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Fabrication and Characterization of Hydroxyapatite Bead for Water Filter Application

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Abstract: Hydroxyapatite and related calcium phosphate compound have similarity in composition with natural bone. From a chemical and structural point of view, HAp with the stoichiometric formula ($Ca_{10}(PO_4)_6(OH)_2$) and a Ca/P molar ratio is 1.67. Natural HAp obtained from animal bones such as pig, bovine, cuttlefish and fish with preserve some properties of the precursor material such as chemical composition and structure. HAp has been used in bone grafts, dental implant coatings, toothpaste and water filter applications. Hydroxyapatite can adsorb bacteria and virus effectively, hence it can be used as a filter to filtrate the bacteria and virus in the air or liquid. The aim of this study was to produce hydroxyapatite (HAp) beads from fish scale for water filter applications and to obtain hydroxyapatite (HAp) from waste fish for producing ion calcium in water. The morphology and physical properties of hydroxyapatite (HAp) beads were investigate through this study. The calcined HAp powder and HAp beads were characterized by Fourier Transform Infrared Spectroscopy (FTIR) to analyzed the chemical bonding, elemental analysis by using Energy Dispersive X-Ray (EDX) and Scanning Electron Microscope (SEM) to analyze the microstructure. The calcination of black tilapia fish scale to derive HAp was evaluated at the different temperature, namely 700℃ and 800℃. The HAp beads were sintered at two different temperature of 1000℃ and 1250℃ in 3 hours. FTIR results revealed the presence of carbonate and hydroxyl groups at low calcination temperature and disappear when the temperature rises. From the SEM result, the crystallinity increases when the temperature increases. In terms of correlation with water, high sintering temperature producing high calcium concentrations. It can be concluded that HAp can be produced from natural sources.

Keywords: Hydroxyapatite, Water Filter, Ion Calcium

1. Introduction

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Hydroxyapatite is a hexagonal mineral composed of calcium, phosphorus, and oxygen. Hydroxyapatite (HAp) of biological or man-made origin is being applied for bone healing and regeneration as granules, blocks, alone or as a composite material with polymers or other ceramics, or as a covering on orthopedic or dental implants. In general, natural hydroxyapatite is produced from mammalian bone, marine or aquatic sources, shell sources, plants, and algae, in addition to mineral sources.

This project aims to develop a water filter using hydroxyapatite beads derived from the scales of black tilapia fish. Hydroxyapatite (HAp) is also used as calcium ion (Ca^{2+}) beads in water filtration applications. The water-soluble bead is used to generate calcium ions (Ca^{2+}). Calcium in the blood is needed for many things, like clot formation, nerve signals transmission, muscle function, cell membrane stability, and metabolic functions.

Some countries do require halal certification for bottled water, although not because of the water itself but because of the filtering procedure it undergoes. Dr. Sirajuddin Suhaimee, who runs the largest halal certification organisation in the world, the Department of Islamic Development's Halal Hub Division in Malaysia, says that the technique, not the product, is certified. Therefore, the development of water filters with 'Halal' certificates is important to consume by Muslim people that about 61.3% in Malaysia according to the Departments of Statistics Malaysia.

2. Materials and Methods

The processes and tests included in this study include sample preparation, calcination, sample powder characterization, fabrication beads, heat treatment on beads HAp and calcium concentration analysis.

2.1 Materials

The black tilapia fish were gathered as by-product waste from the fish market in Parit Raja, Johor. The black tilapia was washed and cleaned before being boiled for one hour at 100°C. The fish scales were then washed with tap water to eliminate any attached fish meat and other impurities. This procedure is then repeated twice to verify that the sample is fully cleaned. In addition, all the scale components were dried in the oven for 3 hours at 120°C. Table 1 illustrates the step preparation process of black tilapia fish.

Table 1: Step preparation process of black tilapia fish

Step	Preparation Process	Description
1		Black tilapia fish were collected from the market at Parit Raja, Batu Pahat, Johor.
2		Black tilapia fish were washed and cleaned by using the tap water.
3		Boiled the black tilapia fish with temperature 100℃ at 1 hour to remove the meat and inorganic substances from fish scales.

