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COMPARATIVE STUDY OF HYDROXYAPATITE SYNTHESIZED FROM FISH SCALE WASTE AND BY CHEMICAL METHODS

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Abstract - *Hydroxyapatite (HAp) was synthesized via both chemical and bio-waste routes. The chemical route employed the chemical precipitation method, wherein calcium nitrate tetrahydrate and di-ammonium hydrogen phosphate were directly mixed without any preliminary mixing or pH adjustment. The solution was then vigorously stirred for 6–8 hours to ensure complete precipitation. The resulting precipitate was separated from the mixture using a filtration unit and subsequently dried in an oven for 24 hours. After drying, the HAp powder was calcined in a programmable furnace at 1000 °C to achieve crystallization. The cleaned scales were subsequently deproteinized by soaking them in 0.1 M hydrochloric acid (HCl) for 12–14 hours to eliminate organic matter. After the HCl treatment the fish scales are stirred in 1N NaOH solution whilst maintaining a temperature of 70oC. The stirring is done at a rotational speed of 1000 rpm for 5 hours. After this a white colored precipitate was formed in the bottom of the beaker. The solution is then filtered using Whitman filter paper alongside washing was continued till the pH of the solution becomes normal. The filtered material is left for drying at a temperature of 60 to 80oC for 24 to 36 hours. Thus it is evident that we can produce hydroxyapatite using fish scales. This will make the production of hydroxyapatite inexpensive. Through this we can thus have waste to wealth approach as the hydroxyapatite is a very valuable ceramic, which can be used for medical as well as for the water treatment purpose.*

Keywords: Hydroxyapatite (HAp), chemical precipitation method, calcined, deproteinized, Whitman filter paper, FTIR analysis

1. INTRODUCTION

Hydroxyapatite (HAp) is a well-known material and have numerous of application like bio-medical (tissue engineering, bone, dentistry, oral and maxillofacial surgery), filter cartage, adsorbent (especially heavy metal i.e. defluoridation), coating material, chromatographic application, prosthesis development and translucent materials for bone-china industries.

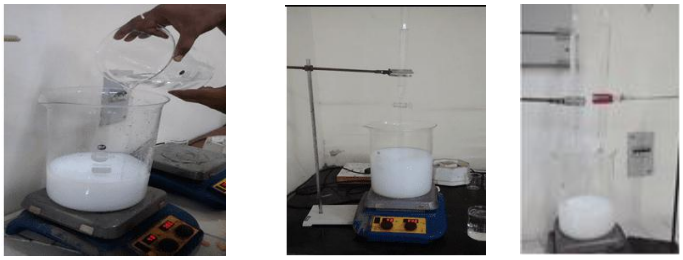
2. Hydroxyapatite (HAp): it is an apatite family mineral structural formula of which is X3Y2(TO4)Z. In this formula X and Y can be represented by Ca, Re, Pb, U, Mn, Ba, Sr. While T by P, As, V, Si, S, or C (as CO3) and Z by F, Cl, OH, or O. The chemical formula of hydroxyapatite (HAp) is Ca10(PO)6(OH)2. The HAp structure have two subsystems one consisting of calcium channels where the OH groups are systematically arranged that provide the framework to form chains of calcium phosphate [51-55].

The decomposition of HAp is not an issue due to excellent biocompatible inorganic substance. A numerous of synthesis processes were earlier cited by various researchers like wet chemical processes (e.g. precipitation, combustion preparation, spray pyrolysis, mechano-chemical and sol–gel process). These processes used costly chemicals and multistep chemical processes that seem to be tedious process resulting in high cost. Hence in this study, the HAp was synthesized via both chemical as well as bio-waste route. Fish scales are used for the synthesis of HAp.

