

# SYNTHESIS, CHARACTERIZATION AND PHASE STABILITY OF POROUS HYDROXYAPATITE

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**Abstract** - Hydroxyapatite (HAp) exhibits excellent biocompatibility with human body making it ideal for orthopaedic and dental applications. However, the low mechanical strength of hydroxyapatite generally restricts its use to low load-bearing applications. Synthetic hydroxyapatite has been widely used as composite or as coating of implants or as void filler materials. Hydroxyapatite has been synthesized by conventional wet chemical precipitation technique with calcium nitrate and ammonium dihydrogen phosphate as raw materials. Polymeric sponge method is employed here for preparation of porous Hydroxyapatite. Investigations from XRD results concluded the formation of hexagonal crystal structure of hydroxyapatite prepared from wet chemical synthesis. The crystal structure of porous hydroxyapatite is hexagonal one confirmed from diffraction results. In addition to the crystal structure the particle size was found to be in nanometer range. Further FTIR results confirmed the presence of O-H bond, C=O bond and  $PO_4^{3-}$  for hydroxyapatite from wet chemical synthesis and for porous hydroxyapatite. SEM images reveal the spherical structure of hydroxyapatite powder with some agglomerations present. SEM also revealed porous structure along with pore interconnectivity. EDX results showed that the presence of the calcium and phosphorous with the stoichiometric ratio of Ca/P=1.68 which is in close with 1.6777 for both hydroxyapatite powders synthesized from wet chemical method and for porous hydroxyapatite scaffolds prepared from polymeric sponge method.

**Key Words:** Porous Hydroxyapatite, Wet Chemical Synthesis, Stoichiometric ratio, Polymeric Sponge Method

## 1. INTRODUCTION

A biomaterial is a substance that has been engineered to take a form which, alone or as interactions with components of living systems in the course of any diagnostic procedure in humans or animals. In other words any substance (other than a drug) or combination

of substances, either synthetic or natural in origin, which can be used for any period of time, as a whole or as a part of a system which treats, augments or replaces any tissue, organ or function of the body are called biomaterials. Biomaterials are used in medical devices, particularly in those applications for which the device either contacts or is temporarily inserted or permanently implanted in the body. Among different classes of biomaterials, bioceramics are the most emerging trends in the field of biomedical applications. Some of the bioceramics widely used are Hydroxyapatite (HA/HAP,  $Ca_{10}(PO_4)_6(OH)_2$ ) and other calcium phosphate minerals as implant materials for many years due to its excellent biocompatibility and bone bonding ability and also due to its structural and compositional similarity to that of the mineral phase of hard tissue in human bones. Naturally occurring Hydroxyapatite is hexagonal in structure and the hydroxyl ion ( $OH^-$ ) of it can be replaced by  $F^-$ ,  $Cl^-$ ,  $CO_3^{2-}$ ,  $Na^+$ ,  $Mg^{2+}$ ,  $Zn^{2+}$ . Hydroxyapatite have also been widely adopted as bioceramics coating in metallic implants to increase the biocompatibility and bioactivity characteristics making it well suited for dental and orthopaedic applications.

## 2. MATERIALS AND METHODS

### 2.1: Materials

#### 2.1.1: Preparation of Hydroxyapatite Powders

Nano-sized hydroxyapatite powders were prepared by wet chemical precipitation method. Calcium nitrate and ammonium orthophosphate were dissolved separately in two different containers with de-mineralized water. The calcium nitrate solution was stirred until the solution is completely dissolved and was filtered using Whatmann grade 1 filter to remove the turbidity formed during the process. The dissolved ammonium orthophosphate is kept aside. The pH during the solution was adjusted and maintained to 11 using calculated amount of ammonium hydroxide ( $NH_4OH$ ) solution.

### 2.1.2 Preparation of Porous Hydroxyapatite

The porous hydroxyapatite scaffolds with 100 wt% have been prepared by 10 wt% of poly vinyl alcohol as pore former.

