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Effect of Calcination Temperature Variation on Hydroxyapatite of Cuttlefish Shell Waste (Sepia Sp.)

S. Nurrahmi*, N. Fuadi, Jumardin, F. Yurdanianti
Universitas Islam Negeri Alauddin Makassar

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Abstract

This study aims to determine the effect of calcination temperature variations on hydroxyapatite from cuttlefish shell waste. Synthesis of hydroxyapatite compounds was carried out by mixing calcium precursors obtained from cuttlefish shell waste and phosphate precursors. Extraction of calcium carbonate (CaCO3) into calcium oxide (CaO) using the calcination method with temperature variations 600□C, 800□C, and 1000□C for 5 hours. The results showed that calcination temperature affects the synthesis of hydroxyapatite compounds. Based on FTIR characterization, the optimum calcination temperature is at 1000°C. Based on SEM analysis result, hydroxyapatite particles from cuttlefish shells appear homogeneous with an average particle diameter of 0.57 µm. EDX result shows that Ca/P ratio of hydroxyapatite from cuttlefish shell waste is 2.08. It can be concluded that the cuttlefish shell waste in this study can be used for biomedical applications, such us a bone implant material because it has a Ca/P ratio of more than 1 so it is not easily dissolved and can be accepted by the body.

*) e-mail: sitti.nurrahmi@uin-alauddin.ac.id

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1. INTRODUCTION

Indonesia is an archipelago with the largest number of islands in the world. Data from the Geospatial Information Agency (BIG) in 2020 shows that Indonesia has 16,771 islands. Thanks to the large number of islands, Indonesia is a source of foreign exchange for the maritime industry. This can be seen from the abundance of marine products such as fish, lobster, sea cucumber, squid, cuttlefish etc. Because it can be used as seafood, the wealth of the marine sector is also a leading export commodity for the world community, one of which is cuttlefish (Sepia sp.). According to 2020 data from the Ministry of Maritime Affairs and Fisheries (KKP), the export value of squid, cuttlefish and octopus (CSG) is $509 million relative to the value of world CSG imports. Both fresh, frozen and other forms of cuttlefish for the development of the maritime industry. However, in the processing process only cuttlefish meat is utilized, while the shell is industrial waste.
Research states that the inorganic elements of cuttlefish shell waste are 75-90%, most of which are calcium carbonate (CaCO3) [1]. Therefore, a solution is needed to utilize this waste into something that has more value. In the synthesis of hydroxyapatite, utilizing cuttlefish shell waste as a source of calcium carbonate (CaCO3) is one of the efforts so that the waste is not wasted [2].

Hydroxyapatite is the main component of bone minerals and can be used as a biomaterial because it is a ceramic material with stable chemical properties compared to metal and polymer materials, is bioactive and biocompatible and non-toxic [3]. Since hydroxyapatite has so many uses in the healthcare industry, the demand for hydroxyapatite is increasing. Hydroxyapatite synthesis is usually done using synthetic chemicals. The use of synthetic chemicals in the hydroxyapatite synthetic process affects the price of hydroxyapatite, the market price of hydroxyapatite in Indonesia is 1.5 million per 5 milligrams and its availability still depends on imported products. Thus, biomaterials from natural materials are needed that can replace synthetic hydroxyapatite, in order to obtain hydroxyapatite at a lower price but with the same or even better quality. With the abundant availability of cuttlefish shell waste and its advantages, cuttlefish shell waste was chosen as a source of hydroxyapatite in this study.

Hydroxyapatite has been studied for many years and is widely used for the manufacture of implants due to its similarity to the mineral phase of bone and is proven to be biocompatible with human bones and teeth. Many studies have shown that hydroxyapatite does not show toxicity, inflammatory response, pyrogenetic response. In addition, the formation of fibrous tissue between the implant and bone is excellent, has the ability to bond directly with the host bone, and is bioactive and osteoconductive. Bioactive and osteoconductive properties can stimulate bone cells around the implant material to infiltrate so as to accelerate the process of mineralization of new [4].

Several researchers have conducted research on the synthesis of hydroxyapatite from cuttlefish shell waste including [5] . The results of the synthesis show that using XRD, cuttlefish shells both calcined at 800□C and 1000□C each have one phase which is a hydroxyapatite compound (Ca5(PO4)3(OH)). Whereas in samples using synthetic calcium carbonate (CaCO3), three phases were obtained, namely calcium oxide (CaO), hydroxyapatite (Ca5(PO4)3(OH)), and magnesium oxide (MgO) compounds, of which CaO and MgO are the more dominant phases formed compared to hydroxyapatite compounds. So it can be concluded that calcium contained in cuttlefish shells can be used as hydroxyapatite material.

