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SYNTHESIS AND CHARACTERIZATION OF HYDROXYAPATITE PRODUCED FROM EGGSHELL

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ABSTRACT

Hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ is an important biomaterial and is the principal inorganic constituent of bones and teeth. It is also used as the replacement of heart valves, hip joints and other implants in the human body. A novel procedure to produce porous hydroxyapatite from the waste eggshells is reported. The thermal decomposition of the clean and dry egg shells were carried out by DTA/TG analysis. The eggshells were thermally treated and hydroxyapatite was produced from the calcined eggshells through chemical route. The powder was characterized by X-Ray Diffraction and particle size analysis.

Keywords: Hydroxyapatite; eggshells; implant; calcium carbonate and calcium oxide.

1. INTRODUCTION

Recently, an ambiguous activity has been observed in the field of material science to develop a new generation of biomaterials for bone replacement which has both the mechanical strength as well as the capability of forming a stable interface with living host tissue. The material thus produced may be bio-inert (e.g., alumina and zirconia), resorbable (e.g., tricalcium phosphate), bio-active (e.g., hydroxyapatite, bio-active glass and glass ceramics) or porous for tissue ingrowths (e.g., hydroxyapatite-coated metals). Ceramics which deals with the repair and reconstruction of diseased and damaged part of musculo-skeletal system is termed as Bio-ceramics. Bio-ceramics are needed to alleviate pain and restore function to diseased and damaged part of the body[1]. Calcium-Hydroxyapatite (HA: $Ca_{10}(PO_4)_6(OH)_2$) is the main inorganic component of hard tissues in bones. They are the member of 'apatite' family having similar structure but not necessarily of identical composition[2]. The similarity of synthetic Hydroxyapatite in chemical and crystallographic structure with that of bone material and its excellent biocompatibility has increased its use in clinical field[3-5]. One of the main components of synthetic Hydroxyapatite as well as of all living hard tissues is Calcium. So the source of calcium needed of the preparation of Hydroxyapatite can be obtained from living bodies. This will also minimize the chances of finding impurities like silica in the material which will in turn help its implant in the living bodies. Moreover, the cost of production can be reduced a lot as there is no need to purify. Eggshells are one of the richest sources of calcium. 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]. A huge amount of eggshells are produced daily which are basically of no use causing environmental pollution. So an attempt has been made to produce clinical grade Calcium-Hydroxyapatite from the waste eggshells.

2. EXPERIMENTAL

Egg-shells of hen were collected in bulk. They were cleaned mechanically by de-ionized water, dried and grinded to very fine particles. This powder was then pre-sintered in a platinum crucible at different temperature starting from 400^0C to 1000^0C at a regular interval of 50^0C. The calcinations of eggshells were carried out in an oven in air to determine the weight loss due to thermal decomposition. Each stage consists of heating the eggshells for two hours at a heating rate of 5^0C/min. The detail thermal analysis of the eggshells was done by DTA/TGA of raw eggshells. The XRD analysis was also carried out for all sets of calcined powder obtained to study the morphological changes during heat treatment. The eggshells transformed into calcium oxide and evolved carbon dioxide above 850^0C as follows:

$$CaCO_3 \rightarrow CaO \quad + \quad CO_2 \uparrow \text{ ---------- (i)}$$

The CaO obtained from eggshells were converted to calcium nitrate [$Ca(NO_3)_2$] by treating with requisite amount of concentrated nitric acid followed by dilution with distilled water. The resulting solution was neutralized with liquor ammonia solution. The ammonia was added in excess to maintain a definite pH during formation of hydroxyapatite. The ammonical $Ca(NO_3)_2$ solution was added drop-wise over a period of approximately 20 – 25 minutes in a mixture containing di-ammonium hydrogen phosphate, liquor ammonia solution and distilled water. The resulting suspension was boiled for 10mins, cooled in an ice-bath and filtered[7]. The Hydroxyapatite thus produced was dried in an oven at 40^0C. The XRD and particle size analysis of the HA powders were carried out.

3. RESULTS AND DISCUSSION

X-Ray Diffractometry was carried out using a Cu-$K_\propto$ 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 250^0C, which is due to the physical absorbed water. But till 450^0C 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 450^0C all the organic compounds are oxidized and so this weight loss.

In temperature between 500^0C and 600^0C, there is a small endothermic peak along with 1.04% weight loss. This is due to the slow decomposition of Mg CO_3 having peak at 540^0C and it also confirms trace amount of $MgCO_3$ in the egg shell.

$$MgCO_3 \rightarrow MgO \; + \; CO_2 \uparrow \text{ ---------- (ii)}$$

In between 750^0C and 900^0C, 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 850^0C. After that, there is a very slight weight loss which may be due to the decomposition of unreacted $CaCO_3$ left behind.

