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Synthesis and Characteristics of Calcium Phosphate from White Mussel Shell

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Abstract

Biomaterials are materials that have been developed for repair, recovery of function, and replacement of diseased or damaged parts of the body especially in cases of fractures. The material for biomaterial that is commonly used is calcium phosphate ($Ca_3(PO_4)_2$). The purpose of this research is to synthesize calcium phosphate and study its characteristics. The source of calcium carbonate in this study was from white mussel shells. The experiment was carried out by reacting calcium carbonate ($CaCO_3$) and phosphoric acid (H_3PO_4) to form the liquid phase of calcium phosphate. The calcium phosphate solution was filtered and the filtrate obtained was added with a solution of NaOH as a pH controller, stirred using a magnetic stirrer in the time range from 10 to 50 minutes to form a calcium phosphate crystal. Filtration is carried out to separate the calcium phosphate crystals from the solution. The results showed calcium phosphate products containing 62% of β-dicalcium phosphate (β-$Ca_2P_2O_7$) and 38% of hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) so that it could be stated that the product was biphasic calcium phosphate. The raw material of white mussel shell powder was analyzed using X-Ray Fluorescence (XRF), while the calcium phosphate solution was analyzed by Spectrophotometry, Gravimetry, and AAS (calcium test). Hydroxyapatite products were analyzed by XRF, XRD (X-Ray Diffraction), FTIR (Fourier Transform InfraRed), and SEM (Scanning Electron Microscopy).

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Keywords: biomaterial, calcium phosphate, hydroxyapatite, white mussel

Introduction

Animal health management will help increase livestock production to the desired optimal extent. Production productivity is the achievement of beef cattle production which is expected to reach a certain average weight gain every day (ADG) (Fathurohman *et al.*, 2018).

Specially designed material has been developed for the repair, recovery of function, and replacement of diseased or damaged body parts such as in cases of fractures. This material is called a biomaterial. A biomaterial is a material that is used as a system in tissues, organs, or bodily functions as well as bone implantation which is expected to interact with tissue without any backreaction or rejection by the human body. In this case, it is necessary to have an ingredient that is expected to be an alternative to replace or speed up the process of repairing the damaged bone. Hydroxyapatite (HA) in powder form is often used in biomedical applications such as bone bioimplants (Ghosh *et al.*, 2008; Carrodeguas and Salvador, 2012; Borges *et al.*, 2015). This is because HA has excellent biocompatibility properties (the ability of the material to match the bone tissue in the body), bioactivity (the ability of the material to provide a suitable framework for bone formation), osteoconductivity, and the chemical elements and structure have

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similarities with natural bone minerals (Chaair *et al.*, 2017; Shahni *et al.*, 2012). In general, the biomaterial used is Calcium Phosphate ($Ca_3 (PO_4)_2$) because this material has a chemical composition that is close to the inorganic components that are in the bones (Yashima *et al.*, 2003; Franca *et al.*, 2014). Hydroxyapatite (HA) is an apatite mineral compound with the chemical formula $Ca_{10} (PO_4)_6 (OH)_2$ made with a Ca / P concentration ratio of 1.67 (Tas *et al.*, 1997; Jaw, 2006; Hung *et al.*, 2012; Zyman *et al.*, 2013; Xidaki *et al.*, 2018). In the HAp structure, there are two parts of the structure, hexagonal and monoclinic (Duncan *et al.*, 2014). The monoclinic structure is caused by the arrangement of OH- forming the OH-OHOH-OH sequence which makes the lattice parameter b be 2 times a. However, hexagonal structures can also be obtained under stoichiometric conditions if the OH arrangement is irregular (Kannan *et al*,.2010).