Furthermore, [2] have also conducted research on hydroxyapatite from cuttlefish shells as a bone scaffold biomaterial preparation, combining hydrothermal and calcination methods to synthesize cuttlefish shells into hydroxyapatite material. The results showed that the optimum condition for extracting calcium oxide from cuttlefish shells was calcination treatment at 700°C for 6 hours, which was characterized by the absorption of functional groups at wavelengths of 1,654; 1,468; 1,116 and 875 cm-1. The characteristics of hydroxyapatite selected with a combination of hydrothermal and calcination at an optimum temperature of 1,000 °C for 1 hour which has a calcium phosphate (Ca/P) ratio of 1.66, crystallinity level of 90.10%, amorphous 9.90 and rod-shaped particle morphology, although the value obtained has not met the 2015 International Organization for Standardization (ISO) 13175 standard, which requires a hydroxyapatite Ca/P ratio of 1.67 and hydroxyapatite crystallinity of 95% [6].

In the process of producing cuttlefish as hydroxyapatite, calcination temperature greatly affects the quality of hydroxyapatite produced. However, there is no optimal calcination temperature that produces the best hydroxyapatite according to the International Organization for Standardization (ISO) 13175 2015 standard, which requires a hydroxyapatite Ca/P ratio of 1.67 and hydroxyapatite crystallinity of 95% [2]. Thus, research was conducted on calcination temperature variations in cuttlefish shell waste (Sepia sp.) hydroxyapatite.

Based on the above, a study was conducted to see the effect of calcination temperature on hydroxyapatite from cuttlefish shell waste, using Fourier Transform Infra Red (FITR) characterization to see the functional groups contained in hydroxyapatite from cuttlefish shell waste, Scanning Electron Microscope (SEM) to see surface morphology and particle size, and Energy Dispersive X-ray (EDX) to determine the elemental composition of the material contained in hydroxyapatite from cuttlefish shell waste.

2. MATERIALS AND METHOD

This research uses a combined method, namely the calcination method and precipitation method to produce hydroxyapatite from cuttlefish shells. The tools used in this research include oven, furnace, Whattman filter paper no 42, crucible, magnetic stirrer, pH meter, beaker glass, cup, funnel, erlenmeyer, pipette, spatula, electric balance. The materials used are cuttlefish shell waste (Sepia sp.), KH2PO4, NaOH, and distilled water. The characterization tools used are FTIR and SEM/EDX.

The research steps include washing the cuttlefish shells obtained then soaking them in distilled water for 30 minutes to clean the remaining dirt. Next, dry the soaked cuttlefish shells at room temperature for 24 hours. After drying, crush the cuttlefish shells using a mortar and pestle. Furthermore, the extraction of calcium carbonate (CaCO3) from cuttlefish shells is carried out using the calcination method. The dried cuttlefish shells were calcined using a furnace with temperature variations of 600□C, 800□C, and 1,000□C for 5 hours respectively. After extraction, CaO powder was obtained from cuttlefish shell waste. Furthermore, hydroxyapatite synthesis from cuttlefish shells was carried out by dripping 50 ml of KH2PO4 solution (0.3 M) on CaO solution (0.5 M) using a magnetic stirrer on a hot plate at 37□C with a speed of 700 rpm for 3 hours using the precipitation method. Next, dry the precipitate using a furnace at 1000□C for 1 hour. After the drying process, a white powder was obtained to be characterized by FTIR and SEM-EDX.

3. RESULTS AND DISCUSSION

Hydroxyapatite is the main material that makes up bone with the chemical formula $Ca_5(PO_4)_3OH$. Hydroxyapatite is one of the calcium phosphate compounds that can be utilized as a bone scaffold biomaterial because it is a ceramic material that has chemically stable properties compared to metal and polymeric materials, is bioactive and biocompatible, and is non-toxic [7].

In the synthesis of hydroxyapatite compounds can be done by mixing calcium precursors and phosphate precursors [8]. In this study, calcium precursors were obtained from cuttlefish shells which contain inorganic elements in the form of calcium carbonate ($CaCO_3$) by 85% and in the synthesis of hydroxyapatite has the potential as a source of calcium oxide (CaO) which is a calcium precursor [2]. Extraction of calcium carbonate ($CaCO_3$) into calcium oxide (CaO) using the calcination method with temperature variations of 600°C, 800°C, and 1000°C for 5 hours.

In the study of hydroxyapatite synthesis using cuttlefish shell waste, characterization was carried out using FTIR and SEM-EDX. FTIR characterization was carried out to see the functional groups of hydroxyapatite from cuttlefish shell waste. Functional groups are carried out to determine the structural decomposition of $CaCO_3$ to CaO [2]. This structural decomposition process is based on changes in transmission intensity and absorption regions due to bond breaking.

