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Conference Paper

Synthesis of Calcium Phosphate from Boiler Egg Shells as Raw Material for Hydroxyapatite

Luluk Edahwati[1]*, Sutiyono[1], Rahmaniar Naulita Hutagalung[2], Siti Robiatuz Zahrotun Nukhuf[2]

[1]Mechanical Engineering Department, Universitas Pembangunan Nasional "Veteran" Jawa Timur, Surabaya, 60294, Indonesia
[2]Chemical Engineering, Universitas Pembangunan Nasional "Veteran" Jawa Timur, Surabaya, 60294, Indonesia

*Corresponding author:
E-mail:
lulukedahwati@gmail.com

ABSTRACT

Hydroxyapatite (Ca10(PO4)6(OH)2) is one of the biomaterials that can be used for replacement bones for survivors of fractures that can be caused by accidents or natural disasters. Hydroxyapatite biomaterials are now a necessity, but the high price of imported hydroxyapatites has resulted in difficulties in obtaining them. The purpose of this study is to synthesize calcium phosphate from the eggshells of purebred chickens so that they can be used as raw materials for making hydroxyapatite. The stages in the manufacture of calcium phosphate are calcination as a pretreatment process of purebred chicken egg shells which is continued with the synthesis process. The research variables used are variations in phosphoric acid concentrations and also pH variations. The results presented were regarding calcium content through XRF analysis, diffraction patterns from calcium phosphate through XRD analysis, and morphology of calcium phosphate through SEM analysis. From the results of the analysis, it can be used as a reference for the characteristics of calcium phosphate which will be used as a raw material for making hydroxyapatite.

Keywords: Calcium phosphate, hydroxyapatite, SEM, synthesis, XRD

Introduction

Increased cases of accidents, bone diseases, and natural disasters can cause paralysis and even death, besides that the increasing cases of bone damage in Indonesia are caused by age as well as factors of unhealthy diet and lifestyle. Thus, a bone graft replacement biomaterial is needed that has bioactive properties, namely the physical properties of the graft in carrying out its function as a scaffold to support bone healing (osteoconduction). Traditional bone replacement materials that are common such as allografts, autografts, and xenografts do not last long and can cause the risk of infection and have an impact on the immune system, which will affect the quality of the replacement bone (Fitriawan et al., 2014). The addition of tissue or bone and dental implants used today uses calcium phosphate-based hydroxyapatite (Ningsih et al., 2014). Hydroxyapatite (HAp) is one of the biomaterials which is the main component of body tissues and teeth. The main property of hydroxyapatite is the ability of a material to interact with living cells or tissues or metabolic systems that do not cause toxicity (biocompatibility) and can develop together with natural bone or good bone regeneration (Fitriawan et al., 2014).

Hydroxyapatite (HAp) with the molecular formula $Ca_{10}(PO_4)_6(OH)_2$ has a lattice character of a = 9.433Å, c = 6.6874, and the ratio Ca/P = 1.67 (Garreta et al., 2002) is a bioceramic calcium apatite that can be found in human bones and teeth (Fitriawan et al., 2014). Hydroxyapatite has two structures, namely monoclinic and hexagonal (Mangkuasih & Rohmawati, 2021). In the world of health, hydroxyapatite is widely used to replace damaged human bones and teeth

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because its structure is the same as natural human bones and teeth. Hydroxyapatite can be produced from natural materials that contain a lot of calcium in the form of calcium carbonate ($CaCO_3$) (Fitriawan et al., 2014), calcium nitrate ($Ca(NO_3)_2$), calcium hydroxide ($Ca(OH)_2$) (Agustiyanti et al., 2018), calcium acetate ($Ca(CH_3COO)_2$) (Henggu et al., 2019). Such as egg shells, gypsum, blood clams, quail shell (Ningsih et al., 2014), fish bones, beef bones (Fadhilah et al., 2016), buffalo bones, pearl oyster shell (Asril & Rahayuningsih, 2020), beef teeth, fish scales, catfish bones (Asril & Rahayuningsih, 2020), cuttlefish shells (Henggu et al., 2019), crab shells (Akbar et al., 2021). While the source of phosphate using diammonium phosphate ($(NH_4)_2HPO_4$), monobasic ammonium phosphate ($NH_4H_2PO_4$), dipotassium phosphate (K_2HPO_4), and phosphoric acid (H_3PO_4) (Henggu et al., 2019). The hydroxyapatite material used is usually quite expensive because the material is still imported and the price reaches 1 million per gram (Wahdah et al., 2014). One of the ingredients that have a high calcium content is chicken eggshell. According to data from the Directorate General of Livestock in 2014 it was 1,244,312 tons and an increase of 3.65% in 2015 to 1,289,716 tons (Yahya et al., 2016). The use of purebred chicken egg shells is only for making karabang flour, a mixture of animal feed, and craft materials. To increase the economic value of broiler egg shells, one of the efforts made is to utilize the calcium content in it (Agustiyanti et al., 2018). Chicken egg shells have a high calcium carbonate composition, which is 98.43% (Puspita & Cahyaningrum, 2017). High levels of calcium carbonate can be used as a source of calcium in the synthesis of compounds containing calcium metal, one of which is the synthesis of calcium phosphate as raw material for hydroxyapatite.