4		The all parts of fish bone were dried using oven at temperature 120℃ in 3 hours.
5		Raw material which is fish scales of tilapia after dried.

2.2 Methods

2.2.1 Drying process

The drying method was necessary to use heat drying to remove the excess water from the mixture and eliminate other undesirable gems. It is crucial to today's mineral processing. The drying oven (SOV140B, China) in the research is used to complete the drying process. The material is preserved during the drying process and the oven-dried method is effective and suitable. A closed chamber was used to complete the oven drying process, which took 1 hours at a 100 ℃.

2.2.2 Grinding process

The bones were first crushed using home drying blender to minimise their size. The rotary mill machine (Fritsch Planetary Pulveriser 14 rotational, German) is utilised to crush fish scales into powder form. The scales are grinded in a milling machine rotating at 10RPM. The diameter of the powder is 150 μm.

2.2.3 Calcination process to produce HAp powder

The dried samples were calcined in a furnace (Protherm, Turkey) at various rates of temperatures. The parameter of the study to heat the powder is using different rate of temperature which are 700 ℃ and 800℃ for 3 hours to produce different sample with heating and cooling rate of 5 ℃/min. In a furnace (Protherm, Turkey), the powder is heated for 3 hours before cooling naturally. Any reaction that occurs throughout the process is recorded.

2.2.4 Fabrication of HAp beads

After powdered hydroxyapatite has been analysed, the optimal temperature for heat treatment or calcination is determined, 800℃ is the optimal heat treatment temperature for producing HAp beads. To make a single bead during the manufacture of HAP slurry, a mixture of 1.2 g HAp powder and 0.1 g starch is combined with 0.5 ml of distilled water. The homogenous mixture was then manually circulated. Subsequently, the beads were sintered at 1000℃ and 1250℃ to generate compact beads.

2.2.5 HAp beads sintering process

The furnace (Protherm, Turkey) is used to heat the beads to eliminate moisture, undesirable materials, and organics. The beads are sintered at temperatures of 1000℃ and 1250℃ with heating and cooling rates of 5℃/min and a 3 hours' dwell time.

2.2.6 Morphological analysis

The morphological characteristics of the produced powder and beads is examined (JEOL JSM-7600F) using high resolution SEM. By sputtering the samples with a 230 V, 50 Hz direct drive 2-stage

vacuum pump, the samples are gold-plated. The photos are magnified between 150 and 30000 times. Energy Dispersion was used to examine the sample surface for X-ray examination (EDX). With the aid of a 20 kV secondary electron image scanning electron microscope made in Germany, the morphology of the material was assessed.

2.2.7 Fourier-transform infrared spectrometer (FTIR)

The functional groups contained in the fish bone and HAp samples were identified using Fourier-transform infrared (FTIR) spectroscopy. To get the pellet for FTIR investigation, use an infrared absorption spectra wave number between 600cm−1 and 4000cm−1 of ATR. With a scan average of 32 scans, the acquisition resolution is 4cm1. Because of the sample, a molecular fingerprint of the sample is formed. The molecular fingerprint of the material is represented by the FTIR spectrum. The Perkin Elmer FTIR Spectrometer 100, UK, was utilised in this experiment to characterise the equipment.

2.2.8 Atomic absorption spectrometer

Atomic absorption spectrometer (Analyst 800) is a device for determining the concentration of metallic elements in solution. The absorption uses flame or flameless (graphite furnace) approach, in which the free atom determines whether to emit or absorb light energy (radiation) from hollow cathode lamp (HCL) sources. Liquid samples are the types of samples that can be tested. In 50 ml of distilled water, 0.5 g of HAP beads heated to 1000 °C and 1250 °C were soaked. The solution is left for 24 hours at room temperature. The solution was then filtered through filter paper to separate the HAP beads from the water. Comparisons were made between the sample and calcium standards of 5 ppm, 3 ppm, and 1 ppm.