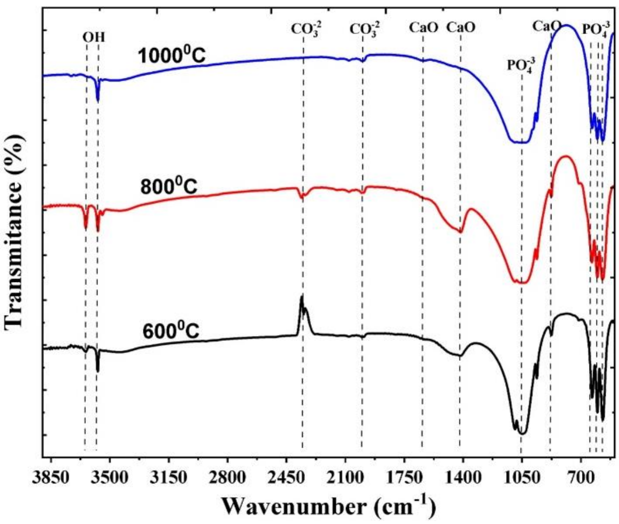

Figure 1. FTIR spectra of cuttlefish shells at calcination temperatures of 600°C, 800°C, and 1000°C.

FTIR characterization results can be seen in Figure 1. Absorption transmission at calcination temperature of 600°C shows split inplane bending vibration of phosphate ion (PO43-) at wave numbers 570, 602, and 632 cm-1, streching vibration of assimmetryc carbonate ion (CO32-) at wave numbers 2002 and 2347 cm-1, and symmetric streching vibration of CaO at wave numbers 1048, 1091, 1420 cm-1. The absorption transmission at 800°C calcination temperature shows the inplane split bending vibration of phosphate ion (PO43-) at wave numbers 571, 602, and 634 cm-1, the assimmetryc streching vibration of carbonate ion (CO32-) at wave numbers 2003 and 2361 cm-1, and the symmetric streching vibration of CaO at wave numbers 1049, 1091, 1414 cm-1. Meanwhile, the absorption transmission at calcination temperature of 1000°C shows the inplane split bending vibration of phosphate ion (PO43-) at wave numbers 570, 602, and 632 cm-1, the assimmetryc streching vibration of carbonate ion (CO32-) at wave numbers 2002 and 2078 cm-1, and the symmetric streching vibration of CaO at wave numbers 981, 1025, 1638 cm-1. According to [9] the main characteristics of cuttlefish shell CaCO3 were identified in the range of wave numbers 2876, 2515, 1800 and 712 cm-1. The presence of carbonate vibrations in the wavelength range is thought to be type A CO32- pnalar vibrations. [10] stated that type A CO32- pnalar vibrations are generally in the range of 1650-2330 cm-1, but at 1000°C calcination treatment some of the CaCO3 structure has been decomposed into CaO.

SEM or Scanning Electron Microscope is a tool that can be used to see the surface morphology of a material. This tool works by using electrons for the imaging source and electromagnetic field for the lens. SEM can be equipped with EDX or Energy Dispersive X-ray to determine the elemental composition of the material. SEM-EDX results are in the form of graphs that are analyzed for characterization based on the intensity peak or quantity of elements. Then the comparative value or ratio of the elements contained therein is calculated.

SEM results in Figure 2 show that the surface of hydroxyapatite powder from cuttlefish shells is regular granular. The granular shape indicates the growth of hydroxyapatite crystals. In addition to the surface, the particle size was also observed. Hydroxyapatite particles from cuttlefish shells appear homogeneous with an average particle diameter of 0.57 µm. This small particle size will be beneficial to increase the bioactivity of hydroxyapatite [11]. The smaller the particle size, the larger the surface area. Thus, the bond between hydroxyapatite and surrounding tissue when applied will also increase [12].

