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Valorization of a Good Bioceramic from Moroccan Waste Fish Bone by a Heat Treatment Method

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Abstract: A tricalcium phosphate (TCP) material was produced from sardine and mackerel waste using a heat treatment method after a Soxhlet extraction to obtain the non-soluble portion of fish waste. The bones were annealed at temperatures between 400°C and 1200°C. The thermal analysis (TG-DTA) was carried out to investigate the thermal stability of TCP and to confirm the removal of organic matter from the raw fish. The calcined bones were characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), and field emission scanning electron microscopy (FE-SEM). The calcium to phosphorous weight ratio was determined by ICP- AES. FT-IR and XRD confirmed the similarities to synthetic β-TCP (JCPDS-09-169), FE-SEM results revealed the formation of nanostructured TCP. These results suggest that varying the isolation temperature between 600-1200°C has tremendous impact on the production of TCP from fish bone waste with the required properties.

Keywords: Hydroxyapatite; tri-calcium phosphate; fish bone; heat treatement; bioceramic

1 Introduction

The valorization of fish waste and by-products has been gaining attention in recent years to obtain valuable compounds. One reason for this is the production of increasingly large amounts of waste and/or by-products, which need to be disposed of. The Food and Agricultural Organization (FAO) estimates that the world fish production utilized for direct human consumption has increased significantly, more than 146 million tones, in 2014, and 21 million tones was destined for non-food products, about 50-60% of this catch is been used for human consumption, while the rest is considered discard [1]. In the fish waste, the fish scale was estimated 4% by weight [2]. Bones are composed of 30% organic compounds and 70% inorganics by weight [3]. The inorganic phase could be used as a cheap source of calcium phosphate (also termed as hydroxyapatite HA or tricalcium phosphate TCP) contributing at the same time to give added value to fishing by-products as well as reducing the undesirable environmental impact. Treated fishbone and other fish waste have been utilized in food industry [4], biofuel production [5], medical applications because HA and TCP are biocompatible, bioactive, non-toxic, non-inflammatory and non-immunogenic [6], and as a natural and low cost heavy metal sorbent [7-10]. Fishbone is a natural resource of P and Ca, and actually is the natural supply of HAp that can be partially transformed into β-tri-calcium phosphate (β -TCP) when calcined above 600°C [11]. Several methods have been employed to prepare HAp from fish scales including enzymatic hydrolysis [12], alkaline hydrolysis [13], ionic liquid pretreatment [14], and heat treatment [15].

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In the present study, we use two basic pelagic fish of morocco sardine and mackerel as main raw material to developed calcium phosphate through thermal treatment method, in order to find out the optimum conditions for TCP isolation. The objective of the present study is the extraction of TCP powder from inexpensive and eco-friendly source that can be used for various medical and industrial applications.

2 Materials and Methods

2.1 Fish Bones

Sardine and mackerel waste (scales, skin and bones) was obtained from local market and industrial companies. The extraction of a lipid from a solid material of waste fish was carried with n-hexane using a Soxhlet extractor for 3 hours at 50°C. After extraction the solvent is removed, typically by means of a rotary evaporator, yielding the extracted compound that was used as a feedstock to produce biodiesel in another study [16]. The non-soluble portion of the extracted solid remains in the thimble then placed in a furnace. Annealing was performed in air, and the heating rate was 10 °C min^{-1} and the annealing time was 4 h. Several annealing temperatures (400°C, 600°C, 800°C, 1000°C, and 1200°C) were tested for the untreated bones. The removal of the organic portion from the non soluble portion of waste fish was observed at different temperatures with changes in the color of the bone as observed in Fig. 1. The color of the raw waste fish bone was observed as light yellow, which consequently changed into black, tan and off-white when subjected to calcinations at 100°C, 400°C, 800°C and 1000°C temperatures, respectively.