3. Results and Discussion

In this section, results obtained for Hydroxyapatite powder and bead are highlighted. It covers:

i. Characterization of Hydroxyapatite powder
ii. Characterization of Hydroxyapatite bead

3.1 Characterization of Hydroxyapatite powder

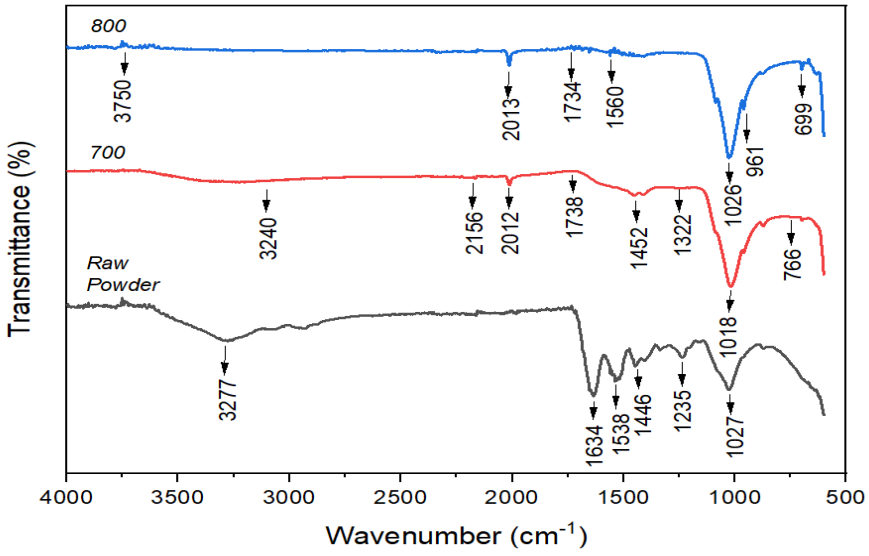

Figure 1: FTIR spectrum of sample before calcined and after

Figure 1 shows the FTIR spectrum of sample before calcined and after. Both stretching of (OH^{-}) group were observed in the absorption bands of uncalcined raw fish scales at 3284cm^{-1} are strong board spectrum. When calcined at 700℃ (OH^{-}) group observed at 3240cm^{-1} are medium spectrum whereas

when calcined at 800℃ the (OH^-) group were barely seen due to hydroxyl ion is more sensitive with temperature and disappears when the higher temperature is applied [1]. The bands of the highest intensity within the wavenumbers range 1200-1000cm^{-1} correspond to the vibrations of the (PO_4^{3-}) group. The phosphate ion was identified through the band at 1027cm^{-1} (uncalcined), 1019cm^{-1} (700℃) and 1026cm^{-1}, 1095cm^{-1} (800℃). As the temperature of calcination increase, the strong appearance of the group (PO_4^{3-}) can be observed. The carbonate ion (CO_3^{2-}) have a strong spectrum and high peak of the raw fish scale, 1615cm^{-1}, as approaching the temperature of 700℃ (1434cm^{-1}) and 800℃ the ion carbonate slowly demolish. This shows that the highest temperature of calcination removes ion carbonate.

