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Synthesis of Hydroxyapatite Bioceramic from Cuttlefish Shell Waste and Coral Using Microwave Hydrothermal

N. Nurbaiti[a,b], M. K. Herliansyah*[a], A. E. Tontowi[a], M. G. Widiastuti[c], H. V. Hoten[a,b]

[a] *Mechanical and Industrial Engineering Department, Universitas Gadjah Mada, Yogyakarta, Indonesia*
[b] *Mechanical Engineering Department, Universitas Bengkulu, Indonesia*
[c] *Oral and Maxillofacial Surgery Department Gadjah Mada, Yogyakarta, Indonesia*

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ABSTRACT

Indonesia is an archipelagic country with two continents and an ocean, where it produces abundant marine products and the second largest marine source in the world, such as cuttlefish. Besides, it was for food, cuttlefish also produced shells as waste. Actually, this waste has been used for animal feed but in small scale. Others are still waste and cause pollution if not handled properly. Cuttlefish shell waste (CSW) is the basic ingredient for making hydroxyapatite (HA), while it was the main bone compound. Meanwhile, HA demand in the market is very high due to bone defects. The novelty of the research was to fulfil the increasing need for HA at low price and prevent air, water, and soil pollution by using circular economic principles (reused), and it has economic value. Synthesis HA was used microwave hydrothermal method. The CSW and coral were obtained from the pet market in Yogyakarta. They were crushed and calcined to the temperature of 900°C to obtain calcium oxide (CaO). Then, CaO was synthesized by microwave hydrothermal to obtain HA powder. Synthetic HA was characterized by the Fourier transform infrared (FTIR), X-ray diffraction (XRD), scanning electron microscope (SEM), energy dispersive X-ray (EDX), and thermogravimetric analysis (TGA). The Ca/P ratio of HA CSW and coral are 1.7 and 1.87, respectively. Moreover, coral HA has higher crystallinity than CSW (48%). The TGA shows that the highest weight loss occurred in HA CSW (16.57%). The conclusion is that both CSW and coral are raw materials used to produce HA.

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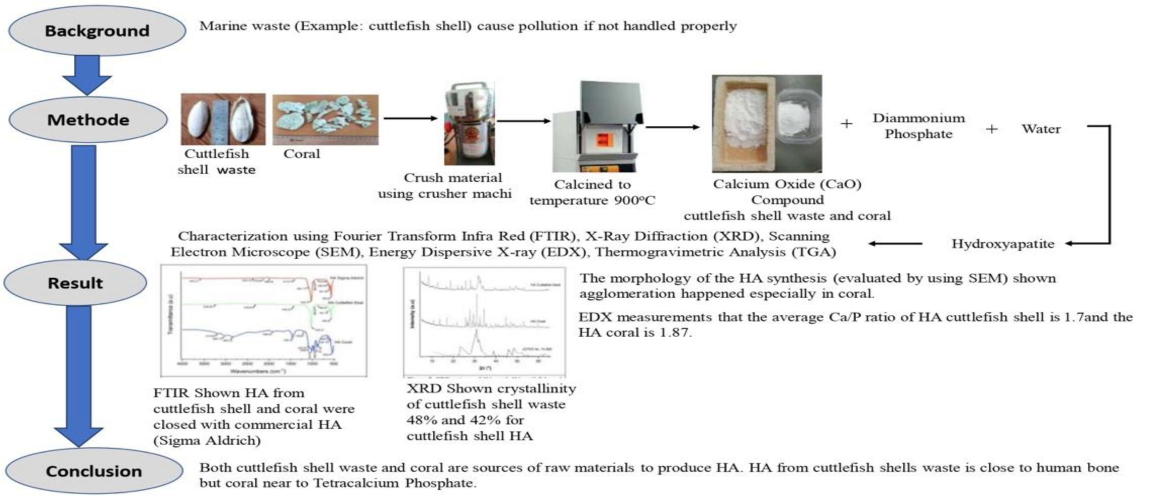
Graphical Abstract



*Corresponding Author Email: herliansyah@ugm.ac.id (M. K. Herliansyah)

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1. INTRODUCTION

Indonesia is an archipelagic country with more than 17,000 islands (1, 2). The country is a megadiverse transcontinental country enriched with unique fauna scattered between the Pacific and Indian oceans and Asian and Australian continents (3). Indonesia has the second largest marine source in the world (4). One marine resource used in large quantities in the food industry is cuttlefish. However, shells are discarded as waste after use (5). There are 6-8 million tons of shell waste annually (6).