### 2.2 Methodology

The dissolved calcium nitrate solution is called Solution X and the ammonium dihydrogen-phosphate solution is called as Solution Y. Solution Y was added drop wise into Solution X and the solution was stirred vigorously and maintained at temperature of 70°C for 45 minutes. By the end of the process a milky solution will be formed confirming the formation of hydroxyapatite as shown in Fig 1

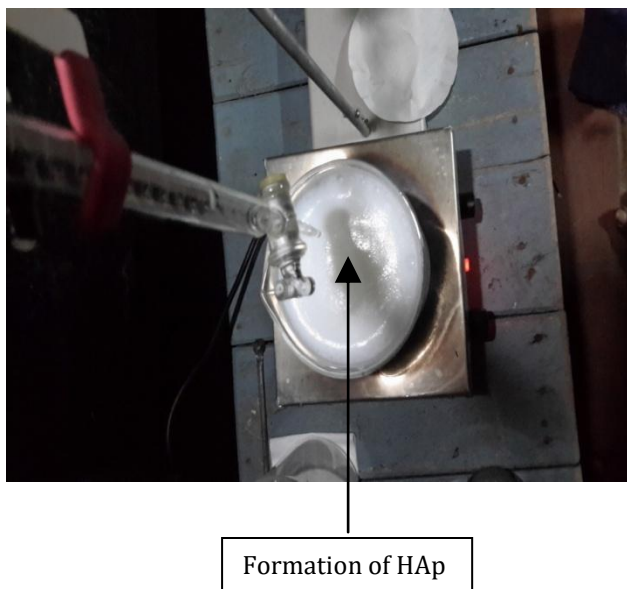


Figure 1: Aerial view of formation of Hydroxyapatite

After the reaction is complete the contents are transferred to a plastic container and covered it with aluminium foil and left undisturbed for 24 hrs allowing the settlement of hydroxyapatite. After 24 hours the mother liquid is decanted leaving the precipitate behind. The precipitate is washed with de-mineralized water for 2-3 times and the liquid solution is fed into centrifuge machine for further cleaning where hydroxyapatite will be obtained in gel form. The gel is collected from centrifuge tubes and transferred onto the petri dish and then placed in hot air oven till the moisture contents are all evaporated. The dried samples are then crushed and made into powders by piston-mortar grinding as shown in Fig 2



Figure 2: Hydroxyapatite Powder

Calculated amount of hydroxyapatite, de-mineralized water and polyvinyl alcohol were taken and the mixture is vigorously till the macropores were converted into fine ones. The complete flow diagram for preparation of porous hydroxyapatite is shown in Fig 3

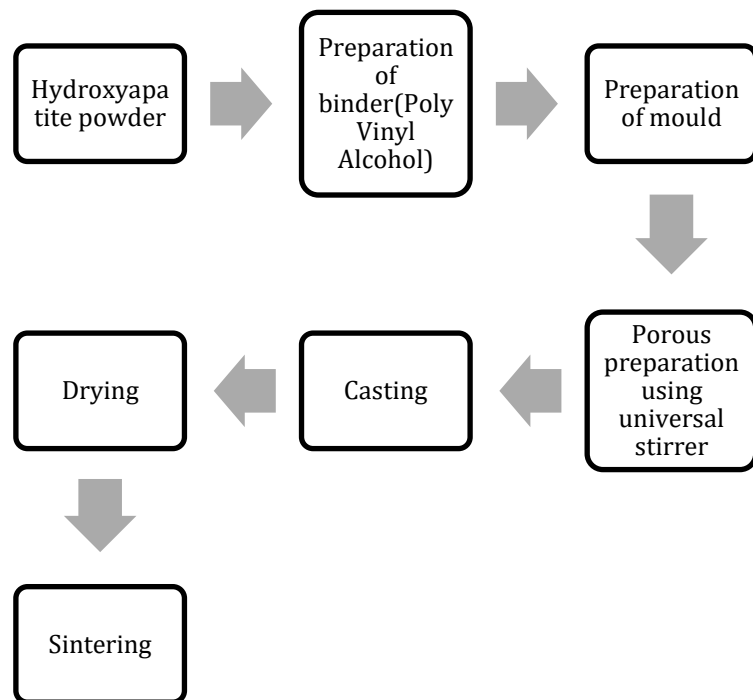


Figure 3: Flowchart for preparation of porous Hydroxyapatite

## 3. RESULTS

### 3.1 Structural Characterization

From the XRD (X-Ray Diffraction) pattern as shown in Fig 6, it is evident that there are a number of peaks (noise) at each level of intensity showing improper growth of crystallites and from Fig 4 it was observed that each of the