The weight losses incurred during calcinations of egg shells were also noted. The Fig (2) shows the weight loss at different temperatures which matches with the DTA/TGA plots.

The Fig (3) and Fig (4) show the composite XRD of the calcined sample. Fig (3) shows the composite XRD graphs of calcined powder from 400^0C to 625^0C and confirms the presence of calcium carbonate. So, $CaCO_3$ is the main constituent in the egg shell below 650^0C.

Fig (4) shows the next set of XRD pattern of calcined powder from 650^0C to 1000^0C. The patterns show the presence of both $CaCO_3$ and $Ca(OH)_2$. But at higher temperature, peaks corresponding to $CaCO_3$ gradually diminish and $Ca(OH)_2$ peaks appear. It is due to the decomposition of $CaCO_3$ to CaO as the temperature goes on increasing. This confirms the decomposition of $CaCO_3$ 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.

$$CaO + H_2O \rightarrow Ca(OH)_2 \quad \text{----------} \ \text{(iii)}$$

The thermal processing used for elimination the organic component of eggshells at 1000^0C produce the conversion of calcite into calcium oxide. This CaO thus produced is treated with nitric acid to produce calcium nitrate. This $Ca(NO_3)_2$ was reacted with di-ammonium hydrogen phosphate in ammonical medium to hydroxyapatite.

$$CaO + HNO_3 \rightarrow Ca(NO_3)_2 + H_2O \quad \text{----------} \ \text{(iv)}$$

$$10\ Ca(NO_3)_2 + 6\ (NH_4)_2H(PO)_4 + 8\ NH_4OH \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 20\ NH_4NO_3 + 6\ H_2O \quad \text{----------} \ \text{(v)}$$

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.

Particle size analysis of the synthesized powders was carried out by LASER technique and average particle size was found to be 4.77μm.

4. CONCLUSIONS

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

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TABLES AND FIGURES

Table – 1: Thermal Decomposition of Egg Shells in Air

Serial No.	Temperature (^{0}C)	Percentage Weight Loss
1	400	05.03
2	450	05.11
3	500	05.03
4	550	05.48
5	600	05.54
6	625	13.24
7	650	27.44
8	675	29.02
9	700	28.86
10	750	35.17
11	800	42.44
12	850	45.46
13	900	46.07
14	950	46.18
15	1000	46.21

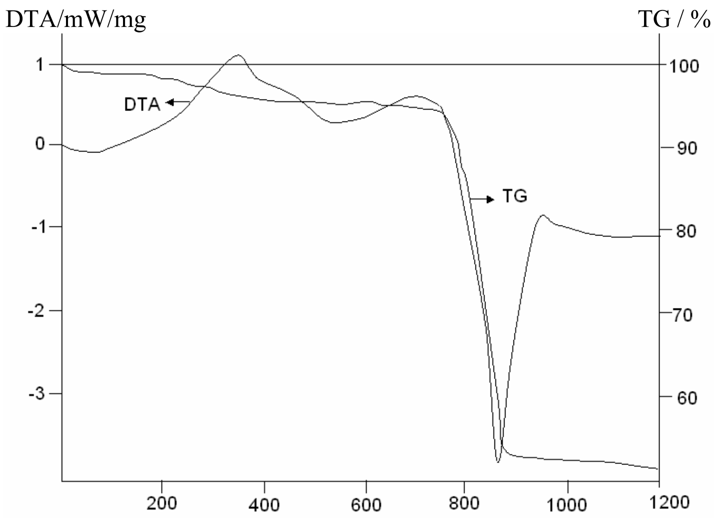

Figure – 1: DTA/TGA of Eggshell.