Cuttlefish shell (CS) is a widely available and inexpensive material (7). It can cause soil, water and air contamination. It is estimated that consumption of natural resources, including cuttlefish waste, will increase in 2050, with the estimated world population reaching 9.8 billion (8). Moreover, an estimated two-thirds of the global population will live in cities, consuming 75% of the world's natural resources and producing 50% of global waste (9). Therefore, to overcome this waste problem, the principles of reduction, reuse, and recycling must be used, which is known as circular economics (CE) (10, 11). It eliminates traditional economic principles or linear economy, namely take, make, and dispose (12). Using CE will maximize the usage of agricultural waste, which can contribute to environmental preservation and improve economic conditions by generating income (13). The waste materials are biodegradable, biocompatible, and less toxic (14).

The cuttlefish shell has a porous structure and consists of organic groups such as peptides, polypeptides, proteins, polysaccharides, and lipids (15). It is composed of organic (3-4.5 wt.%) and it has 93% porosity (5). It consists of 95-98% calcium carbonate ($CaCO_3$), while the shells constitute about 59-75% of the total weight of the organism (16). In fact, CS waste is used for animal feed but in small quantities (17). Others, it can be used to produce large quantities of Hydroxyapatite (HA), which is the result of $CaCO_3$ synthesis (15). Meanwhile, commercially available $CaCO_3$ is expensive (18) .

Hydroxyapatite is a bioceramic material that is made of inorganic and bioactive materials (19–21). It is used as substitute material in the biomedical field, such as bone substitutes, bone fillers, drug delivery agents, and dental implants. Synthetic HA ($Ca_{10}(PO_4)_6(OH)_2$) chemically resembles the naturally occurring mineral phase of bone and it is used clinically as a bone substitute material (22, 23). The need for HA will increase due to disease, osteoporosis and bone injuries. Bone injuries are caused by accidents, old age, and mechanical strikes (24). Around 4 million bone grafting or bone substitutes are used for surgeries every year to treat bone defects (25). More than 9 million osteoporotic fractures occur every year globally (26). Injuries occurring in earthquake victims are one of the uses of HA. In Yogyakarta, Java, Indonesia earthquake that occurred on May 27th 2006, injured more than 36,000 people (1).

There are some methods to synthesis HA, namely wet chemical methods precipitation, electrodeposition, biomimetic deposition, hydrothermal method, and sol-gel method. The hydrothermal method has the advantages of more crystallinity, good homogeneity, and direct and straightforwardness, which gives all the characteristics (27). It is the main component of bone (around 70%) (28). Sources of synthetic HA come from natural bone ash, eggs, mussels, or sea shells, which can show better biological properties due to the presence of beneficial cations such as Na^+, K^+, Mg^{2+}, Sr^{2+}, Zn^{2+}, and Al^{3+} or anions such as F^-, Cl^-, SO_4^{2-} and CO_3^{2-}or the presence of both is proven (27). The ratio of calcium/phosphorus (Ca/P) of HA is between 0.5 and 2. Then, the Ca/P ratio of 1.67 is the stoichiometric ratio of good for biocompatibility (29, 30).

Some researchers conducted a study to synthesis HA from the CS using hydrothermal. Tkalčec et al. (31) were investigated the phase composition, crystal structure and morphology of synthetic HA from cuttlefish using the hydrothermal method. It shows that the synthetic HA from cuttlefish shell was successfully made and stable until 1300ºC. Additional heat treatments can be used to obtain carbonated hydroxyapatite with the desired chemical composition and specific structural and microstructure features. Furthermore, HA is compatible with osteoblast cells, has an ideal pore size and supports biological activities such as bone growth and vascularization. Moreover, it has an excellent proliferation of osteoblasts.

