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Synthesis of Nano Crystalline Hydroxyapatite from Egg Shells by Combustion Method

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Abstract Hydroxyapatite (HA) has been widely used as a biocompatible ceramic in many areas of medicine, but mainly for contact with bone tissue, due to similarity in composition and crystal structure of natural bone. This paper reports for synthesizing hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$] powder wirh Ca/P molar ratio 1.67 from egg shells ,orthophosphoric acid. Fourier-transform infrared (FT–IR) and X-ray diffraction (XRD) techniques were employed to investigate the formation of the HAP phase. Thermal analysis (TG–DTA) was carried out to investigate the thermal stability of HAP powder. FT–IR spectra show the characteristic peaks for phosphate and hydroxyl groups.

Keywords- *hydroxyapatite,eggshell,citric acid,diammonium hydrogen phosphate.*

I. INTRODUCTION

The demand of bioceramics has increased dramatically over past two decades. Hydroxyapatite (HAp, $Ca_{10}(PO_4)_6(OH)_2$ is biocompatible and bioactive, meaning that it will support bone ingrowth and osseointegration when used in orthopaedic, dental and maxillofacial applications(1) .Hydroxyapatite (HA) is the main component of mineral bone. It is the one of the most versatile material used for implantation due to similarity in properties of natural bone, but it can't be used directly for load bearing application (hip replacement) because of its poor mechanical properties and sinterabitily(2,3). Hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$] HA) is an organic biomaterial .it is most produced and less expensive industrial calcium phosphate biomaterial. (4)It exist under two crystallographic structures: β tri calcium phosphate (β TCP) and α tri calcium phosphate (α TCP). The form is unstable at low temperature and is obtained by heating β form above 1200˚C. The precise temperature remaining unclear . the β form cannot be obtained by direct precipitation it results from calciningg at 800-900 C of Ca deficient apatite with loss of water according to the equation:

$$Ca_9(HPO_4)(PO_4)_5(OH) \longrightarrow 3Ca_3(PO_4)_2 + H_2O$$

A number of synthesis techniques using various sources of Ca and P have been developed which includes wet chemical method (precipitation), sol-gel method, hydrothermal synthesis procedure, continuous precipitation, thermal deposition and solid state reaction method(5) . we have adapted wet chemical method to synthesize pure HA bioceramics with Ca/P ratio 1.66, using egg shell as Ca source.The eggshells constitute the 11% of the total weight of the egg and are composed by calcium carbonate (94%), calcium phosphate (1%), organic matter (4%) and magnesium carbonate (1%)6.India, currently ranks fourth in worldin egg production with an annual production of 17,32,500 tons of egg. By taking 11% of the weight, nearly it comes around 1,90,000 tons of eggshell waste is created.(6) The egg shells are useless after the utilization of egg contents and wasted egg shells lead to environmental pollution since these favor microbial growth. This waste is available in huge quantity from food processing, egg baking and hatching industries. Accordingly, the aim of the present work is to propose a cheap way for the production of Hap(7).

II. METHODOLOGY

The major constitute present in eggshell is $CaCO_3$, which account around 94% of total weight .Egg shells of hen were collected in bulk. They were cleaned manually by de- ionized water and boiled in water for 30 minutes. The Uncrushed and washed eggshell were taken in a porcelain crucible and were calcined in a muffle furnace for 1 hr. the eggshells transformed into calcium oxide and evolved carbon dioxide above 850°C The expected reaction is as follows:

$$CaCO_3 \longrightarrow CaO + CO_2$$

A stoichiometery amount of calcined eggshell was dispersed in well degassed distilled water. After dispersing in distilled water the CaO converts into $Ca(OH)_2$ as follow

$$CaO + H_2O \longrightarrow Ca(OH)_2 \text{ (exo)}$$

Under vigorous stirring reagent grade orthophosphoric acid solution (0.6M) was added in drops at a controlled rate to the suspension at room temperature. Initially, the pH of the solution was found to be 12 but at the end of addition of

orthophosphoric acid, it decreases to 8.5. after completion of addition of orthophosphoric acid precipitate were formed .the precipitate formed was subjected to aging treatment for 24 hr. for aging treatment the preicipitate is kept at room temperature in flask. Solution was then stirred for another 30 min without heating and then left for another 10 hr for complete precipitation occur. The expected reaction is as follow:

$$10Ca(OH)_2 + 6H_3P \longrightarrow Ca_{10}(PO_4)_6(OH)_2 + H_2O$$

The precipitate were filtered and thoroughly washed with double distilled water and filtered again .after drying at 80°C for 3 hr, the precipitate was calcined at 900°C for 2 hr. After calcinations at 900°C in muffle furnace white crystalline agglomerates were formed as end result in crucible.

III. CHARACTERIZATION

Phase purity of the synthesized Hydroxyapatite sample was analyzed in Siemens D-500 X-Ray Diffractometer, using Cu Ka, Ni filtered radiation.Differential thermal analysis is done to check the themal analysis by extracting water vapors from the sample.