Figure 1: Preparation of TCP from fish waste

2.2 Characterization of the Powder

Infrared spectral data were collected in the 4000-400 cm^{-1} range by co-adding 16 scans at a resolution of 4 cm^{-1} on a VERTEX 70 spectrometer equipped with an ATR MIRACLE DIAMANT technique. Spectra were recorded as transmittance values at each data point in triplicate. TG-DTA analysis were performed using a SHIMADZU 60H thermobalance, with a heating rate of 5 °C min^{-1} The temperature range employed was 18-1200°C. The room temperature X-ray diffractograms of both the samples were recorded using MiniFlex 600 X-ray diffractometer (Cu Ka, k = 1.5406 A°, 2h = 10-80, step size (2h) = 0.02, and scan step time = 0.15 s) for phase confirmation. ICP-AES was used for determination of elements (Ca, P, Cu, Fe, Mg, Mn, Na, Ni, Sr, and Zn) and controlled with ICP-Expert Sequential software. The instrument was calibrated with 0.1 mg/L, 1.00 mg/L, 10.00 mg/L and 25.00 mg/L concentrations using ICP multi- element Standard solution VIII (Merck, 24 elements) and Na_2HPO_4. Each measurement was repeated three times and then standard means were calculated. The morphology of the HAP powder was viewed by scanning electron microscopy Jeol JSM-7000F FE-SEM, Japan.

3 Results and Discussion

3.1 Thermogravimetric Analysis of Waste Fish Bone

The TG-DTA analysis of the fish bone powder is shown in Fig. 2. TG analysis shows that there is weight loss observed in three steps. The first step occurred up to 200°C (10.34%). It is due to the evaporation of water. The second step is observed between 200°C and 600°C (68.11%). It is resulted from the decomposition of organic material in the fish bone. The final step is between 600°C and 883°C (1.62%). It could be due to the dehydroxylation and the formation of PO_4^{3-} ions. Beyond 883°C to 1200°C no significant weight loss was observed, which indicates thermal stability of the produced powder. The total weight loss at 1200°C is 80.07%. On the other hand the ATD curves show various Thermal behavior: one of an endothermic nature at a 46.5°C attributable to the evaporation of the water adsorbed on the surface of the solids and the others of an exothermic nature, located above 330°C and 548.94°C, are due at the same time to the combustion of organic matter and to the structural transformation of fish bone to the TCP phase.