Neto et al. (32) studied calcium phosphate from cuttlefish shell (hydrothermal method), sintered process and coated with poly(ε-caprolactone) (PCL) or poly(DL-lactide) (PDLA), and a poly(ester amide) (PEA) or a poly(ester urea) (PEU). Regarding in vitro results, it shows that the scaffold is promising for bone tissue engineering.

Scaffolds must repair possess an open pore and are fully interconnected with a highly porous structure, allow cell in-growth, facilitate the neovascularization of the construct from the surrounding tissue, diffusion of nutrients and gases and the removal of metabolic waste resulting from the activity of the cells (33, 34). Moreover, the pore size for bone tissue engineering should range 200–900 µm (35). The pore size required by osteoblasts is 200 µm (36). Porosity is inversely proportional to mechanical properties, whereas increasing the porosity of material will cause a decrease in mechanical properties (37). The mechanical properties, such as tensile strength and compressive strength of bone tissue engineering, are similar to native bone. In the cortical bone, tensile strength and elastic modulus are 49-114 MPa and 3.9-11.7 GPa, respectively. Furthermore, the tensile strength of the trabecular bone is 2-11 MPa (38).

The purpose of the research was to fulfil the increasing need for HA due to bone defects such as osteoporosis and fractures that cause accidents and natural disasters. Furthermore, the synthesis of HA using hydrothermal was an alternative to getting HA at a low price because producing HA with chemicals impacts the price (2). Moreover, it was used to prevent air, water, and soil pollution using circular economic principles (reused), and it has economic value. The synthesis of coral into HA was carried out by comparing it with cuttlefish shell waste.

2. METHODS

2. 1. Material Preparation Cuttlefish shell waste and coral were purchased from PASTY (Yogyakarta Animal and Ornamental Plants Market). The waste of cuttlefish is in the shells. It was raw material, as shown in Figure 1. Diammonium phosphate ($(NH_4)_2HPO_4$), M-132.05, Merck, Germany) was used for the chemical reaction. The experiment was carried out at the Materials Laboratory and Product Design Laboratory, Department of Mechanical and Industrial Engineering, Universitas Gadjah Mada (DTMI UGM) and Engineering Riset and Innovation Center Universitas Gadjah Mada (ERIC UGM) Yogyakarta with the following steps: material preparations, calcination, synthesis HA and characterization.

2. 2. Calcination Process Cuttlefish shell waste and coral were cleaned using water. Then, it was dried under direct sunlight for about 5 hours. The material was crushed using a crusher machine until in powder form. Cuttlefish shell waste and coral powder were then calcined at 900ºC for 5 hours with a temperature rate of 5ºC. This temperature will remove the organic content in the coral and cuttlefish shell. Furthermore, it was held for approximately 2 hours (120 minutes). This process is carried out to ensure that organic compounds are removed completely. The calcination process was carried out in an air-exposed oven (Carbolite Merk, RHF 16/3 type with a maximum temperature of 1600ºC). Moreover, for the calcination chamber to be free from gas and contamination, pressurized air was blown to the inside of the oven using a compressor. Furthermore, the cuttlefish shell powder and coral were put into the oven.

Figure 1. Raw material from waste (a) cuttlefish shell (b) coral

2. 3. Synthesis HA The hydroxyapatite process was carried out by a chemical reaction between calcium oxide (CaO) powder and water. Regarding the chemical reaction, HA ($Ca_5(PO_4)_3(OH)$), NH_4OH and H_2O will be produced. The reaction process is carried out using a hotplate magnetic stirrer. The chemical reaction that occurs is expressed in Equation 1.

$$5\mathrm{CaO} + 3(\mathrm{NH_4})_2\mathrm{HPO_4} + 2\mathrm{H_2O} \rightarrow \mathrm{Ca_5(PO_4)_3}OH + 6NH_4OH \quad (1)$$

There are several steps involved in HA synthesis. Firstly, 100 ml of distilled water was put into the reaction glass and heated on a magnetic stirrer hotplate (temperature 105ºC and rotation 200 rpm). Then, 14.02 grams of CaO (the calculation results to get 1/20 part of hydroxyapatite) were added to the distilled water reaction glass. Additionally, the $(NH_4)_2HPO_4$ (19.8 grams). After mixing the ingredients, the solution was left until precipitation HA formed. This process takes approximately 45 minutes. Finally, the HA precipitate was put into the incubator for approximately 24 hours at a temperature of 60ºC. This aim was to remove the liquid still present in the HA, and the form of HA was in the fine powder.