IV. RESULT AND DISCUSSION

X-Ray Diffractometry was carried out using a Cu-K∝ X-Ray Diffractometer (PW-1830, Philips, Netherlands) and particle size analysis was performed in Malvern Particle Size Analyzer (Model – Micro-P, UK). DTA-TG was done in NETZSCH DTA-TG/DSC Thermal Analyzer (Model – STA409C).The Fig (1) shows the thermal decomposition of eggshells. The graph shows a weight loss of 1.4% below 2500C, which is due to the physical absorbed water. But till 4500C there is a remarkable weight loss of total of 4% with an exothermic peak in DTA. Exothermic peak indicates oxidation of sample. This shows at temperature below 4500C all the organic compounds are oxidized and so this weight loss. In temperature between 5000C and 6000C, there is a small endothermic peak along with 1.04% weight loss. This is due to the slow decomposition of Mg CO3 having peak at 5400C and it also confirms trace amount of MgCO3 in the egg shell.

$$MgCO3 \rightarrow MgO + CO2 \uparrow \text{ ---------- (ii)}$$

In between 7500C and 9000C, the peak shows a huge weight loss of 39.76% with a big endothermic peak in DTA. At this temperature range almost all the calcium carbonate decomposes into calcium oxide with a peak at 8500C. After that, there is a very slight weight loss which may be due to the decomposition of unreacted CaCO3 left behind. The weight losses incurred during calcinations of egg shells were also noted. The Fig (2) and Fig (3) show the composite XRD of the calcined sample. Fig (2) shows thecomposite XRD graphs of calcined powder from 4000C to 6250C and confirms the presence of calcium carbonate. So, CaCO3 is the main constituent in the egg shell below 6500C. Fig (3) shows the next set of XRD pattern of calcined powder from 6500C to 10000C. The patterns show the presence of both CaCO3 and Ca(OH)2. But at higher temperature, peaks corresponding to CaCO3 gradually diminish and Ca(OH)2 peaks appear. It is due to the decomposition of CaCO3 to CaO as the temperature goes on increasing. This confirms the decomposition of CaCO3 to CaO. Due to the presence of moisture in the atmosphere, CaO absorbs water and changes to Ca(OH)2. So the XRD peaks for Ca(OH)2 are observed instead of CaO.

$$CaO + H2O \rightarrow Ca(OH)2 \text{ ---------- (iii)}$$

The thermal processing used for elimination the organic component of eggshells at 10000C produce the conversion of calcite into calcium oxide. This CaO thus produced is treated with nitric acid to produce calcium nitrate. This Ca(NO3)2 was reacted with di-ammonium hydrogen phosphate in ammonical medium to hydroxyapatite.

$$CaO + HNO3 \rightarrow Ca(NO3)2 + H2O \text{ ---------- (iv)}$$

$$10\ Ca(NO3)2 + 6\ (NH4)2H(PO)4 + 8\ NH4OH \rightarrow Ca10(PO4)6(OH)2 + 20\ NH4NO3 + 6\ H2O \text{ ---------- (v)}$$

The XRD of the hydroxyapatite thus produced was taken. The peaks thus found matches with pure hydroxyapatite. This confirms that the sample produced was pure hydroxyapatite with no other chemical impurities. The conventional chemical analysis of the final powder also confirms that the material is extra pure.

V. Conclusions

The high purity hydroxyapatite can successfully be synthesized through chemical route usingwaste eggshells. This is a novel technique to produce a high value material and final cost of thepowders produced through this route is very low. The process parameters, mainly the amount ofprecursors and pH of the media, are optimized. The bio-compatibility of the synthesized material will be worked out.

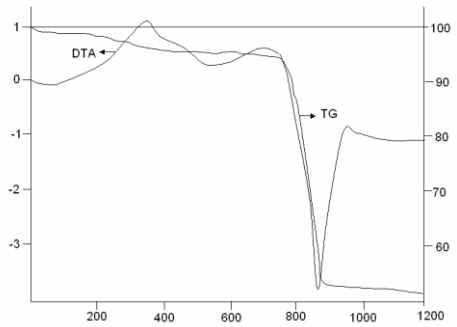

Figure – 1: DTA/TGA of Eggshell.

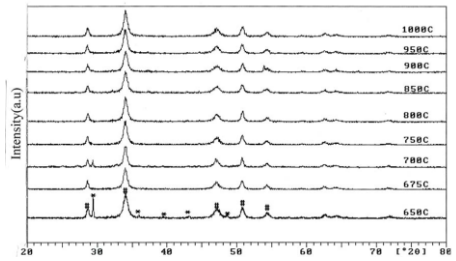

Figure 2: Composite XRD of Calcined Eggshells at Different Temperatures The abbreviation for the phase * represents CaCO3 peaks

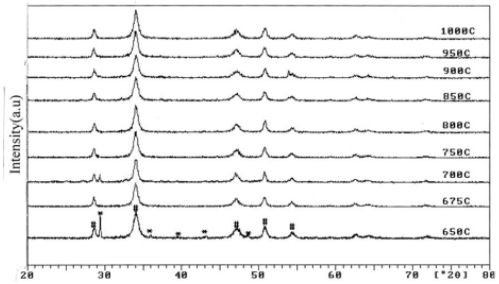

Figure3: Composite XRD of Calcined Eggshells at Higher Temperatures. The abbreviation for the phases: * for CaCO3 peaks and # for Ca(OH)2 peaks.

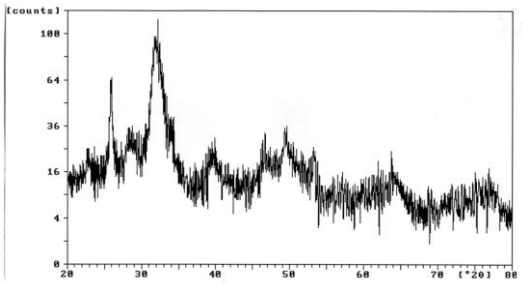

Figure 4: The XRD of Hydroxyapatite Produced from Egg Shell

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