In this study, hydroxyapatite was synthesized using the precipitation method using broiler egg shells as raw material. Chicken egg shells are used as a source of calcium, while phosphoric acid (H_3PO_4) is used as a source of phosphate. The synthesis of hydroxyapatite can be carried out by several methods, namely the wet method and the dry method. Wet methods include precipitation, hydrothermal, and hydrolysis (Hanin & Sande, 2021). The method in this study uses the precipitation method, the precipitation method is a simple method that can produce mostly amorphous hydroxyapatite (Gago & Ngapa, 2021). Or it can be said that it requires a simple chemical reaction and the size and homogeneity of the particles obtained are quite good (Mangkuasih & Rohmawati, 2021). The advantages of this method are that it requires relatively low cost, uses easily available materials, and obtains high-purity hydroxyapatite (Yuliana et al., 2017).

Based on research by Pangestu et al. (2021) on snail shell material, it is known that snail shell contains 99.10% calcium composition. Furthermore, another study said that with baung fish bone material, the yield of calcium phosphate produced was 61.8% (Akbar et al., 2021). In the synthesis of hydroxyapatite, a calcination process is required in a furnace at a temperature of 900℃ for 4 hours. Calcination is needed to remove organic components and convert calcium carbonate compounds ($CaCO_3$) into calcium oxide (CaO) which is used as a calcium precursor and causes a decrease in mass (Wardiana & Cahyaningrum, 2019). After the calcination process is carried out, the synthesis process is continued by mixing the calcium and phosphate precursors used.

For the reactions that occur in the process of making calcium phosphate as raw material for hydroxyapatite, several stages occur, namely the calcination and synthesis stages, the reactions that occur are as follows:

- Calcination Stage

$$CaCO_3 \rightarrow CaO + CO_2 \quad (1)$$

(Wathi et al., 2014)

- Synthesis Stage

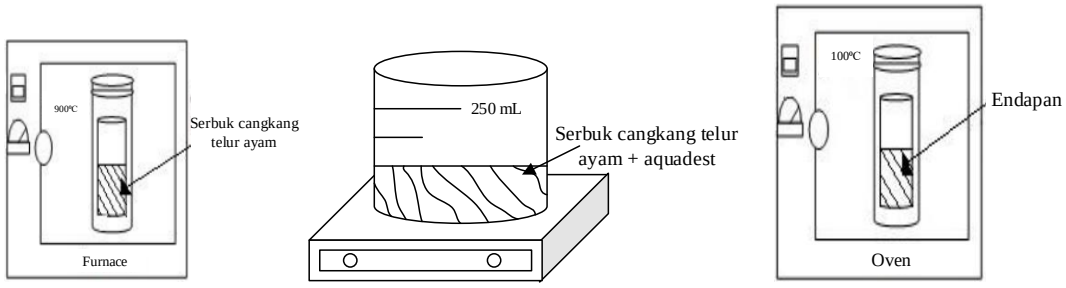
$$CaO + H_2O \rightarrow Ca(OH_2) \quad (2)$$

$$10Ca(OH)_{2(l)} + 6H_3PO_{4(l)} \rightarrow Ca_{10}(PO_4)_6(OH)_{2(s)} + 18H_2O_{(l)} \quad (3)$$

(Mohd Pu'ad et al., 2019)

Material and Methods

This research was carried out experimentally at the Advanced Materials Laboratory, Universitas Pembangunan Nasional "Veteran" Jawa Timur using the test equipment scheme shown in figure 1. The figure shows a schematic of the experimental equipment installation starting from the preparation of raw materials to the results used in the utilization of broiler eggshell waste to make calcium phosphate from broiler eggshells as raw material for hydroxyapatite.