Various synthesis techniques, such as sol-gel synthesis, hydrothermal reaction, solid-state reaction, and chemical precipitation have been developed to synthesize HA powder (Tanimoto *et al.*, 2007; Eshtiagh-Hosseini *et al.*, 2008; Li *et al.*, 2009; Kanman *et al*., 2010; Kang *et al.*, 2017). Using this technique, powder with different morphology, stoichiometry, grain size, and crystallinity can be obtained. In the last two decades, the use of biogenic materials such as eggshells, shells, animal bones, and corals have been widely used. The use of biogenic materials is an interesting way to produce HA powder not only because it uses biogenic resources, but the economic and environmental benefits are obtained through waste recovery. In previous studies, white mussel shells were used as ingredients for the characteristics of β-Tricalcium phosphate by precipitation method (Li *et al.*, 2017). The results obtained from this study are the optimum β-tricalcium phosphate obtained with calcination temperature of 1000°C. Crystal structure of β-tricalcium phosphate formed by rhombohedral crystals and Fluorocence x-ray results obtained Ca / P 2.72 mol (Onoda and Nakanishi, 2012). In addition to using white mussel shells as a source of calcium, the hydroxyapatite can be synthesized using other raw materials such as biological waste, marine corals, eggshells, shells, and other bio-membranes.

This research develops the synthesis of Hydroxyapatite ($Ca_{10} (PO_4) 6 (OH)_2$) from white shells as a source of Calcium Carbonate ($CaCO_3$) which is then reacted with Phosphoric Acid (H_3PO_4) for the production of Hydroxyapatite (HA).

Research Method

Preparation of Hidroxyapatite

The raw of white mussel shell powder 50g which is the source of $CaCO_3$ is reacted with H3PO4, then the product will be in the form of the liquid phase. Phosphoric Acid 85% 34.5 ml diluted with demineralizing water up to 500 ml to obtain a concentration of H_3PO_4 3,375 N.

The formation of HA follows the reaction:

$$10CaCO_3 (s) + 6 H_3PO_4 (l) \rightarrow (Ca_{10} (PO_4) 6 (OH)_2) (l) + 8H_2O (l) + 10CO_2 (g)$$

Thydroxyapatite formed is then filtered to separate solids and filtrate. The filtrate obtained is then stirred using a magnetic stirrer with reaction time in the range of 10,20,30,40, and 50 min, then NaOH solution is added as a pH controller in the range 5,6,7,8, and 9 to form precipitates in the form of crystals HA ($Ca_{10} (PO_4) 6 (OH)_2$). Furthermore, the mixture is filtered to separate HA crystals and filtrate. The precipitation reaction follows the reaction:

$$(Ca_{10} (PO_4) 6(OH)_2) (l) + 3H_2O (l) \rightarrow (Ca_{10} (PO_4) 6(OH)_2) (s)$$

The filtered HA crystals are dried in an oven at 100 C for 24 h and then HA crystals that are already dry enough are burned in a furnace at 800 C.

Characteristic

The analysis was performed on the ingredients of white mussel shell powder and the resulting product. To find out the composition of raw materials analyzed using XRF (X-Ray Fluorescence) method, while the results of mixing white shell powder with phosphoric acid (in the form of filtrate) were analyzed by Spectrophotometry (Phosphor test as PO4), Gravimetry (phosphate test) and AAS (phosphate test) calcium). The resulting product is then analyzed by XRF (X-Ray Fluorescence), XRD (X-Ray Diffraction), FTIR (Fourier Transform InfraRed), and SEM (Scanning Electron Microscopy) methods.

Result and Discussion

Analysis of the composition of white mussel shells used in this experiment was carried out using XRF (X-Ray Fluorescence) with the results presented in Table 1.

Table 1. Composition of white mussel shells

No	Component	Concentration (%w)
1.	Al	0,8
2.	S	0,081
3.	Ca	96,98
4.	Ti	0,05
5.	Mn	0,18
6.	Fe	0,91
7.	Cu	0,083
8.	Zn	0,11
9.	Br	0,01
10.	Sr	0,73

The results of the analysis of calcium phosphate solution (filtrate) using AAS revealed that the calcium (Ca) mole concentration was 0.0165 and using spectrophotometry for the phosphor (P) was 0.0187 mole.

Effect of pH

Figure 1 showed the effect of pH on the Ca/P ratio on various reaction times. The results showed that there were various doses of the use of NPK fertilizer and organic fertilizer doses which could increase NPK fertilizer by several percents, depending on the level of use of inorganic fertilizers.