peaks and lattice points and intensity angles ( $2\theta$ ) of HAp prepared by co-precipitation method are in accordance with the JCPDS value (9-432). Further using this pattern, the lattice constants and the crystallite sizes of the basic precipitate are calculated from cell calc software and Debye-Scherrer equation. The calculated results and experimental results were found to be in close range. It was found that the basic crystallite size was in range of 44.78 nm, which is universally a typical characteristic of calcium precursors synthesised by wet chemical method. However, after calcinations and sintering the peaks showed a significant peak height and an associated drop in peak width, which corresponds to an increase in crystalline nature of porous HAp. Earlier several authors reported the effect of calcinations or sintering might actually be involved in increasing the overall crystal lattice size. Therefore, the sole effect of increasing crystallinity cannot be isolated easily. It was also noted that the presence of  $\beta$ -TCP begins to surface once the calcinations or sintering temperature reaches  $1000^{\circ}\text{C}$  and above. This may not be desirable, as pure, clean powder is an essential criterion for any implantology in biomedical application. But there are no presences of  $\beta$ -TCP peaks. The porous hydroxyapatite intensity and peak values before and after sintering were also found to be in accordance with JCPDS (9-432) value.

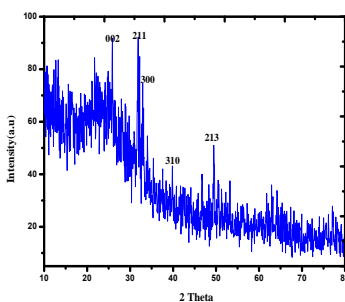


Figure 4: XRD pattern of hydroxyapatite before calcination

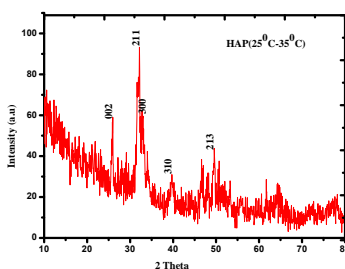


Figure 5: XRD pattern of hydroxyapatite after calcination

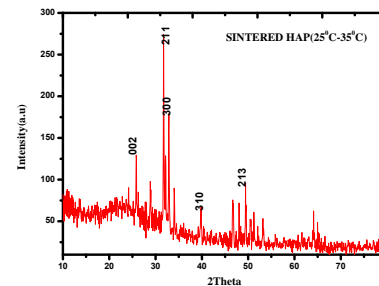


Figure 6: XRD pattern of porous hydroxyapatite before sintering

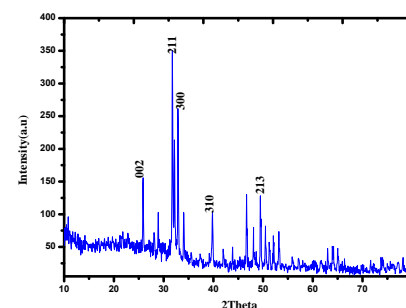


Figure 9: XRD pattern of porous hydroxyapatite after sintering

The FTIR spectrum of the hydroxyapatite is shown in fig 9. The band stretching at  $3861.44, 2001.44\text{ cm}^{-1}$  corresponds to O-H bond linkage and wave number at  $1383.99, 827.49\text{ cm}^{-1}$  corresponds to C=O linkage. The wave number from absorption band corresponding to  $\text{PO}_4^{3-}$  is at  $1026.95, 564.46\text{ cm}^{-1}$ .

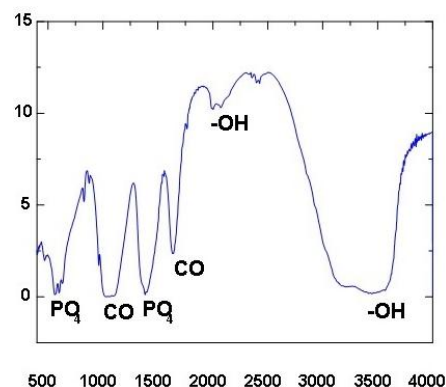


Figure 7: FT-IR of HAp

### 3.2 SEM Micrographs

SEM micrographs revealed hydroxyapatite particles produced by wet chemical synthesis are of dense structure

and spherical shape which is a desirable result as shown in Fig 9. The size of HAp particles varies from 2µm to 6 µm. Fig 10 shows the sintered porous ceramics with presence of micropores and macropores. SEM micrographs also provided information about pore size and shape.

