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Synthesis and characterization of pure natural hydroxyapatite from fishbone biowaste of coastal communities

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Abstract. Fish bone waste has long been used in research laboratories that make it necessary for the program to transfer the knowledge to the community in order to improve its usefulness. Fish bone is a form of waste generated from the fish crackers processing industries that like the highest content of calcium hydroxyapatite (HA or HAp). In the bones, the minerals are mainly deposited in the form of calcium phosphate compounds with the greatest majority existing as apatite and only a small amount of the most carbonate containing apatites. Fish bone was converted to hydroxyapatite by heat treatment method at different temperature and for different conversion durations. Based on the result characterization (at temperature of 1100 °C by FTIR) only the phosphate is exist which is at 1026 cm⁻¹ which almost has no impurities that the compound HA at high temperatures and smaller particle will be produced hydroxyapatite which is the particle size using 25 µm.

1. Introduction

Fish bone is one of many waste produce from fish processing which contains most of calcium in fish and has the potential for economic value to be transferred into bone meal as a bone substitution, food add-on and other purposes. In terms of food and nutrition, fish bones are rich in calcium, phosphorus and carbonate, needed by human. Involvement of the community to use left over fish bone to produce hydroxyapatite is a way to improve society benefit and reduce pollution. Hydroxyapatite with the chemical formula (Ca₁₀(PO₄)₆(OH)₂) is an apatite the major mineral component, composed of calcium and phosphorus as the skeleton and theet[1]. Hydroxyapatite is one of the most common apatites used in dentistry and medicine [2].

It can promote faster bone regeneration and direct bonding to regenerate bone without intermediate connective tissue and its synthetic form is one of the most widely used biomaterials for reconstruction of the skeleton due to the lack of local or systemic toxicity together with its osteoconductive properties. It is used as an implant material both in its bulk mainly porous form, for filling in or reconstructing bone defects, and as a thin coating on metals, titanium and CoCrMo alloys, for hip, knee, and dental prostheses. Although success rates of these kinds of implants are dependent on bone-implant



osteointegration. The success and long-term survival of the implants areal is dependent on the prevention of bacterial infection after implant placement.

Therefore, there is high clinical demand for synthetic bone substitution materials [4]. The main objective of this research is to analysis particle and temperature of the natural derived hydroxyapatite from fish bone. The addition objectives are to prepare, to characterize and to compare hydroxyapatite from fish bone with synthetic hydroxyapatite.

2. Methodology

2.1. *Materials, Sample Preparation and Synthesis of Hydroxyapatite Powder from Fish Bone Waste*

The fish bone waste was abundantly available freshly collected from the cracker processors community in Kuala Terengganu Malaysia. In the sample preparation steps, fish bone was soaked in the acetone for an hour. Then wash it with distilled water to remove salts, blood, dirty substances and let it dried in the laboratory for overnight. Initially, it was de-proteinized through external washing with acetone and rinsed several times with distilled water. The acetone is used too to remove the collagens, fat sand and other impurities.

Fish bones were obtained from cat fish. It was then crushed and turn into powder of hydroxyapatite. The powder of HA pare calcined at different temperatures to synthesis Hydroxyapatite ceramics. The various temperatures, 800 °C - 1100 °C (with different temperature 100 °C a part of temperatures) are performed for 2 h.

2.2. *Calcination Process*

The hydroxyapatite powder was produce after the raw powder of cat fish bone were posses a calcination stages. Calcination process is categorized as intelligent way in produce the HA powder due to low cost and uncomplicated method. The raw sample powders were heated in Naber Therm furnace in temperature range between 800 °C to 1100 °C at a heating rate of 5 °C / min in 2 hour. As soon as the calcination temperature had been reached, the sample will maintain cooled naturally in the furnace.

2.3. *Fourier Transform Infrared Spectroscopy (FT-IR)*

The infrared spectra in this project were recorded using the Alvatar 380 FTIR Thermonicolet. The experiment was done in room temperature to determine the component and phase of the converted fish bone peak in intensity occurs.

2.4. *X-Ray Diffraction (X-RD)*

X-ray diffraction is now a common technique for the study of crystal structures and atomic spacing. X-ray diffraction, based on constructive interference of monochromatic X-ray sand a crystalline sample. These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the sample. The interaction of the incident rays with the sample, produces constructive interference (and a diffracted ray) when conditions satisfy Bragg's Law ($n\lambda=2d \sin \theta$).