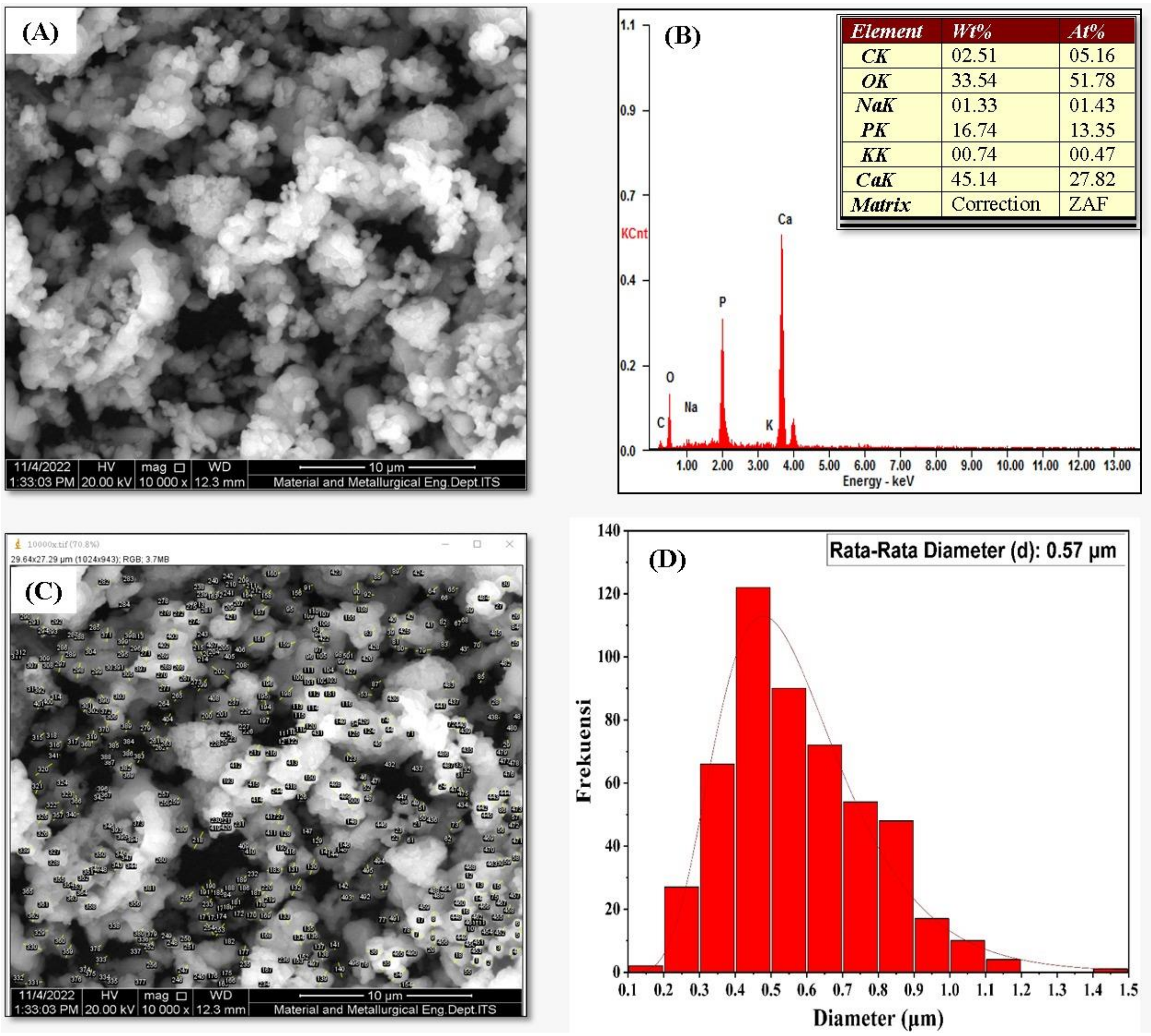

Figure 2. SEM-EDX analysis results of cuttlefish shell hydroxyapatite at 1000°C calcination temperature treatment (A) SEM results with a magnification of 10,000 times (B) EDX results at a magnification of 10,000 times (C) Calculation of sample diameter size using Image-J software (D) Gauss distribution of sample diameter measurement results.

Ca/P ratio is one of the important parameters in calcium orthophosphate compounds. The lower the Ca/P ratio value, the more acidic and soluble it will be. Therefore, cuttlefish shell powder can be used for biomedical applications, one of which is as a bone implant material because it has a Ca/P ratio of more than 1 so that it is not easily soluble and can be accepted by the body [13] . However, the cuttlefish shell in this study has a Ca/P ratio value of 2.08 above the theoretical value of 1.67. This is because the cuttlefish shell powder still contains CaO which will increase the calcium value in the synthesis [14]. Therefore, it is recommended to increase the temperature and prolong the reaction time to obtain purer hydroxyapatite [15] .

4. CONCLUSION

Calcination temperature affects the synthesis of hydroxyapatite compounds. Based on the results of FTIR characterization, the optimum calcination temperature is at 1000°C. Based on the results of SEM analysis, hydroxyapatite particles from cuttlefish shells appear homogeneous with an average particle diameter of 0.57 µm. EDX characterization shows that the cuttlefish shell in this study can be used for biomedical applications, one of which is as a bone implant material, because it has a Ca / P ratio of more than 1 so that it is not easily dissolved and can be accepted by the body. The Ca/P ratio of cuttlefish shell at a calcination temperature of 1000°C has a Ca/P ratio value of 2.08 above the theoretical value of 1.67. This is because the cuttlefish shell powder still contains CaO which will increase the calcium value in the synthesis.

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