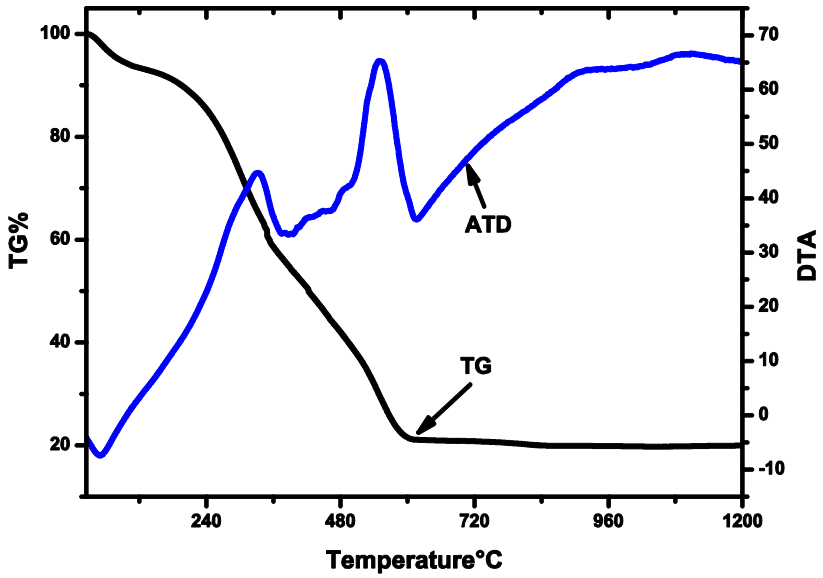

Figure 2: TG-DTA analysis of raw fish bone

3.2 FT-IR Spectroscopic Analysis

The FT-IR analysis was performed to identity unknown substances and to determine the amount of components in the isolated fish bone. Fig. 3 depicts the FT-IR spectrum of raw fish bone, calcined fish bone from 400°C to 1200°C and synthetic β-TCP from Carlo Ebra. The characteristic bands of raw fish bone were observed at 504 cm^{-1}, 531 cm^{-1}, 601 cm^{-1}, 692 cm^{-1}, 778 cm^{-1}, 1168 cm^{-1},1390 cm^{-1}, 1460 cm^{-1}, 1537 cm^{-1}, 1624 cm^{-1}, 1736 cm^{-1}, 2853 cm^{-1}, 2923 cm^{-1}, 2954 cm^{-1} and 3275 cm^{-1}. These bands indicate calcium phosphate and collagen moieties, which is consistent with some previous reports [13, 15]. The bands at 1460 cm^{-1}, 1537 cm^{-1}, 1624 cm^{-1}, 1736 cm^{-1}, 2853 cm^{-1}, 2923 cm^{-1}, 2954 cm^{-1} and 3275 cm^{-1} were reduced above 600°C, suggesting the removal of organic matter. At lower temperature (400°C). The peaks corresponding to the phosphate group at 562 cm^{-1}, 600 cm^{-1}, 962 cm^{-1}, 1019 cm^{-1} and 1087 cm^{-1} was not observed and it appeared only at temperatures above 600 °C. From this temperature the spectra show the characteristic bands for PO_4^{3-} group consisting of three main regions. In the first region a strong band was observed at 1119 cm^{-1}, 1010 cm^{-1}, 1080 cm^{-1} corresponding to υ_3 stretching mode of PO_4 vibration, and 962 cm^{-1} associated to υ_1 stretching mode. The second region of phosphate ions is represented by the υ_4 band with well defined peaks at 556 cm^{-1} and 590 cm^{-1} corresponding to bending

mode. Concerning carbonate ions, there are usually four vibrational bands that can be observed in the infrared spectra of calcium phosphate, but only two are exploitable for infrared studies, υ_2 and υ_3 bands. Indeed the band υ_1 CO_3^{2-} is masked by the band υ_3 PO_4. υ_4 CO_3^{2-} band exhibit very low intensity and is rarely observed [17, 18]. In samples calcined above 600°C carbonate ions are detected at 875 cm^{-1}, 1441 cm^{-1}, and 1644 cm^{-1} with a low intensity peaks.