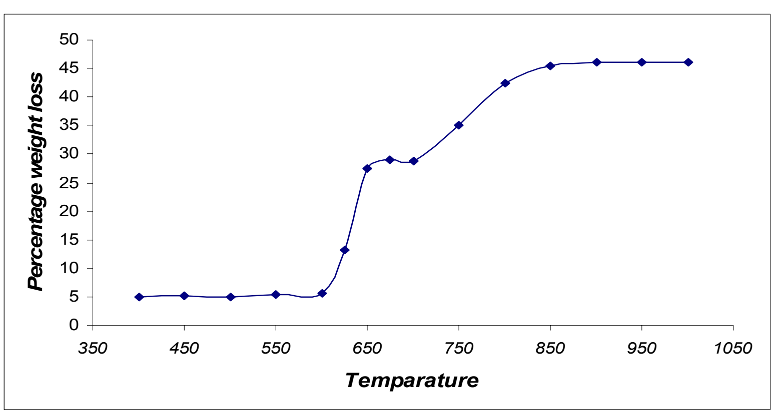

Figure 2: Thermal Decomposition of Egg Shells

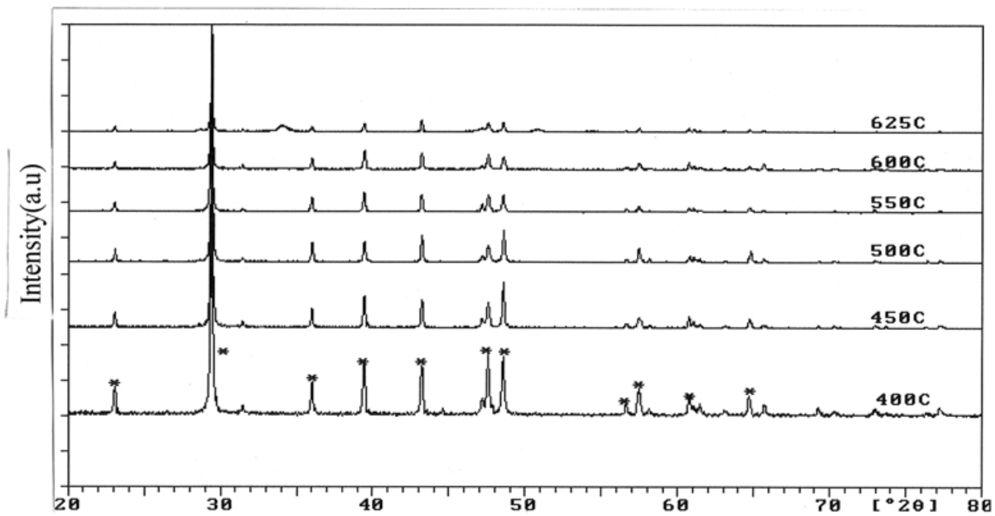

Figure 3: Composite XRD of Calcined Eggshells at Different Temperatures
The abbreviation for the phase * represents $CaCO_3$ peaks.

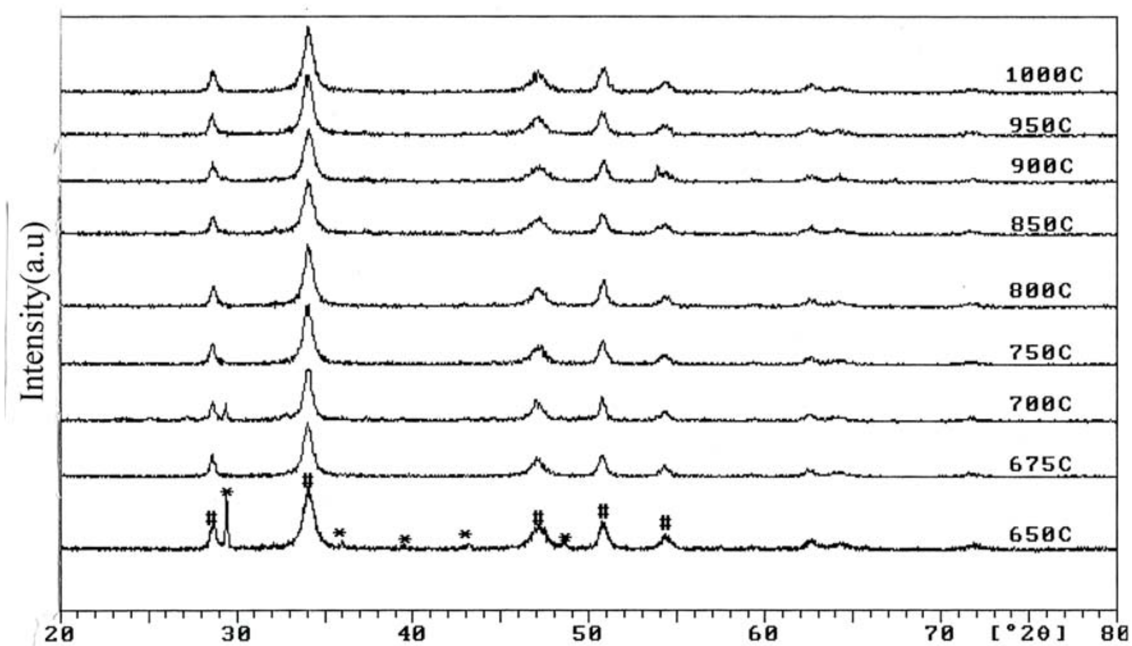

Figure 4: Composite XRD of Calcined Eggshells at Higher Temperatures.
The abbreviation for the phases: * for $CaCO_3$ peaks and # for $Ca(OH)_2$ peaks.