(a) (b) (c)

Fig. 1 Process Set of Tools (a) Calcination, (b) Prepicipitation, (c) Hydroxyapatite synthesis

The material used in this study was chicken eggshell as a source of calcium ($CaCO_3$) obtained from the Blauran Baru market, Surabaya. Aquades (H_2O), Sodium Hydroxide (NaOH), and Phosphoric Acid (H_3PO_4) sources of phosphate. While the tools used are an analytical balance, furnace, magnetic stirrer, burette, and oven. Materials and tools were obtained from the Introduction to Chemical Engineering I Laboratory, Universitas Nasional Pembangunan "Veteran" Jawa Timur.

The conditions determined in this study were particle size through a 100 mesh sieve, calcination temperature of 900℃ with a time of 4 hours. The sample mass is 3.7 grams, the volume of H_3PO_4 is 150 mL, the stirring speed is 400 rpm for 3 hours, the pouring time is 24 hours, and the oven temperature is 100℃. As for the condition variables used in this study, namely variations in the concentration of phosphoric acid (0.2 M; 0.3 M; 0.4 M; 0.5 M; 0.6 M) with variations in pH (9, 10, 11 12 , 13).

To obtain calcium phosphate from the synthesis of broiler eggshells as raw material for hydroxyapatite with the precipitation method, two processes must be carried out, namely the calcination process as a pretreatment process for broiler eggshells, followed by a synthesis process as the process of forming raw materials in the form of purebred eggshell powder from the pretreatment process. to calcium phosphate. The calcination process was carried out by placing chicken eggshell powder with a particle size of 100 mesh to taste in a petri dish, after that it was put into a furnace with an operating temperature of 900℃ for 4 hours. After calcined, let the eggshell powder for a day first to be stable and at room temperature.

Followed by the synthesis process. After calcination, 3.7 grams of broiler eggshell powder was taken and dissolved with 100 ml of distilled water. Then it was mixed with phosphoric acid with a set concentration of phosphate (0.2 M; 0.3 M; 0.4 M; 0.5 M; 0.6 M) as much as 150 mL. Stirring was carried out at 400 rpm for 3 hours while adjusting the pH according to the conditions to be determined (9, 10, 11 12, 13), the solution was stirred at 400 rpm for 30 minutes. Let stand for 24 hours to facilitate the filtering process, the filtering process to separate the precipitate from the filtrate, the precipitate obtained is carried out the next process, namely in an oven at a temperature of 100 until the mass obtained is constant and calcium phosphate is obtained from chicken egg shells as raw material for hydroxyapatite.

Results and Discussion

The results of the calcination of broiler eggshell powder showed that the raw material became smoother and drier because of the release of carbon dioxide from the $CaCO_3$ compound into CaO and CO_2 at an operating temperature of 900℃. Then the calcined broiler eggshell powder was synthesized with phosphoric acid precursor and then the pH was adjusted using sodium hydroxide. The observations obtained are in the form of sediment and filtrate. In this study, an analysis of the raw materials and products produced, the raw material in the form of chicken eggshell powder was analyzed using the XRF (X-Ray Fluorescent) method, while the results or products produced were analyzed using the XRD (X-Ray Diffractor**)** and SEM (Scanning Electron Microscope**)** method.

XRF (X-Ray Fluorescent) analysis result

The analysis of the composition of the chicken eggshell powder using the XRF (X-Ray Fluorescent) method which aims to identify and determine the concentration of substances in the eggshell powder.

Table 1. Ingredients for chicken eggshell powder

Component	Concentration (% weight)
S	0,13
Ca	99,37
Fe	0,099
Co	0,088
Cu	0,03
Er	0,1
Lu	0,17

In the research on the synthesis of calcium phosphate from broiler egg shells after the raw material is calcined, the raw material is analyzed by XRF first to determine the composition of the chicken eggshell powder. As shown in the table above, chicken eggshell powder there contains calcium 99.37%. Based on the analysis results obtained, the calcium in the eggshell powder of broiler chicken can be synthesized using a phosphoric acid precursor to form calcium phosphate as raw material for hydroxyapatite.

SEM (Scanning electron microscope) analysis result

SEM analysis is used for material analysis, especially manometer-sized materials. So that the morphological shape of a material can be enlarged in resolution. SEM is a type of electron microscope that is capable of producing high-resolution images of a sample surface. Therefore the image produced by SEM has qualitative characteristics in two dimensions because it uses electrons instead of light waves and is useful for determining the surface structure of the sample.

The results of the SEM analysis above are the morphology of calcium phosphate crystals using the H_3PO_4 precursor with 1000 times magnification. Calcium phosphate from broiler egg shells produces irregularly sized particles of varying sizes. Some of the particles are plate-shaped. These particles generally agglomerate and collide with each other. For calcium phosphate from egg shells to produce monoclinic crystals in the form of dicalcium phosphate dihydrate (DCPD) with an average size of 100 m and small lumps with an average size of 2 m which are distributed quite well and some are agglomerates, in the crystal, there are no pores on its surface.