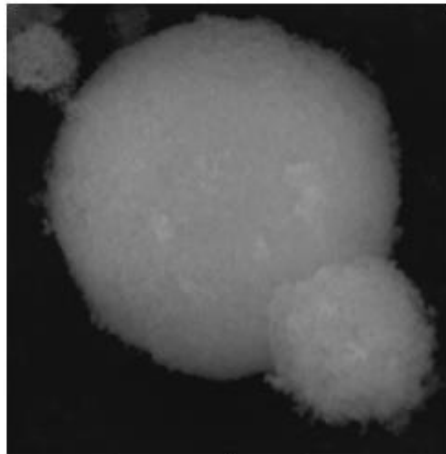


Figure 8: SEM micrograph of HAp at 5 µm scale

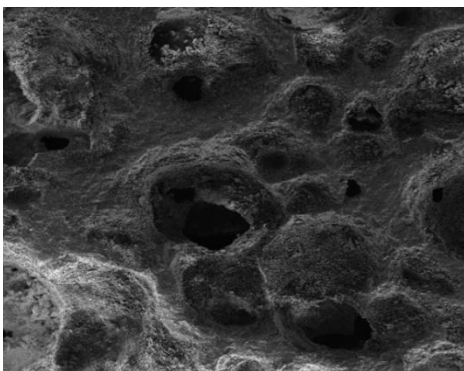


Figure 9: SEM micrograph of porous HAp at 200µm scale

### 3.3 Chemical Composition

Fig 11 illustrates EDX analysis of HAp from SEM demonstrating that they are formed essentially by Ca, P and O. Further the EDX results confirmed that no impurities were present in the samples, and stoichiometric Ca/P ratio was found to be 1.68 which is close to 1.67 for excellent stability of the compound synthesized from calcium and phosphate.

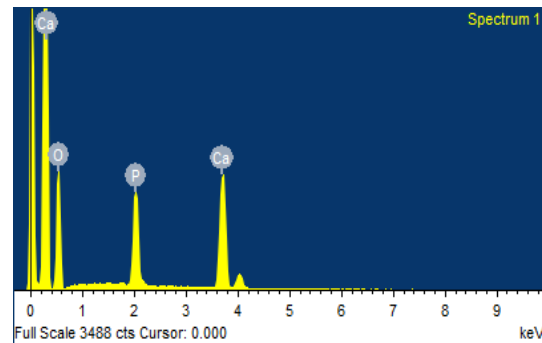


Figure 11: EDX pattern of HAp

### 3.4 TGA Thermogram

The thermogravimetric analysis was carried out between 35°C and 700°C in air at a heating rate of 20°C/min. The thermogram and its differential thermogravimetric trace are shown in Fig 12. The minute weight loss around 130°C is assigned to dehydration of calcium hydroxide. The decomposition trace does not bear any inflection and this process is also not accompanied by any other additional decomposition. Further hydroxyapatite synthesised by wet chemical synthesis exhibited a stable phase.

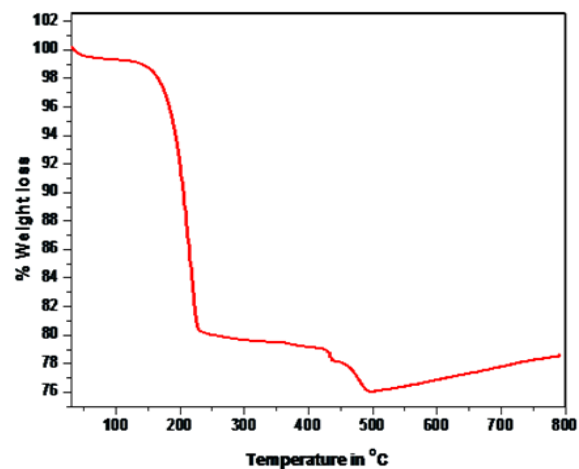


Figure 12: TGA curve of HAp

### 4. CONCLUSION

The present work dealt with the synthesis, characterization and phase stability of hydroxyapatite powder by wet chemical precipitation route and porous hydroxyapatite by polymeric sponge method. The structural characterization results confirmed the presence of elements found in accordance with JCPDS (09-432) value for hydroxyapatite powder and also for porous hydroxyapatite. The FTIR spectra confirmed the bond angles and SEM micrographs revealed the formation of