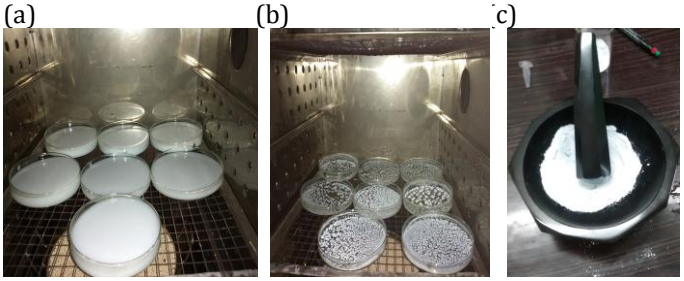
2.1Hydroxyapatite Preparation

The synthesis of hydroxyapatite (HAp) was done using both chemical as well as fish scale route. The FTIR and particle size analysis was done for thus produced HAP. Both the methods are mentioned in the following sections2.2.1 (a) Preparation of HAp using chemical synthesis route:-

0.4M of Ca(NO3)2•4H2O and 0.15M of (NH4)2HPO4 were taken and mixed together in a beaker. The beaker contains distilled water to form aqueous solution of requisite amount of chemicals. After mixing the chemicals were stirred vigorously for 6-8 hrs using a magnetic stirrer with an rpm of about 600. Once mixed these were allowed to precipitate and then the precipitate was put in oven for about 72 hours in temperature of 100 °C to dry off the water. After drying the HAP obtained was put in the programmable furnace for calcination at a temperature of 1000 °C. The systematic pictorial representation of all the process involved during preparation of HAp through chemical route is shown in Figure 2.2.



(a) (b) (c)

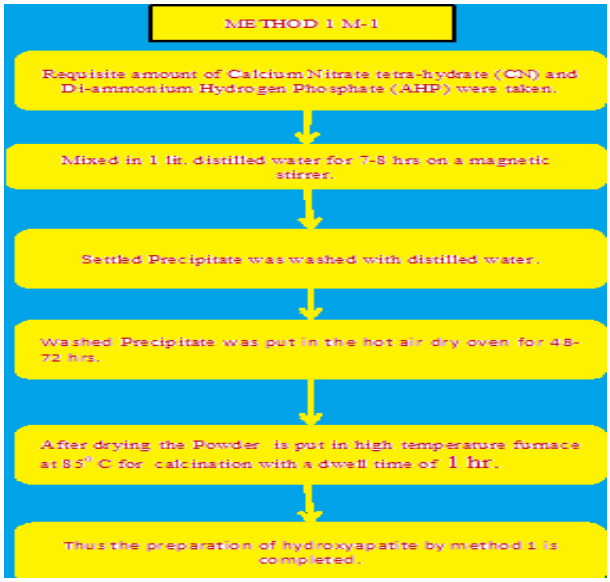


(d) (e) (f)

2.2.1 Chemical Route

The chemicals for the synthesis of HAp through chemical routes are mentioned below:-

Figure shows the flow chart that reveals the systematic processes involved during synthesis of HAp powders.



(a) (b) (c)

Figure 2.3 (a) Planetary mill used for wet balling of HAp for more fine size, (b) Programmable furnace and (c) Thereflek furnace used in FSHAP synthesis.

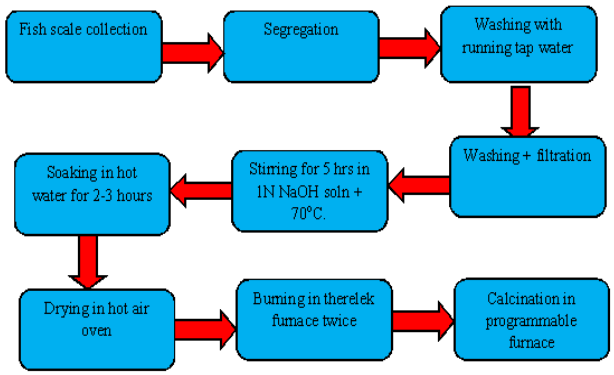


Figure 2.4 Flow chart showing the steps followed for the synthesis of fish scale hydroxyapatite (FSHAp).