2. 4. Characterization of HA Characterization of HA was carried out using the Fourier transform infrared (FTIR), X-ray diffraction (XRD), scanning electron microscope (SEM), energy dispersive X-ray (EDX) and thermogravimetric analysis (TGA). FTIR (Shimadzu) spectroscopy was used to identify the composition of hydrogen bonds and functional groups with transmittance mode using 46 acquisitions recorded in the range of 500 to 4000 cm^{-1}. The crystalline structures of $CaCO_3$ and HA were characterized by using an X-ray diffractometer (Malvern Panalytical, The Netherlands). The characterization was performed using Cu− Kα radiation (λ = 0.154 nm) in the range of 2θ = 10−65°. The speed used was 0.1°/min, operating at 40 kV and 30 mA. The surface morphology of HA was visualized using a scanning electron microscope (JEOL, JXA-ISP100 Electron Probe Microanalyzer (EPMA)) with an accelerating voltage of 0.3–30 kV. The SEM was partnered with an energy dispersive X-ray spectrophotometer (EDS, (JEOL, JXA-ISP100 Electron Probe Microanalyzer (EPMA)) for elemental analysis with the following scanning parameters voltage 15.0 keV and magnification 100x. Thermogravimetric analysis (NetzschSTA 449F3, Germany) was used to evaluate the thermal resistance of HA. The sample was put inside a crucible and heated from ambient temperature to 1200°C in solid form (about 15−20 mg). The heating rate was constant at 10°/min to evaluate the thermal degradation of the raw material and resulting HA under a nitrogen atmosphere.

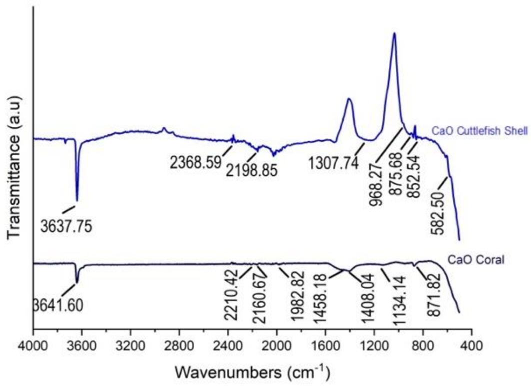

Figure 3. FTIR spectra of cuttlefish shell and coral powder from CaO

3. RESULTS AND DISCUSSION

3. 1. FTIR Spectroscopy Analysis Figure 2 displays the infrared spectra of the cuttlefish shell and coral powder after crushed. It was confirmed that $CaCO_3$ was present in the powder. It was shown that both cuttlefish shell and coral have the same peaks at 698.23, 713.66, 852.54, 1080.14, 1446.61, and 1786.08 cm^{-1}. The reference shows the spectrum will appear at 876 and 712 cm^{-1} for compounds containing calcite ($CaCO_3$) (39).

The calcination process until temperature 900ºC showed CaO compounds, which were used as raw material for HA synthesis. Figure 3 shows the FTIR spectra of cuttlefish shell and coral powder.

The CaO spectrum will appear at a peak of 875 cm^{-1} (40). Figure 3 presents that one of the spectrum peaks appeared at 875.68 cm^{-1} for cuttlefish shell and 871.82 cm^{-1} for coral. It means that the peak value was close to the reference. However, in the cuttlefish shell, a spectrum differed from the reference while the peak was upwards (correctly, the spectrum was way down). This condition may be caused by the presence of other contaminated compounds in the calcined cuttlefish shell powder during the calcination process.