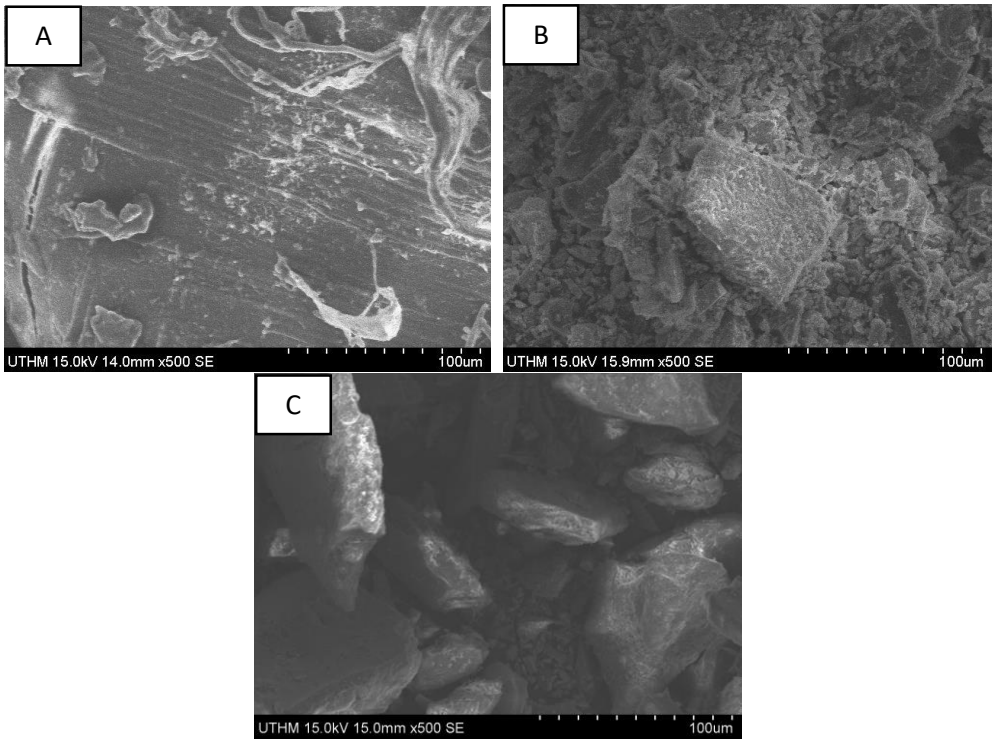

Figure 2: The morphology of A) raw fish scale, calcined powder at B) 700℃ C) 800℃

The morphology of calcined powders at 700°C (Figure 2 (B)) was noted to be distinct from that of raw fish scale (Figure 2 (A)), which morphology consisted of small and long particles. Meanwhile, particles calcined at 800°C (Figure 2 (C)), the particles present in morphology are hexagonal in form. This situation occurred owing to the calcination process, all organic material from the raw fish bone evaporated, leaving just calcium carbonate. The inorganic substances stayed stationary. Furthermore, it was hypothesised that both calcined powders possessed the same chemical composition. It was anticipated that the particle size will rise with regard to the temperature. Therefore, samples calcined at 800°C were reported to have higher particle size than samples calcined at lower temperatures calcined samples at 700°C.

The results of elements compounds in tilapia scale sample calcinated at 800℃ shown in Table 2. As seen from the table, the Ca/P ratio for the sample after calcinated at 800 ℃ is 1.64. Table 2 shows the element compound that had obtained from the EDS analysis. The main element that in the sample is calcium and phosphate. There are a minor peak of elements that appeared with the small percentage value when calcined at 700℃, due to the organic compound not burn completely during calcination process.

Table 2 Elemental analysis of tilapia fish scale

No	Temperature (℃)	Weight of Calcium (%)	Weight of Phosphorus (%)	Ca/P Ratio
1	Raw	-	-	-
2	700	24.67	11.74	2.10
3	800	27.96	17.06	1.64

The calcine temperature of 800℃ have a nearly value to the HAp Stoichiometric (1.67) of Ca/P ratio. Based on the data, the Ca/P weight ratio for derived HAp was calculated and was found to be 2.10 at 700℃ and 1.64 at 800℃. This value of 1.64 is close to the stoichiometric HAp (1.67). The resultant result is consistent were compared with natural HAp extracted from Tuna bone reported by Venkatesan et al., 2010.

