkaline precipitation method showed that the presence of phosphate and hydroxyl groups on limestone hydroxyapatite, indicated that the hydroxyapatite phase had formed quite well. This was characterized by the formation of major groups namely phosphate (PO_4^{3-}), carbonate (CO_3^{2-}), hydroxyl groups (OH^-) and CaO compounds on hydroxyapatite limestone.

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