2.5. *Scanning Electron Microscope Analysis (SEM)*

SEM is used to observe the microstructure of the original bone and converted fish bone. The Scanning Electron Microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derived from electron-sample inter actions reveal in formation about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials, is making up the sample.

3. Result And Discussion

3.1. Elemental composition of fish bone Analysis

Ca and P took over 85.41 wt %, which provided an evidence that fishbone is the natural resource of Ca and P. Besides these two elements, the other elements presented considerably in lower concentrations as shown in Table 1. For FT-IR analysis, in the transmittance mode, shows the presence of carbonate group at around 1410-1450 cm^{-1} and 875 cm^{-1} , hydroxide group at around 3500 – 3200 cm^{-1} [5]. For phosphate group at 1049-1090 cm^{-1} and 1950-2200 cm^{-1} , 962 cm^{-1} and 560 cm^{-1} .

Table 1. Elemental Compound/Composition Of Cat Fish Bone

Compound	P	S	K	Ca	Mn	Fe	Cu	Zn	Sr	Yb	Re
Count Unit (%)	12,20	0,59	0,2	85,41	0,087	0,19	0,082	0,17	0,58	0,45	0,07

3.2. FT-IR spectroscopy Analysis

Fourier Transform Infrared (FT-IR) spectroscopy was employed to characterize the different functional groups of HAp $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, (HAp) powder. Based on the graph FT-IR shows in Figure 1; the value for (a) 713 cm^{-1} , (b) 1034 cm^{-1} , (c) 1513 cm^{-1} and (d) 2985 cm^{-1} . From the result, it is known that (a) producing hydroxyl ion, (b) phosphate ion while (c) and (d) produced carbonate ion. Compare with the three different sizes, pure HA with the size 25 μm has the lowest intensity. So that 25 μm size is chosen since it produces lowest intensity.