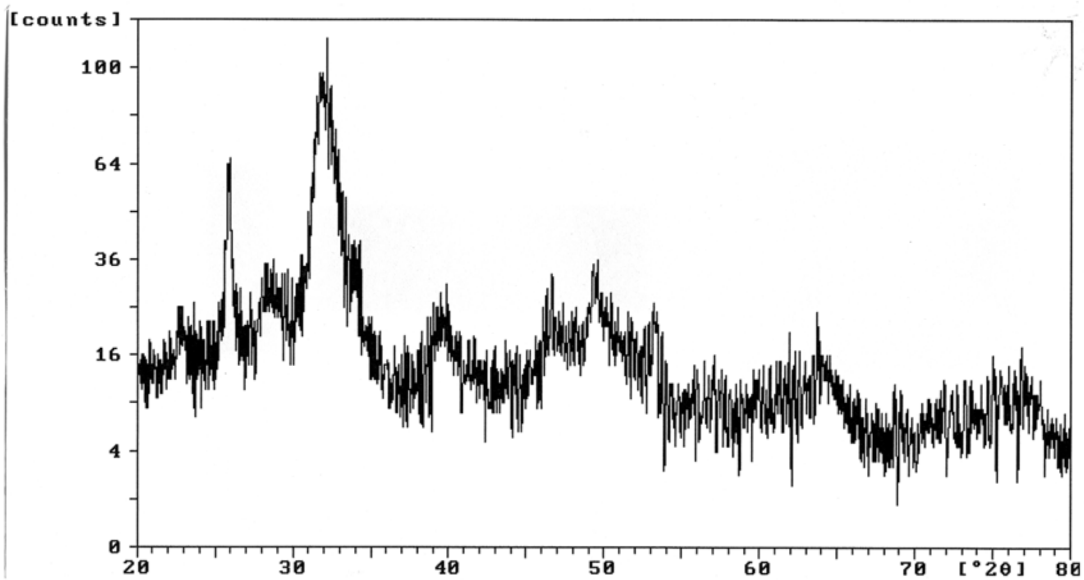

Figure 5: The XRD of Hydroxyapatite Produced from Egg Shell.

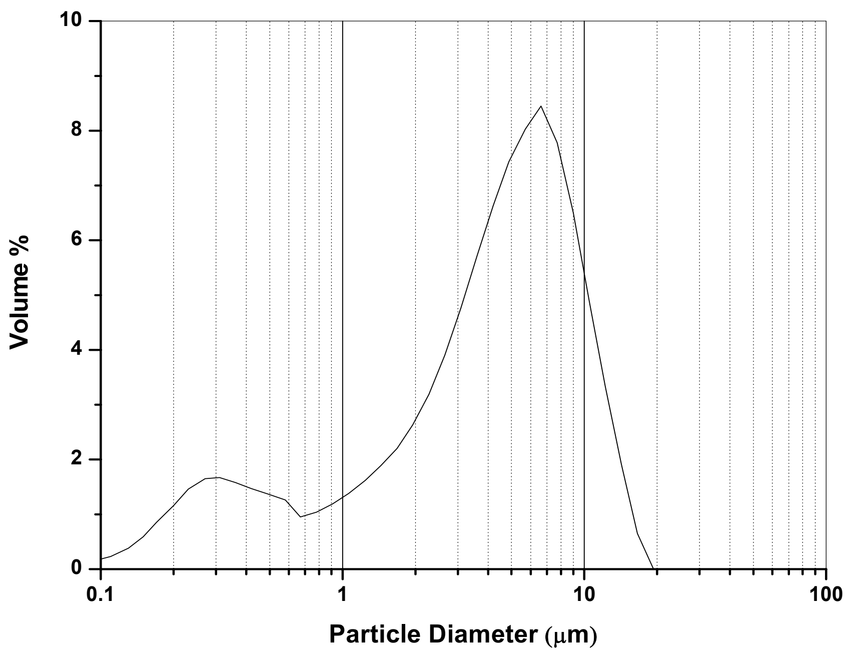

Figure 6: Particle Size Analysis by Laser Technique