The synthesis of cuttlefish shell CaO was HA in the form of a white powder. The FTIR results are shown in Figure 4. It shows that HA from cuttlefish shell and coral were closed with commercial HA (Sigma Aldrich). Spectrum peaks from HA Sigma Aldrich were 559.36 cm^{-1}, 601.79 cm^{-1}, 964.41 cm^{-1}, 1022,27 cm^{-1}. Furthermore, peaks of HA cuttlefish shell were 559.36 cm^{-1}, 601.79 cm^{-1}, 960.55 cm^{-1}, 1022.27 cm^{-1} and peaks of HA coral were 536.21 cm^{-1}, 601.79 cm^{-1}, 968.27 cm^{-1}, 1014.56 cm^{-1}.

3. 2. XRD Analysis The XRD patterns HA cuttlefish shell and HA coral are presented in Figure 5. Standard JCPDS no.74566 are also shown for comparison. Figure.5 shows the crystalline peaks of cuttlefish shell at 2θ = 10.85, 17.05, 21.94, 25.76, 31.065, 32.49, 34.85, 44.72, and 47.044°. Then, the crystalline peaks of coral at 2θ = 12.70, 16.87,18.66, 22.18, 25.90, 31.70, 32.7, 33.99, 44.48, 46.69, and 49.42°. The HA crystallinity index produced from cuttlefish shell and coral is 42% and48%, respectively.

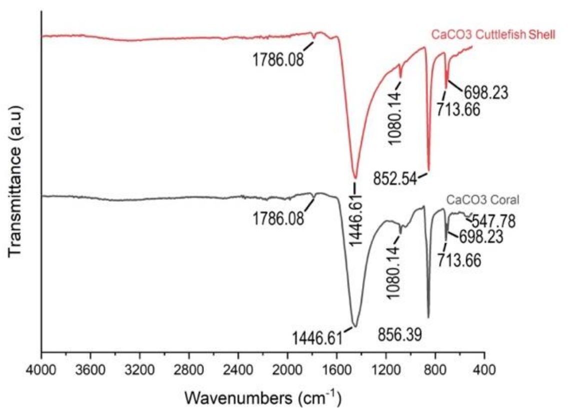

Figure 2. FTIR Spectrum of raw material from waste (a) cuttlefish shell (b) coral

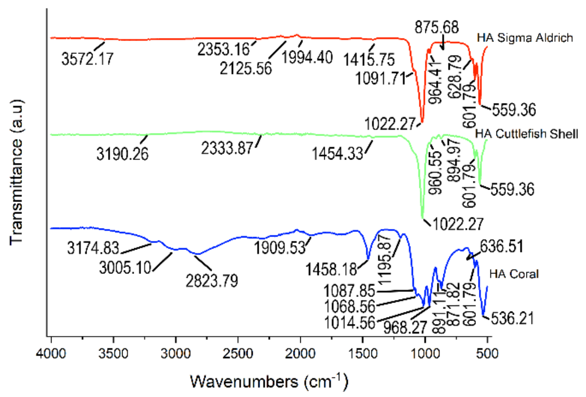

Figure 4. FTIR spectrum of HA Sigma Aldrich versus HA cuttlefish shell powder and HA coral

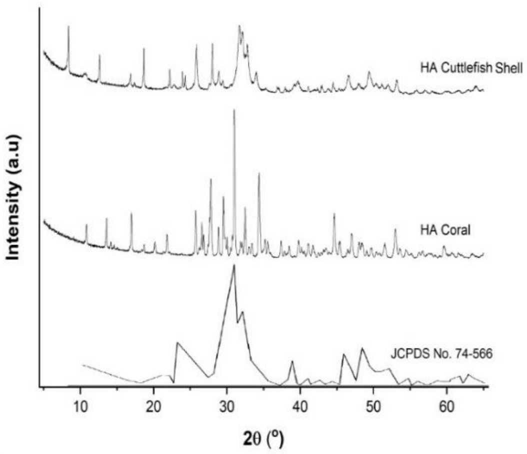

Figure 5. XRD patterns of HA coral, HA cuttlefish, and standard HA in JCPDS No. 74566

3. 3. SEM-EDX Analysis The morphology of the HA synthesis was evaluated by using SEM. It is shown in Figure 6 the size of the HA from coral, but agglomeration happened. The composition Ca/P ratio of HA cuttlefish shell and HA coral was determined with EDX at a certain area previously determined by SEM. Figure 7 shows the EDX spectrum of the HA coral and HA cuttlefish shell.