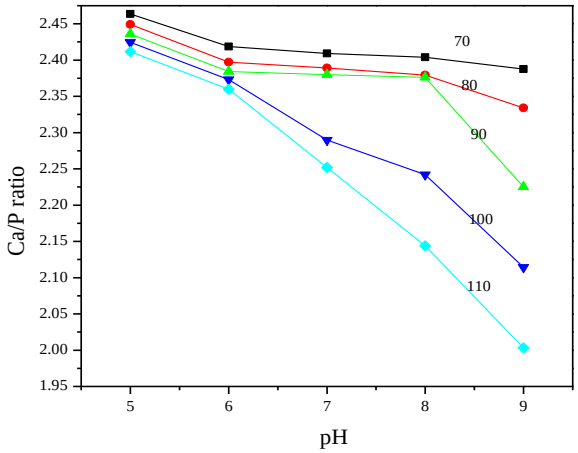

Figure 1. Effect of pH on Ca/P ratio

The mole ratio of Ca / P in HA products tends to decrease with increasing pH. Decreasing the mole ratio of Ca / P is influenced by the solubility of Ca and P in water. The higher the pH, the solubility of Ca, and P decreases. The decrease in P solubility tends to be greater than the solubility of Ca. That's because the rate of precipitation of P increases with increasing pH. Therefore, more P solids are formed than Ca, so the mole ratio of Ca / P is reduced.

Characteristic of Calcium Phosphate from white mussel shell

Characterictic of XRD

The results of XRD analysis for product samples at pH 6, reaction time of 100 minutes, and a temperature of 800 C showed that the percentage of calcium phosphate was 64% and HA 36%.

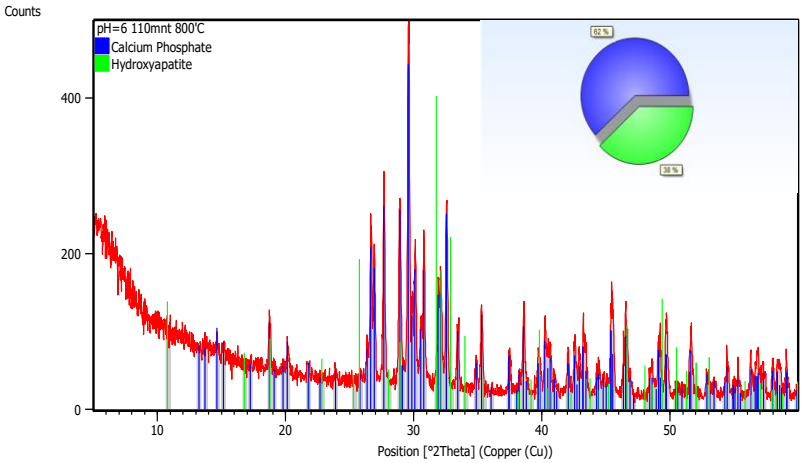

Figure 2. XRD for Calcium Phosphate at 800 °C

To identify the resulting phase is done by comparing the sample data XRD analysis results against JCDPS for Calcium Phosphate and Hydroxyapatite (HA). The results showed that the sample was dominated by Calcium Phosphate type β-Dicalcium Diphosphate (β-$Ca_2P_2O_7$) of 62%, and

Hydroxyapatite (HA) of 38%. It can be stated that the product produced is Biphase Calcium Phosphate (Franca *et al.*, 2014).

Characterictic of IR Spectra

Calcium Phosphate compounds contain several functional groups namely OH^-, PO_4^{3-}, CO_3^{2-} and other functional groups. Figure 3 shows IR spectra for calcium phosphate products. Samples containing OH- functional groups at wave number 3400 cm^{-1}; the C-O function group at the wave number 1208.18 cm^{-1}; $PO4^{3-}$ functional group at wave number 914.44 cm^{-1}, and $P_2O_7^{4-}$ functional groups at wavenumbers 723.17 cm^{-1}.