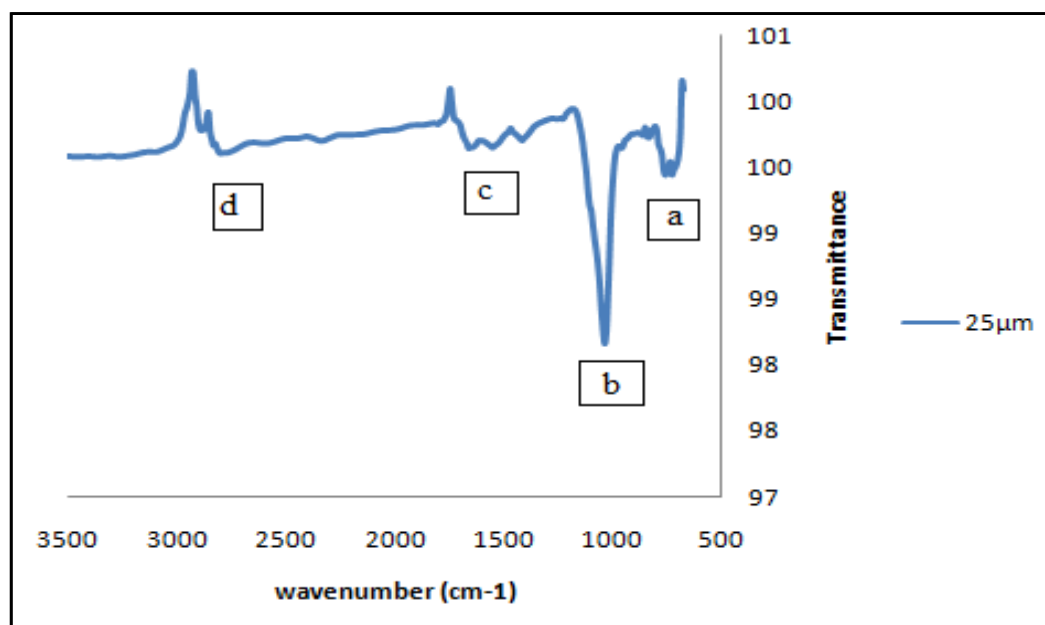


Figure 1. FTIR graph/ patterns for 25 μm of hydroxyapatite before heat treatment

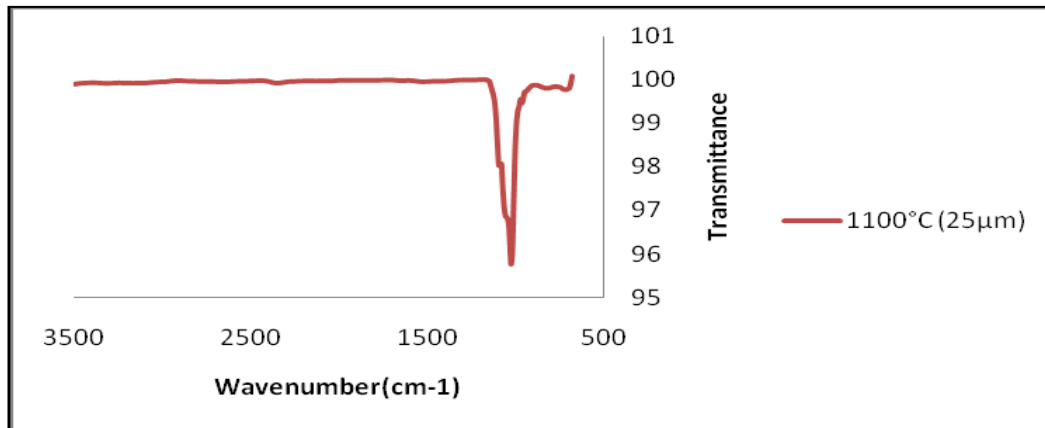


Figure 2. FTIR graph of 25 μm with temperature of 1100 $^{\circ}\text{C}$

From the graph below, the highest temperature which is 1100 $^{\circ}\text{C}$ has the lowest intensity also has the phosphate ion and lowest impurity which is good to produced the best HAp. After the heat treatment, the temperature of 1100 $^{\circ}\text{C}$ only the phosphate is exist which is at 1026 cm^{-1} which almost no impurities as shown in graph FTIR Figure 2.

3.3. X-Ray Diffraction (XRD) Analysis

The mineral phases detection of cat fish bone sample were determined by X-ray diffractometry (XRD, Rigaku) using $\text{CuK}\alpha$ radiation at 44 kV and 30 mA. Specimens were scanned from 2-75 deg (2θ) by 0.02 deg (2θ) / step, and the x-ray irradiation time was 2 s / step. Analysed by X-ray Diffraction (XRD) is to identify the mineralogy of raw bone. The powder was well-crystallized, and all peaks from the XRD pattern were identified as HA. From the graph, the sample with 25 μm size has the highest intensity compared to the other sizes, which are 90 μm and 150 μm . The sample with highest intensity has been chosen to be sintered at 800 $^{\circ}\text{C}$ until 1100 $^{\circ}\text{C}$.

