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SYNTHESIS AND CHARACTERIZATION STUDIES OF HYDROXYAPATITE NANOCRYSTALS

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Abstract. Hydroxyapatite (HAp) is the most emerging bioceramic, which is widely used in various biomedical applications, mainly in orthopedics and dentistry due to its close similarities with inorganic mineral component of bone and teeth. In this paper, hydroxyapatite (HAp) nanocrystalline powder was synthesized via wet chemical technique. Diammonium hydrogen phosphate and calcium nitrate tetra hydrate were used as starting materials and sodium hydroxide solution was used as the agent for pH adjustment. Two samples of hydroxyapatite nano crystalline powders were obtained with a molar concentration of Phosphate solution (HAp-1) and two molar concentration of Phosphate solution (HAp-2). The powder samples were evaluated by techniques such as SEM, FTIR, XRD, and UV. According to the above-experimental results, it was found that hydroxyapatite nanocrystals can successfully be produced through wet precipitation method. The particle size of prepared samples of HAp-1 & HAp-2 are 21.52 nm and 29.84 nm respectively. The absorbance of HAp-1 & HAp-2 are 250.21 nm and 221nm respectively. The functional groups presented in the prepared samples are evaluated by FTIR. The SEM analysis is taken at various orientation and also various magnification range from 200 nm to 1μm.

Keywords: Hydroxyapatite, Biomedical, Wetchemical, Coating.

1. INTRODUCTION

Hydroxyapatite is one of the prominent compounds. It occurs naturally in human bone, which is mainly compound of calcium as one of the main source. These materials are used in coating and porous skeletons. This bio ceramic, Ca10(PO4)6(OH)2, can be synthesized by many wet chemical and mechano-chemical methods. The solgel route is becoming a unique low-temperature technique to produce ultra fine and pure ceramic powders. Recently, hydroxyapatite powders and coatings have been successfully synthesized by the sol gel method. The process parameters have been optimized to produce high purity hydroxyapatite. Among all biomaterials, hydroxyapatite - the mineral component of hard tissues in vertebrates, is the most biocompatible material able to be used in clinical applications of conservation and restoration because of its excellent features such as biocompatibility and bioactivity. Hydroxyapatite shows excellent biocompatibility not only with hard tissue but also with soft tissue. This material is capable of integrating biologically when directly implanted into a bone defect; furthermore, it produces no harmful effect on the immune system, is not toxic, and features an osteoconductive behavior [5].

Hydroxyapatite (HAp) is a calcium phosphate similar to the human hard tissues in morphology and composition [8]. Particularly, it has a hexagonal structure and a stoichiometric Ca/P ratio of 1.67, which is identical to bone apatite [3, 6, 7, 1]. An important characteristic of hydroxyapatite is its stability when compared to other calcium phosphates. Thermodynamically, hydroxyapatite is the most stable calcium phosphate compound under physiological conditions as temperature, pH and composition of the body fluids [3]. With the development of nanotechnology, a major impact on materials science has been noticed. The production of nanomaterials has gained considerable attention for adsorption, catalysis and optical applications, particularly when biomaterials are involved [4]. Motivated by the results, we here by report the synthesis and characterization studies of hydroxyapatite nanocrystals by wet chemical method. The as synthesized hydroxyapatite nanocrystals with different molar ratios are characterized by powder X-Ray Diffraction, Fourier transform infrared analysis, Scanning Electron Microscope analysis and UV Visible spectral studies are reported for the first time.

2. MATERIALS AND METHODS

0.09 molar of Diammonium hydrogen phosphate (1.189 g) was dissolved in water (100 ml) and stirred well. 0.15 molar of Calcium nitrate tetrahydrate (3.54 g) was dissolved in water (100 ml) and stirred well. The appropriate stiochiometric ratio of phosphate solution was added slowly in to the calcium nitrate solution with vigorous stirring. Similarly two molar of phosphate solution was added slowly in to the calcium nitrate solution with vigorous stirring both solutions was brought to pH 11 by addition of concentrated sodium hydroxide solution. The obtained precipitation was hydroxyapatite. The precipitation of hydroxyapatite can be described by Equation (1)

$10Ca^{2+}+6HPO4^{-}+2OH^{-} \rightarrow Ca10(PO4)6(OH)2+ 6H^{+} \ldots\ldots\ldots (1)$

The precipitate was aged overnight at room temperature and was thoroughly centrifuged and washed with deionized water. The processes of centrifuging and washing were carried out three times. The resulting powder was calcined in a furnace at 80 ^{o}C for 8 h after heating at the rate of 5 ^{o}C/min. in air. From the wet chemical method we got 3.64 g and 7.30 g of hydroxyapatite nanopowders for one molar phosphate solution and 2 molar phosphate solutions respectively. The as prepared samples of hydroxyapatite nanocrystals are shown in Fig 1.