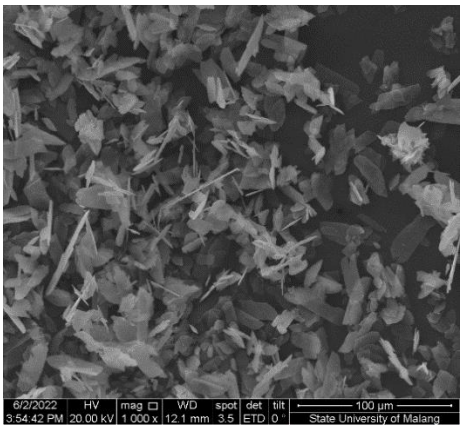


Fig. 2 Results of SEM Analysis of Calcium Phosphate from Chicken Egg Shells with H_3PO_4 Precursor with 1000x Enlargement

Based on the results of the SEM analysis above, shows that the shape of the resulting crystals is different, some crystals are well-distributed and some are lumpy. The difference in distribution could be due to the less-than-perfect deposition and stirring process during the formation of Calcium Phosphate. In addition, the calcination process carried out at high temperatures also gives a tendency for the particles to combine to form lumps.

XRD (X-Ray diffractor) analysis result

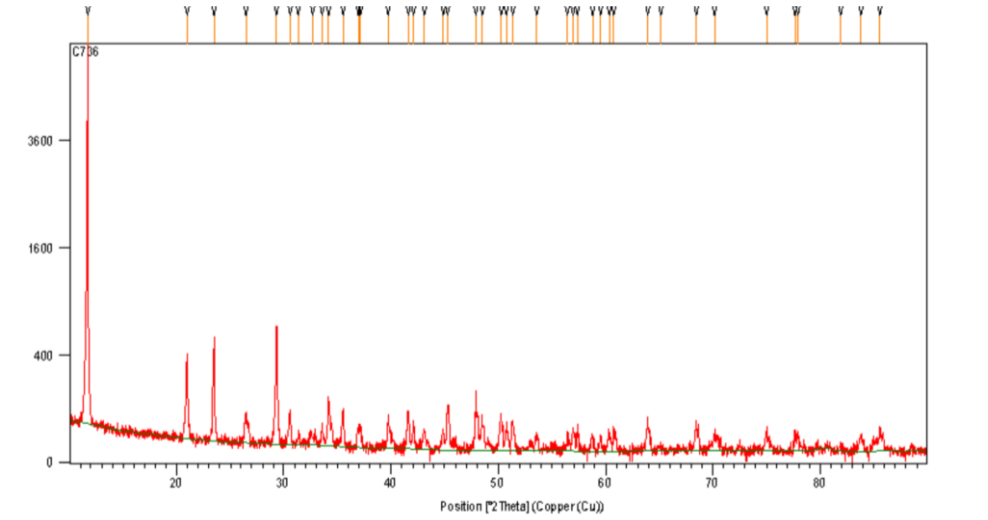


Figure. 3 XRD diffraction pattern of calcium phosphate from chicken egg shell with H_3PO_4 precursor

The picture above shows the results of the crystal composition of calcium phosphate at pH 9 and phosphoric acid concentration of 0.6 M. In the picture the XRD test was carried out at an angle of 2θ of (10-90)^o, and the results of the analysis showed that the sample was dominated by brushite. ($Ca(HPO_4).2(H_2O)$ by 100% or each component contains elements of O by 55.8% by weight, elements of Ca by 23.3% by weight, elements of P by 18.0% by weight, and elements of H by 2,9% by weight Brushite has a monetite-like structure namely calcium diphosphate ($CaHPO_4$) but contains water crystals.

Conclusion

From the results of SEM (Scanning Electron Microscope) analysis, it is known that calcium phosphate derived from the synthesis of broiler eggshell powder with phosphoric acid produces monoclinic crystalline particles in the form of dicalcium phosphate dihydrate (DCPD) with an average size of 100 μm and small lumps of the average size of 2 μm which is distributed quite well and some are clumped, the crystal has no pores on its surface and does not have an irregular shape and varies in size. Calcium phosphate can be synthesized from chicken eggshells which is a source of calcium obtained from XRF analysis, which is 99.37% with phosphoric acid as a precursor to being used as raw material for the manufacture of hydroxyapatite.

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