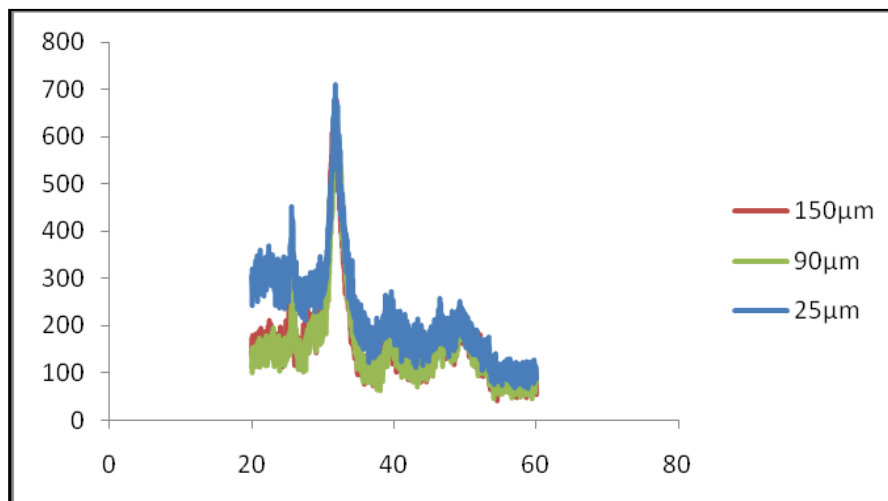


Figure 3. XRD graph of 25 μm for pure hydroxyapatite before heat treatment

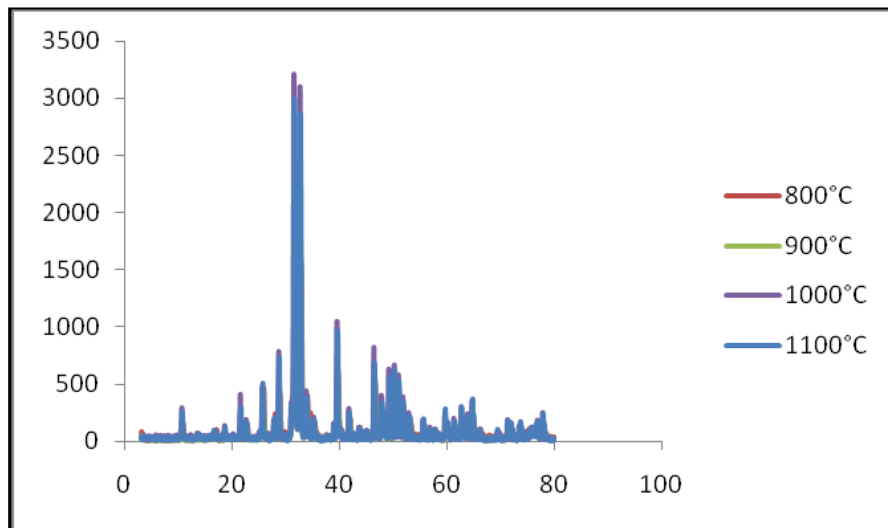


Figure 4. XRD graph of 25 μm different temperature of hydroxyapatite after heat treatment

Shipman in Yoganad, et.al [5] reported that they found there was a gradual increase in hydroxyapatite crystal size associated with an increase in the heat treatment temperature [5]. The black powder, produced in this study, began recrystallization at about 600°C without decomposing to any other compound of the calcium phosphate family. Figure 3 elicit the XRD patterns of fish bone heated at various temperatures which is 800°C, 900°C, 1000°C and 1100°C. These diffraction patterns show a gradual increase in the degree of sharpness of peaks with increasing heat treatment temperatures. These results confirm the previous discussion regarding the effect of the heat treatment temperature on the crystal size of hydroxyapatite [6]. From the graph, it can be seen that the sample with the temperature of 1100°C has the highest intensity compared to the other temperature. The temperature of 1100°C was detected to have the minor impurity elements and the most suitable to produce the best HAp as shown in Figure 4.

3.4. Scanning Electron Microscope Analysis (SEM)

Moreover the powder of fish bone also go through to Scanning Electron Microscope (SEM) machine to analyse the microstructure of the sample powder. The morphologies of the pure fish bone are shown in figures below before calcined in three different sizes which are 25 μm , 90 μm , and 150 μm as shown in Figure 5. These SEM images gave insight into the hydroxyapatite structure with respect to particle size and shape. Compared to the three different sizes, it shows that HAp microstructure for 25 μm has very dense structure which is close to each other. Dense structure has fewer pores than the other two sizes which is 90 μm and 150 μm .

When bone is heated gradually from 200°C to 1600°C, macroscopical (i.e.colour) changes and also microstructural changes occur which include recrystallization of the bone mineral. The image shows that the high temperature will remove all the impurities so that, HAp with the temperature of 1100°C has fewer pores (Figure 6). Result attempted SEM observations of heat treated to human bone and reported that the organic components of the bone tissue are eliminated at 400°C. [7,8].