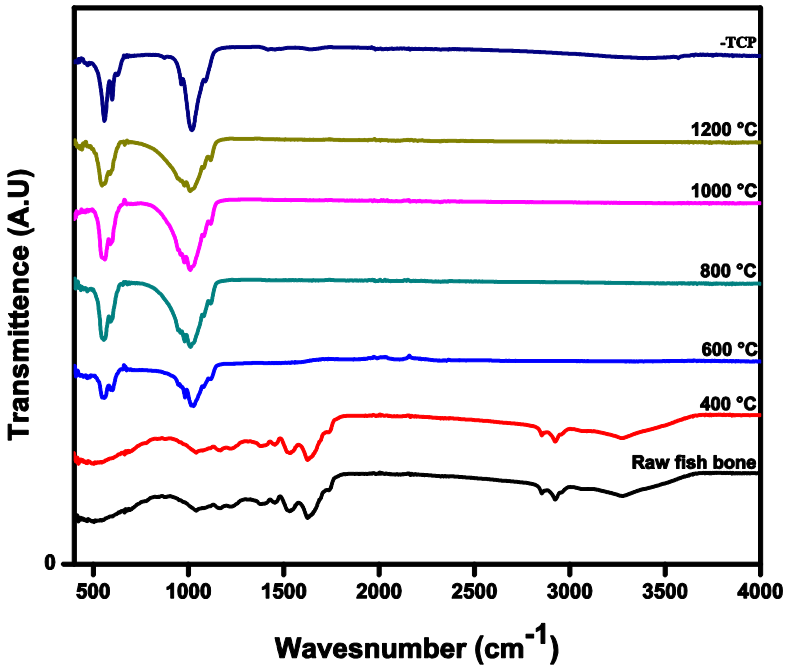

Figure 3: FTIR spectrum of TCP powder synthesized from waste fish bone

3.3 X-Ray Diffraction Analysis

The phase and purity of the calcium phosphate powders obtained at different firing temperatures were confirmed with XRD analysis. Fig. 4 shows the XRD pattern of raw fish bone and treated bone at different temperatures. A broad single peak was observed in the X-Ray diffraction spectrum of raw bone at 32.04, confirming that our simple is amorphous. Waste fish Bones transformed to a calcium phosphate phase was found to be similar to that of synthetic β -TCP (JCPDS-09-169) when calcined between 1000-1200°C, as compared to other researches [13,15,19]. The intensity and sharpness of TCP peaks increase with the increase of the calcinations temperature. The highest intensity of the peaks of the prepared TCP from fish bone (28, 31.28, and 34.6) is similar to that of the standard (JCPDS- 09-169).

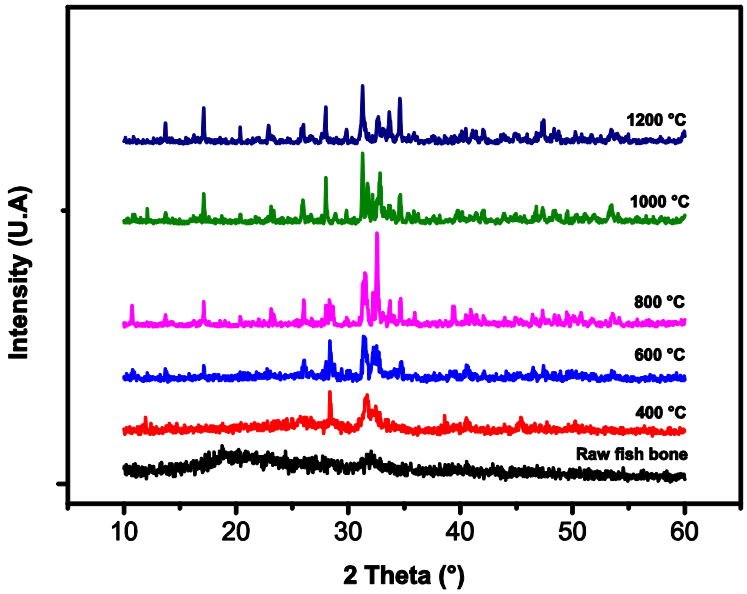

Figure 4: XRD pattern of TCP powder synthesized from waste fish bone

3.4 Chemical Analysis of Fish Bone

In order to determine calcium to phosphorous molar ratio of bone samples, bone sample was digested with a composition of HNO_3/H_2O_2 (2/1) acid mixture at 110°C for 50 minutes until dried and then the samples were dissolved in 50 ml of 5% nitric acid. This procedure was repeated three times for every sample. The minerals (Ca, P, Cu, Fe, Mg, Mn, Na, Ni, Sr, and Zn) were measured with ICP-AES and then concentrations were calculated based on standard deviation after treating three replicates of every sample. Tab. 1 represents chemical composition of HAp at 1200°C. The Ca/P weight ratio for derived TCP was calculated and was found to be 1.49 and refers to tricalcium phosphate phase. the resultant values are consistent with values reported by Sahin et al., 2016 [20].