spherical structure of hydroxyapatite powders. Further all the morphological studies confirmed the porosity, pore size and pore interconnectivity for porous hydroxyapatite prepared by polymeric sponge method. The particle size was found from SEM micrographs. Further the chemical composition of hydroxyapatite was found from EDX results and found to be in close with stoichiometric value of Ca/P=1.68. The particle sizes were found to be in order of nano meters calculated from XRD and SEM results. Therefore, it can be concluded from the structural and morphological studies that there was no existence or formation of secondary phases in synthesized hydroxyapatite powder by wet chemical synthesis and porous hydroxyapatite from polymeric sponge method. Further morphological studies revealed the shape of HAp powder and pore interconnectivity of hydroxyapatite produced by polymeric sponge method.

## REFERENCES

- [1] Aminzarea M., Eskandarib A., Barooniand M.H., Berenovc A., Hesabi Z., Taheria M. and Sadrnezhaade S.K. (2013), 'Hydroxyapatite nanocomposites: Synthesis, sintering and mechanical properties', *Journal of Ceramics International*, Vol. 39, pp. 2197-2206.
- [2] Arcos D. and Regi M.V. (2010), 'Sol-gel silica-based biomaterials and bone tissue regeneration- a review'- *Acta Biomaterialia*, Vol. 6, pp. 2874-2888.
- [3] Dasgupta S., Tarafder S., Bandyopadhyay A. and Bose S. (2013), 'Effect of grain size on mechanical, surface and biological properties of microwave sintered hydroxyapatite', *Journal of Materials Science and Engineering C*, Vol- 33, pp.2846-2854.
- [4] Hong L., Owen C., Tiffany T.Y., Bruno A. and Michael V. (2008), 'Mechanical behaviour of porous hydroxyapatite', *ActaBiomaterialia*, Vol-4, pp.577-586.
- [5] Karimzadeh A., Majid R.A., Bushroa A.R. and Herliansyah M.K. (2014), 'Effect of sintering temperature on mechanical and tribological properties of hydroxyapatite measured by nanoindentation and nano scratch experiments', *Journals of Ceramics International*, doi:10.1016/j.ceramint.2014.01.131.
- [6] Meyers M.A., Mishra A. and Benson D.J. (2006), 'Mechanical properties of nanocrystalline materials', *Journal of Progress in Materials Science*, Vol-51, pp.427-556.
- [7] Monmaturapoj., Yatongchai, (2010), 'Effect of Sintering on Microstructure and Properties of Hydroxyapatite Produced by Different Synthesizing Methods', *Journal of Metals, Materials and Minerals*, Vol.20 No.2 pp.53-61, 2010.
- [8] Muralithran G. and Ramesh S. (2000), 'The effects of sintering temperature on the properties of hydroxyapatite', *Journal of Ceramics International*, Vol.26, pp.221-230.
- [9] Nayak A.K. (2010), 'Hydroxyapatite Synthesis Methodologies: An Overview', *International Journal of Chemical and Technology Research*, Vol.-2, no. 2, pp. 903-907.
- [10] Oghbaei M. and Mirzaee O. (2010), 'Microwave versus conventional sintering: A review of fundamentals, advantages and applications - a review', *Journal of Alloys and Compounds*, Vol-494, pp.175-189.
- [11] Ou S., Chiou S.Y. and Ou K.L. (2013), 'Phase transformation on hydroxyapatite decomposition', *Journal of Ceramics International*, Vol-39, pp. 3809-3816.
- [12] Potoczek M., Zima., Paszkiewicz Z. And Anna S. (2009), 'Manufacturing of highly porous calcium phosphate bioceramics via gel-casting using agarose', *Journal of Ceramics International*, Vol-35, pp.2249-2254.
- [13] Ramay H.R. and Zhang M. (2003), 'Preparation of porous hydroxyapatite scaffolds by combination of the gel-casting and polymer sponge methods', *Biomaterials*, Vol.24, pp.3293-3302.
- [14] Ramesh S., Adzila S., Jeffrey C.K.L., Tan C.Y., Purbolanksono J., Noora A.M., Hassana M.AA., Spoyan C. and Teng W.D (2013), 'Sintering properties of hydroxyapatite synthesise by wet chemical method', *Journal of Ceramic Processing Research*, Vol-39, pp.111-119.