This chapter includes the procedures that were followed in synthesis of HAp, its characterization techniques both physical and chemical and adsorption related experiments that were done. The synthesised HAP was characterised using Fourier transform infrared (FT-IR) spectroscopy, X-ray diffraction (XRD), Field Emission Scanning Electron Microscope (FESEM) and Energy Dispersive X-ray analysis (EDXA). For observing the isotherm modelling the Brunauer, Emmett, and Teller (BET) surface area analysis was also done. The physical properties like bulk density and apparent porosity determination procedures are mentioned in this chapter. Particle size distribution of HAP prepared was also determined.

3.1 Experimental Characterization Techniques:

The characterization of hydroxyapatite was carried out for physical and chemical properties. The microstructural properties were observed in FESEM and particle size distribution was carried out. FTIR and particle size analysis was done for both HAp and FSHAp.

3.1.1 Evaluation of Physical Properties

The Archimedes principle was used to measure the apparent porosity and bulk density. Three samples were taken. The first sample was of beads made of HAp. These beads were made by combining the HAp and polyvinyl alcohol. The second sample was of the FSHAp beads that were analyzed for fish scale derived HAp. The third sample was of HAP M2 pellets.

3.1.2 Size of the Particles

The size of the particles was measured using a Malvern Zetasizer Nano Series shown in Figure 3.1. The samples for particle size analysis were prepared by mixing 10 mg of samples in 10 ml of distilled water. The samples before analysing in the zetasizer were first sonicated for 2 minutes. It helped in breaking down the HAp particles properly and also to maintain the homogeneity of the sample. This system uses DLS technique for the particle size analysis.

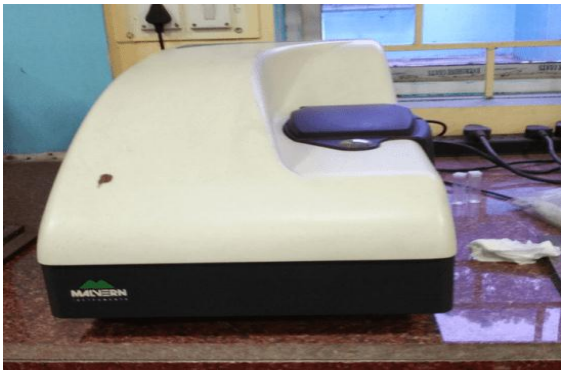


Figure 3.1 Malvern Zetasizer Nano series.

3.1.3 Fourier Transform Infrared Spectroscopy

The infrared spectroscopy characterization was done using FTIR IR Prestige-21, Shimadzu, Japan shown in Figure 3.2. The samples for analysis in FTIR were mixed with potassium bromide (KBr). The mixing ratio of KBr : sample was of 50:1. KBr was taken as reference for background spectrum. Both samples and reference were first crushed in agate mortar for uniform mixing. The mixed powder was kept on standard sample holder and spectrum was recorded in the spectrometer wave in 300-4000cm-1.

Figure 3.2 FTIR IR Prestige-21, Shimadzu, Japan.

3.1.4 X-Ray Diffraction Analysis

Constructive interference of monochromatic X-rays are analyzed through XRD i.e. X-ray beam of a single wavelength and a crystalline sample. The diffract meter attached to the systems is used to detect the X-ray diffraction passed from the sample and continuously record the diffraction intensity as a function of the diffraction angle(2θ). The XRD analysis was done to analyze the phase in HAp on D2 Phaser, Bruker, Make: Germany. The analysis was done for both before and after adsorption. The 2θ range was kept between 20o and 70o. The phase identification of the diffraction data obtained was done by comparing with standards of Joint Committee on Powder Diffraction Standards (JCPDS).

The broadening analysis was used to evaluate the crystallite size of the sintered specimen using Scherrer's formula (Cullity (1978) asshown in Equation 3.3.

$$D = \frac{0.9\,\lambda}{B\cos\theta} \qquad (3.3)$$

Where, D is used to represent crystallitesize, λ is used to represent the wavelength of radiation and θrepresent Bragg's angle. The full width at half maximum is representedby B which is calculated by using Equation 3.4.

$$B^2 = B^2_{meas} - B^2_{inst} \qquad (3.4)$$

Where, Bmeasrepresents the full width at half maximum from peak values and Binst represent the instrumental broadening.