Table 1: Element compositions and Ca/P mole ratios of the produced TCP by ICP-AES

Element (wt %)	P	Ca	Cu	Fe	Mg	Mn	Na	Ni	Sr	Zn	Ca/P ratio	Total (wt %)
	37.35	55.82	0.002	0.002	1.88	0.025	4.94	0.003	0.012	0.003	1.49	100

3.5 Microscopy Results

Fig. 5 depicts the FE-SEM images of HAp waste fich bone at differents magnifications: (A) *1000, (B) ˆ2000 and (C, D) ˆ4000. Agglomeration of the particles was observed. These SEM images illustrate that the morphology is composed of a nano-scale particles along with microscale particles.

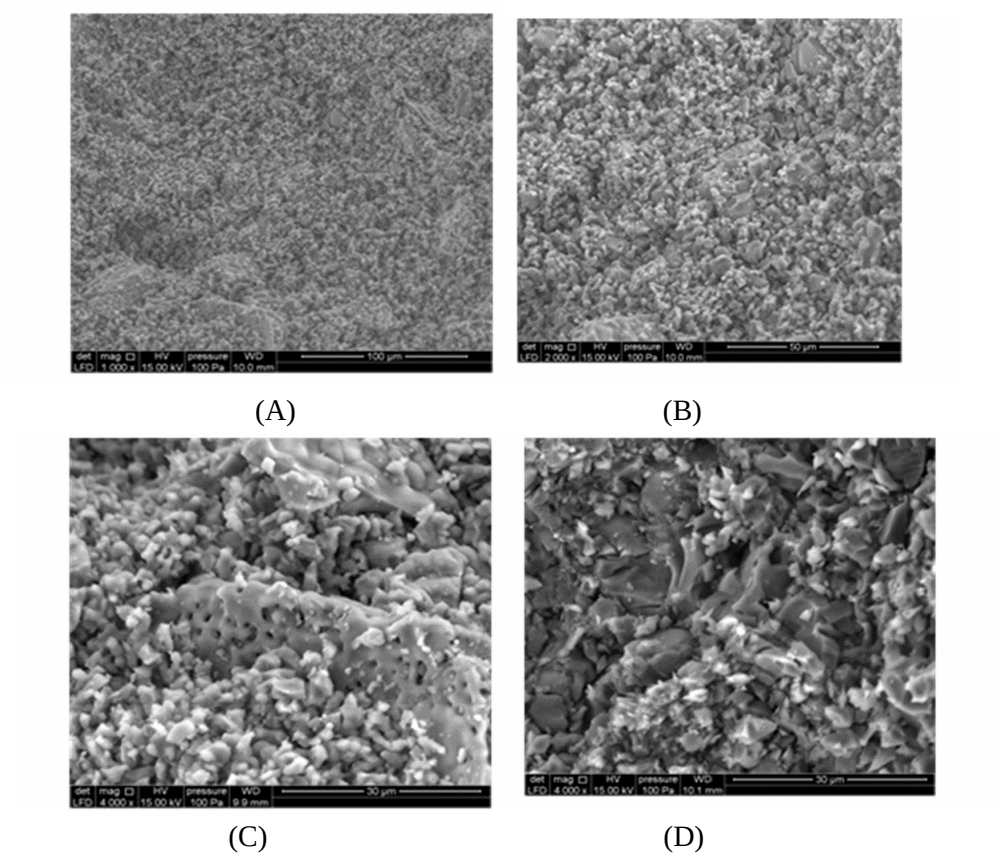

Figure 5: Field emission-scanning microscopy images of the produced TCP at different magnifications. (A) × 1000, (B) × 2000 and (C,D) × 4000

4 Conclusion

We have isolated a tri calcium phosphate from Moroccan waste fish bone using a heat treatment method. This is a very low cost efficient method for the isolation of TCP. From this study we conclude that a temperature between 600-1200°C is optimum for isolation of TCP from fish bone with almost no organic portion, high purity, stability, crystallinity, and nanostructure that could will be useful in biomedical applications, biofuel production and as a natural heavy metal sorbent. This study presents a very simple and green production method of bioceramic from fish bone and can reduce the undesirable environmental impact by recycling fish waste.

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