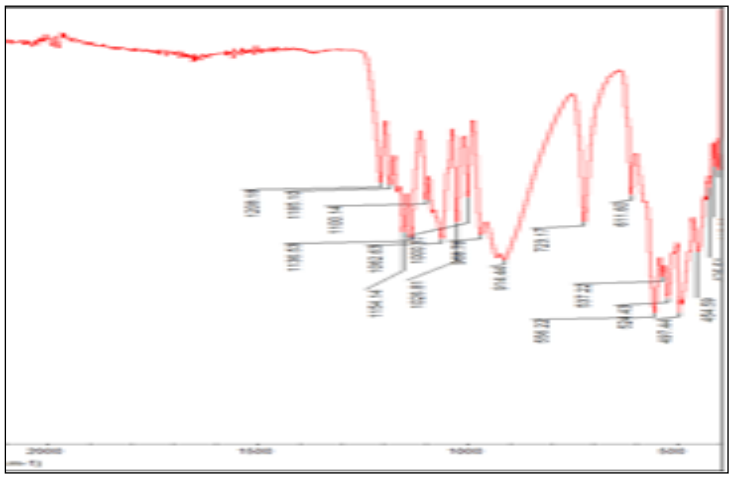

Figure 3. IR Spectra for Calcium Phosphate at 800 °C

Characterictic of SEM Image

Figure 4 showed the results of SEM of calcium phosphate samples.SEM image showed that calcium phosphate is in the form of large particles with an average diameter of 10μm and small particles with an average size of 2 μm. The particles are arranged into a coarse aggregate.

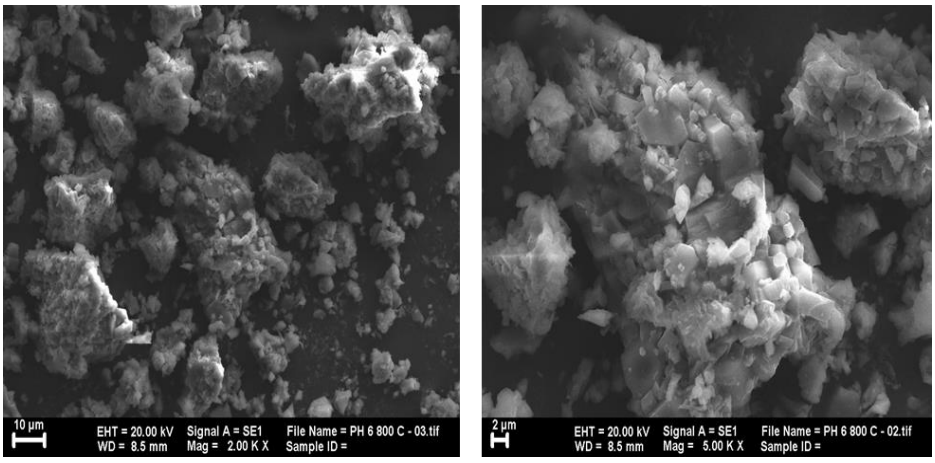

Figure 4. IR SEM image Calcium Phosphate product at 800 °C

Conclusion

The results showed that the problem of miscarriage or brucellosis often

The results of the study can be concluded that:

1. Synthesis of Calcium Phosphate from white shells with a Ca / P mol ratio of 0.88 has been successfully carried out and produces calcium phosphate which has Ca / P in the range of 2 - 2.4.
2. The length of time of stirring causes the mole ratio of Ca / P to decrease.
3. Products are dominated by Calcium Phosphate type β-Dicalcium Diphosphate (β-Ca2P2O7) of 62%, and HA of 38%. Thus, it can be concluded that the product produced is Biphase Calcium Phosphate.
4. β-Dicalcium Phosphate produced has an average size of 2μm-10 μm.
5. Samples contain functional groups OH-, C-O, PO43-, and P2O74-. which indicates the presence of Calcium Diphosphate or Calcium Pyrophosphate (C2P2O7). The provision of bio-sensitive vermicompost combined with a reduction in NPK fertilizers has produced unreal results on the growth and yield of soybean crops.

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