3.1.5 FESEM and EDX Analysis

FESEM and EDX analysis was done using Σigma HD, Zeiss, Germany. Same samples were used for the analysis of EDX and FESEM. FESEM analysis was done to see the morphological features of the prepared HAP. FESEM of HAp M1 nad M2 were done. EDX was done only for HAP M2. EDX analysis is helpful in getting an idea of the chemical composition of the sample. Thus it enables to do elemental and chemical characterization of the sample.

Figure 3.3 FESEM Image analyser

3.1.6 Surface Characterization

The nitrogen adsorption study was done to analyze the surface characters of HAP. Automated Gas Sorption Analyzer, autosorb iQ, Quantacrome, USA was used for the purpose figure 3.4. Specific surface area was determined using both Brunauer, Emmett, and Teller (BET) and Barrett-Joyner-Halenda (BJH) method. The adsorption of nitrogen gas on the HAP sample was studies using liquid nitrogen maintained at a temperature of 77 K.

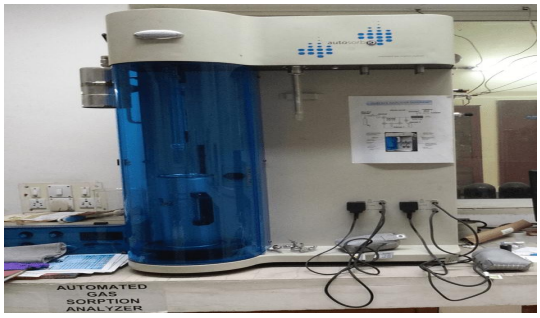
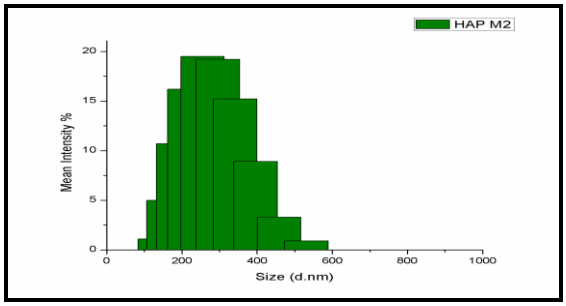


Figure .3.3 Automated Gas Sorption Analyzer, autosorb iQ, Quantacrome, USA

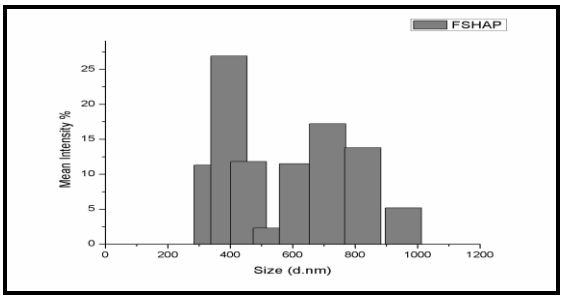
RESULT AND DISCUSSION

There are two methods, one through chemical route and another one for fish scale route. The analysis starts with the evaluation of apparent porosity and bulk density for chemically synthesized as well as fish scales synthesized HAp..

S No.	HAP type	Minimum size (nm)	Maximum size (nm)	Mean size (nm)	Mode (nm)
1	M1	342	955	566	396
2	FSHAp M2	342	458	412	396