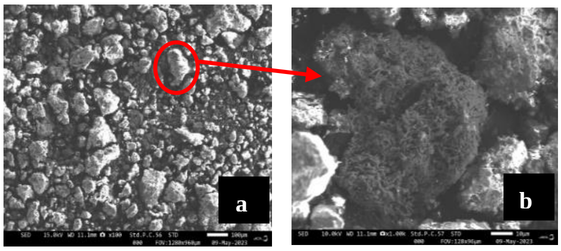

Figure 6. The morphology HA coral (a) microporous structure (b) agglomeration in powder granules

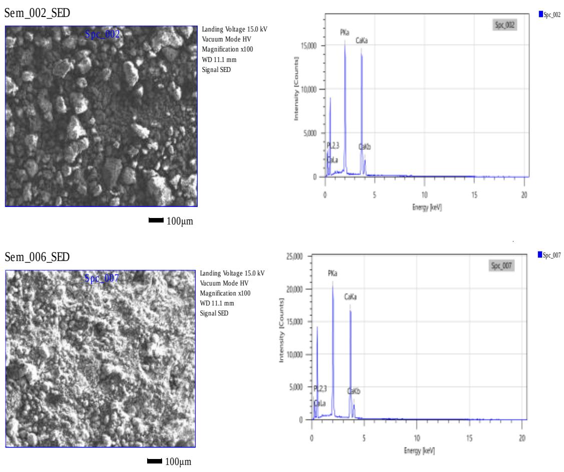

Figure 7. EDX of HA (a) cuttlefish shell (b) coral

It shows the chemical composition of the HA material, especially the ratio of Ca and P. Based on EDX measurements, it is known that the average Ca/P ratio of HA cuttlefish shell is 1.7. Moreover, the average Ca/P ratio of HA coral is 1.87.

Regarding the research obtained, HA from cuttlefish shells is close to the HA from human mandibular. In contrast, HA of the human mandibular as the stoichiometry of $Ca_{10}(PO_4)_6(OH)_2$ with ratio Ca/ P is 1.67 (41). The main chemical elements of cuttle fish shells Ca and P are summarized in Table 1. Furthermore, HA from coral is close to tetracalcium phosphate (TTCP) ($Ca_4P_2O_9$) with Ca and P ratio of 2 (42). This comparative value of Ca and P composition is very important for manufacturing products that approach the chemical composition of bone.

3. 4. Thermogravimetric Analisys Figure 8 shows the thermogravimetric profile depicting changes in the weight of HA coral, HA Sigma Aldrich and HA cuttlefish shell with an increase in temperature. Total weight loss of HA coral, HA Sigma Aldrich and HA cuttlefish were 2.26%, 5.91%, and 16.57%, respectively. HA coral and HA Sigma Aldrich were shown the three stages, whereas HA cuttlefish shell with two stages. The first stage was between 25°C and 400°C, during which weight loss was 0.47% for HA coral and 3.47% for HA Sigma Aldrich. It was indicated the removal of adsorbed physical and chemical water. The second stage was between 400°C and 800°C, where 0.81% weight loss for

TABLE 1. The main chemical elements Ca and P

Cuttlefish shell				Coral			
Area	P	Ca	Ca/P	Area	P	Ca	Ca/P
1	37.01	62.99	1.70	1	34.52	65.48	1.90
2	37.11	62.89	1.69	2	34.86	65.14	1.87
3	36.96	63.04	1.71	3	35.28	64.72	1.83
	Average		1.70		Average		1.87

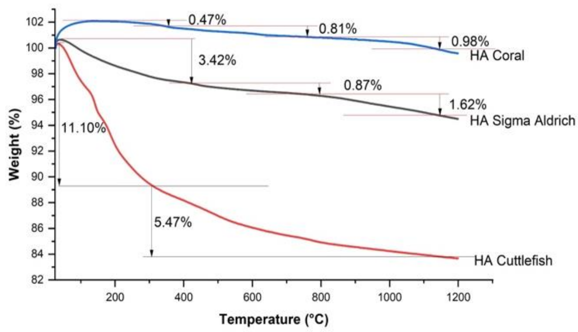

Figure 8. TGA of HA Coral, HA Sigma Aldrich and HA Cuttlefish Shell

HA coral and 0.87% for HA Sigma Aldrich were attained, which accounted for the removal of organic content. The third stage was between 800ºC and 1180 ºC. It shows the decomposition of biomolecules present in HA.