3.2 Characterization of Hydroxyapatite bead

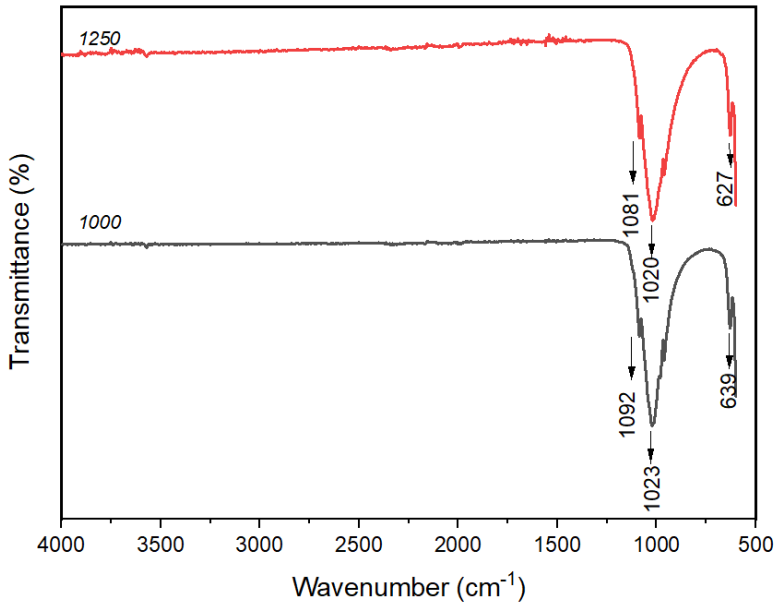

Figure 3: FTIR spectrum of HAp Beads

At sintering temperature 1000℃, the HAp was confirmed by the definite clear peak at intensity 1023 cm^{-1} and 1092 cm^{-1} (Figure 3) which similar to the previous study. Regardless of high calcination temperature, the libration band at 639cm^{-1} originating from (OH^-) group. The persistence of the (OH^-) group band suggests that the basic apatite structure of the sample is not affected by the calcination, whereas the chemically absorbed water disappeared as the calcination temperature was increased. The region of carbonate ion has disappeared when sintering at 1000℃, compared to the powder at calcine 800℃. With increasing sintering temperature to 1250℃, the same pattern when sintered at 1000℃ could be observed. The small peak of hydroxyl ion at 3750 cm^{-1} has been disappeared completely, while at peak 627 cm^{-1}, the group of (OH^-) could be observed. The clear peak at 1081 cm^{-1} and 1020 cm^{-1} belong to phosphate ion group. The band appears strong and narrow.

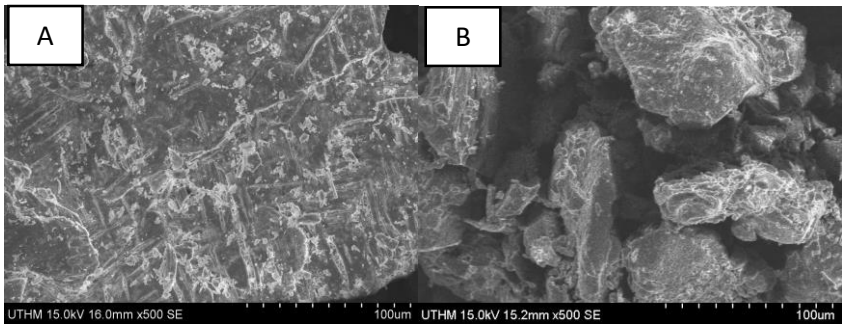

Figure 4: Surface morphology of HAp beads A) 1000℃ B) 1250℃

As observed in the images of HAp powder (sample No. 1), a porous structure with a spherical form has developed. Due to the organic presence of carbonate and hydroxyl, a porous structure has developed. From a picture of beads sintered at a temperature of 1000℃ (Figure 4 (A)), nanoparticles were created. The particle has a spherical shape and a grain size of around 874.8 nm. The carbonate group begins to diminish relative to the quantity of carbonate in the HAp powder 800°C sample.

Table 3: Chemical composition of material after sintered

No	Temperature (℃)	Weight of Calcium (%)	Weight of Phosphorus (%)	Ca/P Ratio
1	1000	36.57	19.76	1.85
2	1250	27.95	15.04	1.85

Table 3 represent the EDS data for derived HAp at 1000℃ and 1250℃ respectively. Based on the data, the Ca/P weight ratio for derived HAp was calculated and was found to be similar on both. The resultant result is consistent were compared with natural HAp extracted from Venkatesan et al., 2010. As the Ca/P weight ratio of the derived HAp at the different temperatures did not show any considerable difference, it can be inferred that Ca/P weight ratio is independent of sintering temperature.

4. Conclusion

In conclusion, the results of this study showed that Hydroxyapatite (HAp) could be made using natural resources from the scale of tilapia fish. The two steps needed to make HAp are calcination and sintering. Calcination is a process that uses heat to treat the raw bone in order to make HAp powder. On the other hand, the HAp powder is turned into HAp beads through the sintering process. It has been found that calcination at 800°C and sintering at 1000°C, respectively, are the best temperatures for turning tilapia fish scales into hydroxyapatite.

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