FIGURE 1. As prepared samples of hydroxyapatite nanocrystals

3. RESULTS AND DISCUSSIONS

The prepared sample of Hydroxyapatite (HAp-1 & HAp-2) was characterized by X-Ray Diffraction analysis (XRD), Scanning Electron Microscope analysis (SEM), Fourier Transform Infra Red spectroscopic studies (FTIR) and Ultra Violet visible spectroscopic studies (UV).

3.1. **X-Ray Diffraction Analysis.** The structural analysis of sample was done by powder X-Ray diffraction. The XRD patterns of synthesized nano hydroxyapatite (HAp-1 and HAp-2) is shown in Fig 2 The XRD pattern of nano hydroxyapatite shows sharper peaks which indicate better crystallinity. By comparing the XRD results of HAp -1 and HAp-2, HAp-2 has sharper peaks and less noise. This is due to presence of more HAp molecules compared to HAp-1. From this we conclude that by increasing the ratio of molar concentration of phosphate increases the particle size. The average crystallite size of HAp-1 and HAp-2 are 21.52 nm and 29.84 nm respectively.

From the XRD results calculate the crystallite size of the materials was calculated using the relation.

$$D = \frac{K\lambda}{\beta D cos\theta}$$

Here, **D** is the particle size, **K** is a constant (0.9), β**D** is the peak width at half-maximum intensity, λ is the wave length, θ is the peak position.

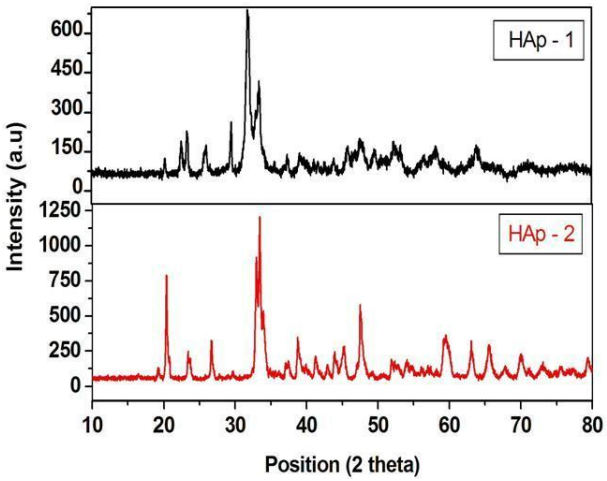

FIGURE 2. XRD PATTERN OF HAp-1 and HAp2

3.2. **Fourier Transform Infrared (FTIR) Analysis.** The FTIR spectra for all prepared samples are analysed using Bruker, Alpha T, model spectrometer. The functional groups of the synthesized hydroxyapatite nanoparticles is analyzed by FTIR spectrometer. Fourier Transform spectroscopy is a technique which is used to obtain an infrared spectrum and to measure the vibrational frequencies of bonds in the molecule. Fig 3 shows the FTIR spectrum of the HAp-1 and HAp-2 nanoparticles synthesis by wet chemical method. A number of vibration bands can be seen in the region of 4500-500 cm^{-1}. The functional groups presented in HAp-1 and HAp-2 are tabulated in Table 1 & 2 respectively.

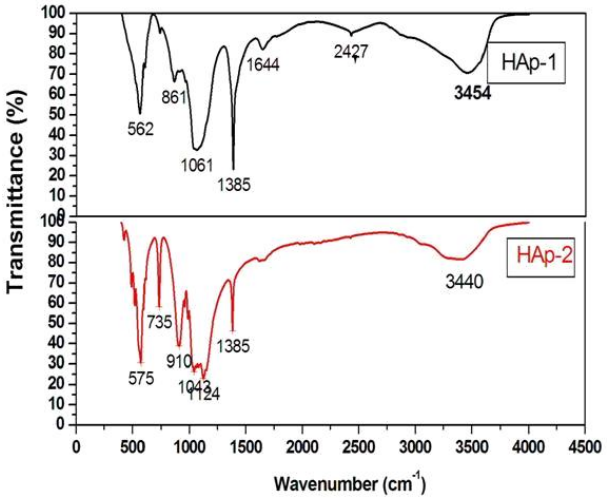

FIGURE 3. Ftir Spectra of HAp-1 and HAp-2 nanocrystals

EXPERIMENTAL VALUE	ASSIGNMENT
562	PO4 bend $\nu 4$
861	Out of plane bending mode [$CO3^{2-}$]
1061	Asymmetric stretching [$PO4^{-3}$]
1385	$CO3^{2-}$
1644	$CO3^{2}$
2427	$CO3^{2-}$
3454	H20 adsorbed

TABLE 1. Vibrational Assignments of HAp-1 nanocrystals

EXPERIMENTAL VALUE	ASSIGNMENT [CHEMICAL GROUPS]
575	Asymmetric bending Vibration [$PO4^{3-}$]
735	[P_2O7^{4-}] [begins showing up if $1.5 <$ Ca/P < 1.67]
1042	Asymmetric stretching [$PO4^{-3}$] & 3 bending mode
1124	β-TCP
1385	NO3-(Synthesis residue that disappears during the calcifying)
3440	OH-Ions prove presence of HAp