Furthermore, the First stage of HA cuttlefish shell was between 25 and 300ºC with 11.10% weight loss. It indicated the removal of physical and chemical water. Furthermore, the second stage showed a weight loss of 5.47% in temperatures between 300 and 1100ºC to remove the organic content decomposition of biomolecules present in HA.

4. CONCLUSION

The current investigation confirms the possibility of producing HA from cuttlefish shell waste and coral, which are abundant in nature. From the results obtained, the HA cuttlefish shell is close to the HA bone, while the HA coral is close to the tetracalcium phosphate (TTCP) ($Ca_4P_2O_9$) value. This is confirmed by the Ca/P ratio value obtained from EDX testing. HA human bone is 1.67, while HA cuttlefish shell is 1.7, and HA coral is 1.87. Cuttlefish shell has a crystallinity of 42%, and coral has 48%, which was obtained from XRD testing. TGA indicated that the weight loss occurred from temperature 25ºC to 1180 ºC with the value 2.26% (HA coral), 5.91% (HA Sigma Aldrich), and 16.57% (HA cuttlefish shell). However, HA coral can be used as an alternative source of HA, but further research is needed.

5. ACKNOWLEDGEMENTS

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Persian Abstract

چکیده

اندونزی کشوری مجمع الجزایری با دو قاره و یک اقیانوس است که در آن محصولات دریایی فراوان تولید می کند و دومین منبع دریایی بزرگ در جهان مانند ماهی های دریایی است. علاوه بر این، آن را برای غذا بود، صدف نیز به عنوان زباله تولید صدف. در واقع از این ضایعات برای خوراک دام استفاده شده است اما در مقیاس کوچک. برخی دیگر همچنان زباله هستند و در صورت عدم مدیریت صحیح باعث آلودگی می شوند. ضایعات پوسته سگ ماهی (CSW) ماده اساسی برای ساخت هیدروکسی آپاتیت (HA) است، در حالی که ترکیب اصلی استخوان بود. در این میان تقاضای HA در بازار به دلیل نقص استخوان بسیار بالاست. تازگی این تحقیق، رفع نیاز روزافزون به HA با قیمت پایین و جلوگیری از آلودگی هوا، آب و خاک با استفاده از اصول اقتصادی دایره ای (استفاده مجدد) بوده و دارای ارزش اقتصادی است. سنتز HA از روش هیدروترمال مایکروویو استفاده شد. CSW و مرجان از بازار حیوانات خانگی در یوگیاکارتا به دست آمدند. برای به دست آوردن اکسید کلسیم (CaO) آنها را خرد و تا دمای ۹۰۰ درجه سانتیگراد کلسینه کردند. سپس، CaO توسط هیدروترمال مایکروویو برای به دست آوردن پودر HA سنتز شد. HA مصنوعی با تبدیل فوریه فروسرخ (FTIR)، پراش اشعه ایکس (XRD)، میکروسکوپ الکترونی روبشی (SEM)، پرتو ایکس پراکنده انرژی (EDX) و تجزیه و تحلیل حرارتی وزن (TGA) مشخص شد. نسبت کلسیم به فسفر HA CSW و مرجان به ترتیب ۱.۷ و ۱.۸۷ است. علاوه بر این، مرجان HA بلورینگی بالاتری نسبت به (48٪) CSW دارد. TGA نشان می دهد که بیشترین کاهش وزن در (16.57٪) HA CSW رخ داده است. نتیجه این است که هم CSW و هم مرجان مواد خامی هستند که برای تولید HA استفاده می شوند.