(a) HAp M1,



(b) FSHAp M2

Figure 4 Particle size distributions in the form of histogram

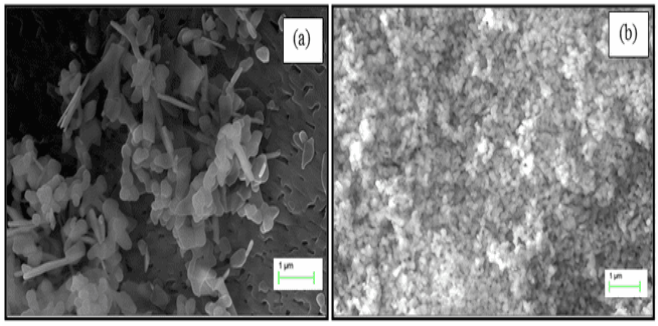


Fig Typical FESEM images of HAp as synthesized by different methods. (a) HAp M1, and (b) FAHAp M2 at same magnifications

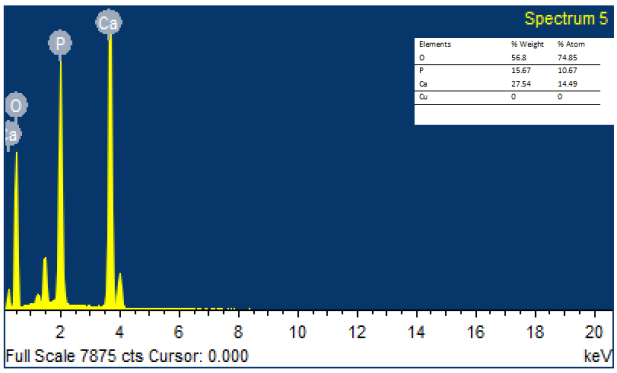
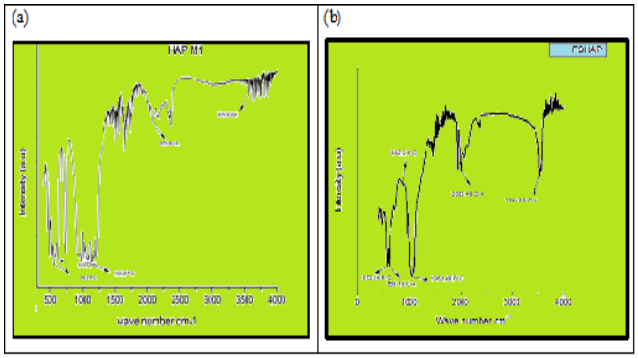
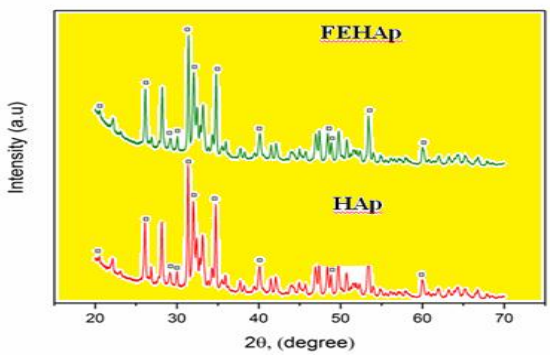


Figure 4.3 EDX analysis of FSHAp M2.



FTIR image of HAP (a) HAp M1, and (b) FSHAp M2



CONCLUSION

The hydroxyapatite was synthesized using both chemical route and bio-waste route. As per chemical precipitation method different processes were adopted. It is evident from these process adaptations that the hydroxyapatite synthesis depends critically on both stirring process and the way the different chemicals are mixed. HAP M1 synthesis was done by mixing calcium nitrate tetra hydrate and Di-Ammonium hydrogen phosphate together without any separate premixing or pH adjustment. It can be seen from the FESEM image analyses that the shape of particles in all the processes respectively is different.

The formation of hydroxyapatite as per fish scale route is also confirmed by FTIR analysis. The particle size analysis of fish scale indicates larger sized particles as compared to the former synthesis processes. The particles being smaller in size can be confirmed from various research papers as has already been mentioned in chapter 3. Thus it is evident that we can produce hydroxyapatite using fish scales. This will make the production of hydroxyapatite inexpensive. Through this we can thus have waste to wealth approach as the hydroxyapatite is a very valuable ceramic, which can be used for medical as well as for the water treatment purpose.

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BIOGRAPHIES

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