TABLE 2. Vibrational Assignments of HAp-2 nanocrystals

3.3. **Scanning Electron Microscope Analysis (SEM).** Scanning electron microscopy is used for inspecting topographics of specimens at very high magnifications using a piece of equipments called the Scanning Electron Microscope. In order to obtain insight information about surface morphology and particle size of the samples, SEM analyses were performed. SEM images were obtained on a Parl Zesis evo18 instrument. The SEM images of HAp-1 nanoparticles are analyzed at magnification 1μm and 2μm. Fig 4 shows the SEM images of HAp-1 nanocrystals. The SEM images of HAp-2 nanoparticles are analyzed at various position and its magnification 200nm to 1 μm also varied. Fig 5 shows the SEM images of HAp-2 nanocrystals.

3.4. **Ultra Violet Visible Studies.** The UV-Vis spectrum was obtained by using systronics, 2202 model spectrometer. The obtained absorption and transmittance of the nanoparticles are one of the important properties to be studied to understand the behavior of nanoparticles. The absorption and transmission spectrum of hydroxyapatite nanoparticles were taken in the wavelength range 200-1000nm. The absorbances of HAp-1 and HAp-2 are obtained at the wavelength of 250.21 nm and 221 nm respectively. The absorbances peak of HAp-1 and HAp-2 are shown below in Fig 6 and Fig 7 respectively.

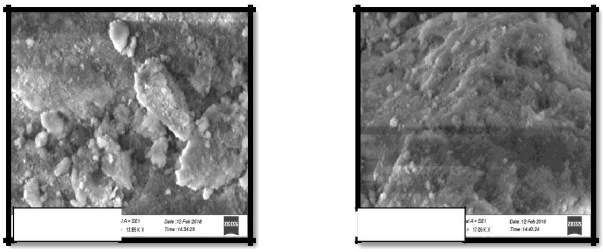

FIGURE 4. SEM Image of HAp-1 nanocrystals

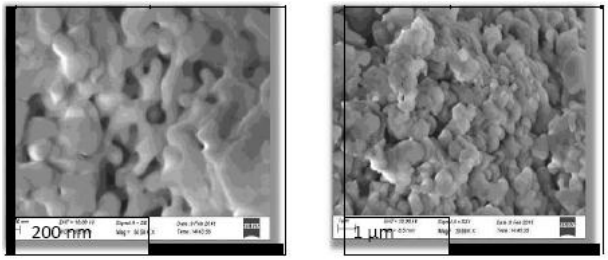

FIGURE 5. SEM Image of HAp-2 nanocrystals

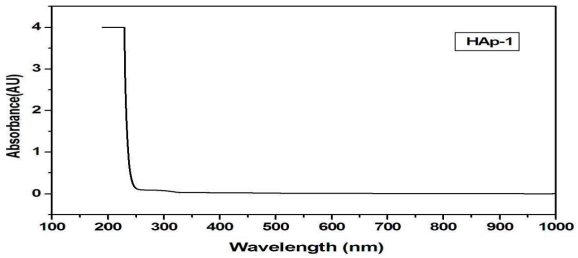

FIGURE 6. Absorbance peak of HAp-1 nanocrystals

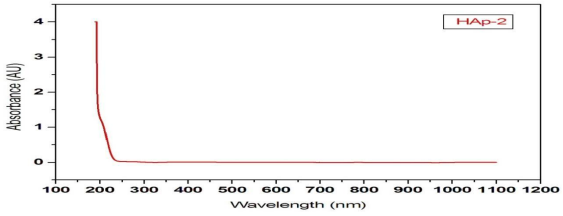

FIGURE 7. Absorbance peak of HAp-2 nanocrystals

4. SUMMARY AND CONCLUSION

In this paper, we have successfully synthesized hydroxyapatite nano powders by wet chemical method. Two samples of hydroxyapatite nano crystalline powder were synthesized with one

molar concentration of phosphate solution (HAp-1) and two molar concentration of phosphate solution (HAp-2). The nano powder samples were evaluated by the following techniques, such as XRD, FTIR, SEM and UV. From XRD the crystalline size of the nano particle was calculated using De-Bye Scherer equation. The prepared crystallite size of HAp-1 and HAp-2 are evaluated by the XRD and the crystallite size of prepared samples of HAp-1 and HAp-2 are 21.52 nm and 29.84 nm respectively. Various functional groups are confirmed using FTIR analysis. The absorbance of the prepared nano powders was evaluated using UV-V is analysis. The absorbance of HAp-1 and HAp-2 are evaluated by the UV Visible studies and the absorbance of HAp-1 and HAp-2 are 250.21 (AU) and 221(AU) respectively. From images of SEM the structure of the hydroxyapatite was identified. The SEM analysis is taken at various positions and also various magnification range 200nm to 1μm.

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