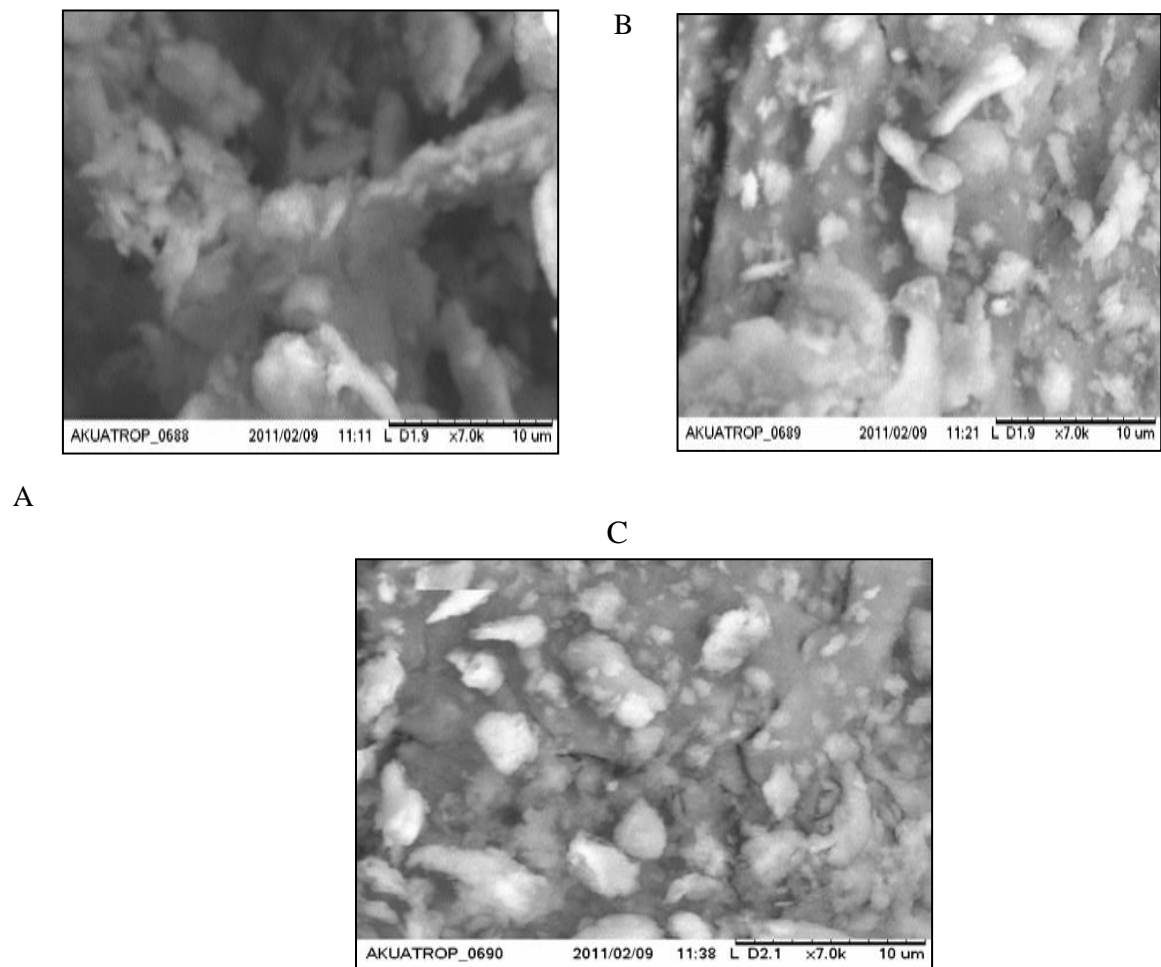


Figure 5. Image For HAp before treatment (A) with the size of 25 μm ; (B) with the size of 90 μm and (C) with the size of 150 μm

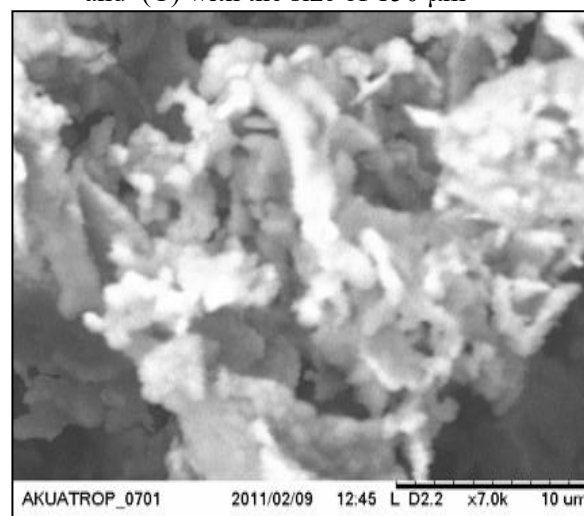


Figure 6. HAp with temperature 1100 $^{\circ}\text{C}$

4. Conclusions

Fish bone can be used as a natural source for production of hydroxyapatite. Based on the Fourier transform infrared spectroscopy analysis, 25 μm has the lowest intensity compared to the other two sizes which are 90 μm and 150 μm and the highest temperature of 1100 $^{\circ}\text{C}$ has the lowest intensity and lowest impurity provide the good quality of HAp. For XRD analysis, the smallest particle which is 25 μm has the highest intensity compared to the other sizes. The best size to be sintered then has been calcined with the temperature of 1100 $^{\circ}\text{C}$ which has the highest intensity. From the SEM analysis, the size with minor impurities is 25 μm which is the most suitable one to produce of HAp. The highest temperature has removed all the impurities. The best temperature that has been used is 1100 $^{\circ}\text{C}$. The process will produce hydroxyapatite acceptable for use in orthopaedic and dental applications. This study showed the optimum heat treatment temperature to prevent phase transformation of hydroxyapatite. In addition, heating the fish bone at temperatures up to 1100 $^{\circ}\text{C}$ indicated the fact that this natural hydroxyapatite is stable at temperatures lower than 1100 $^{\circ}\text{C}$. The highest temperature and the smaller size will produce the best hydroxyapatite.

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