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Synthesis of Hydroxyapatite mesoporous nanoparticles at low temperature via chemical precipitation

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Abstract:

In the present study, mesoporous hydroxyapatite (HA) nanopaticles was succesfully synthesized via aqueous chemical precipitation. Sample was characterized with BET-BJH, XRD, FE-SEM. It was found that HA Nanoparticles with hexagonal structure can be synthesized at low temperatures. X-ray diffraction was approved this. FE-SEM images of HA nanoparticles showed spherical morphology with 40 nm in diameter. BET analysis approved mesoporous structure.

Keywords: Hydroxyapatite, Mesoporous, Chemical precipitation, Characterization.

Introduction:

Hard tissues of mammals, bone, dentin and enamel, are composites consisting of mineral particles, organic materials such as proteins and water. In fact, the bone can be used as a natural nanocomposite with high percentage of inorganic phase that considers the final shape and forms the skeleton.

Mineral phase of bone and teeth mainly consists of a particular class of calcium phosphates called hydroxyapatite (HA). Particles of hydroxyapatite in bone had a crystal structure consisting of OH^-, PO_4^{3-} and Ca^{2+} ions and ionic impurities (M.sadat-Shojai, 2010).

The most stable phase of calcium phosphates is Hydroxyapatite (HA) with $Ca_{10}(PO_4)_6(OH)_2$ chemical formula at low temperatures and pH between 4 and 12, that because of its biocompatibility and bioactivity is recognized as an important substituing material of bones and in orthopedic, dental prostheses and implants (X. Wu et. al., 2012, D.N. Ungureanu et. al., 2011).

Molar ratio of Ca / P changes from 1.2 to 2 in Hydroxyapatite and stoichiometric ratio of is 1.67 (M.H. Santos et. al. , 2004).

Nowadays, hydroxyapatite is very in attention. The main reason for this, is biocompatibility and bioactivity of hydroxyapatite as well as its similarity to mineral phase of bone and teeth.

On the other hand it has been predicted that hydroxyapatite nanoparticles are capable for inducing bone growth. The ability of these materials to restore lost bone is one of the main reasons for use of hydroxyapatite in a variety of bone biomaterials.

Applications of hydroxyapatite is not limited only to the field of medical applications but also it is used in a wide range of technologies and industries such as catalysts, liquid chromatography, gas sensors, water treatment, chemical fertilizers and drug delivery systems.

In order to build a biomaterial similar to bone structure, several studies on synthesis of mineral phase of bone, hydroxyapatite nanoparticles, have been done (M.sadat-Shojai, 2010).

Despite the different methods of synthesis, chemical deposition from aqueous solution is a versatile and economic method for synthesis of pure hydroxyapatite. So that HA can be easily synthesized at low temperatures ranging from 40-100℃ (S. Polarz, 2002).

1. Experimental:

1.1 Synthesis of mesoporous Hydroxyapatite (HA):

Calcium chloride de-hydrated, Potassium dihydrogen phosphate were used as Calcium and Phosphor precursors, respectively. Ammonia Solution was used for adjusting pH. All chemicals were from Merck Millipore Chemicals.

2 g of calcium chloride de-hydrated ($CaCl_2.2H_2O$) with 33 ml of distilled water were mixed. In a separate container 1.1 grams of powdered potassium dihydrogen phosphate (KH_2PO_4) with 20 ml of distilled water and placed on the stirrer. Then two solutions were mixed together. The pH of solution adjusted by ammonia solution at 12 and milky solution was obtained. After mixing, milky solution was poured into a round-bottom flask under reflux using an oil bath for 24 hours at 90 ° C. After reflux, the solution was divided into equal parts for centrifuging three times with 4500 rpm for 5 minutes. After centrifugation, the separated water from sediment was removed. The precipitated

powder was dried at 100 ° C for 24 hours and named “HA”. Schematic of synthesis procedure is given in Fig. (1).

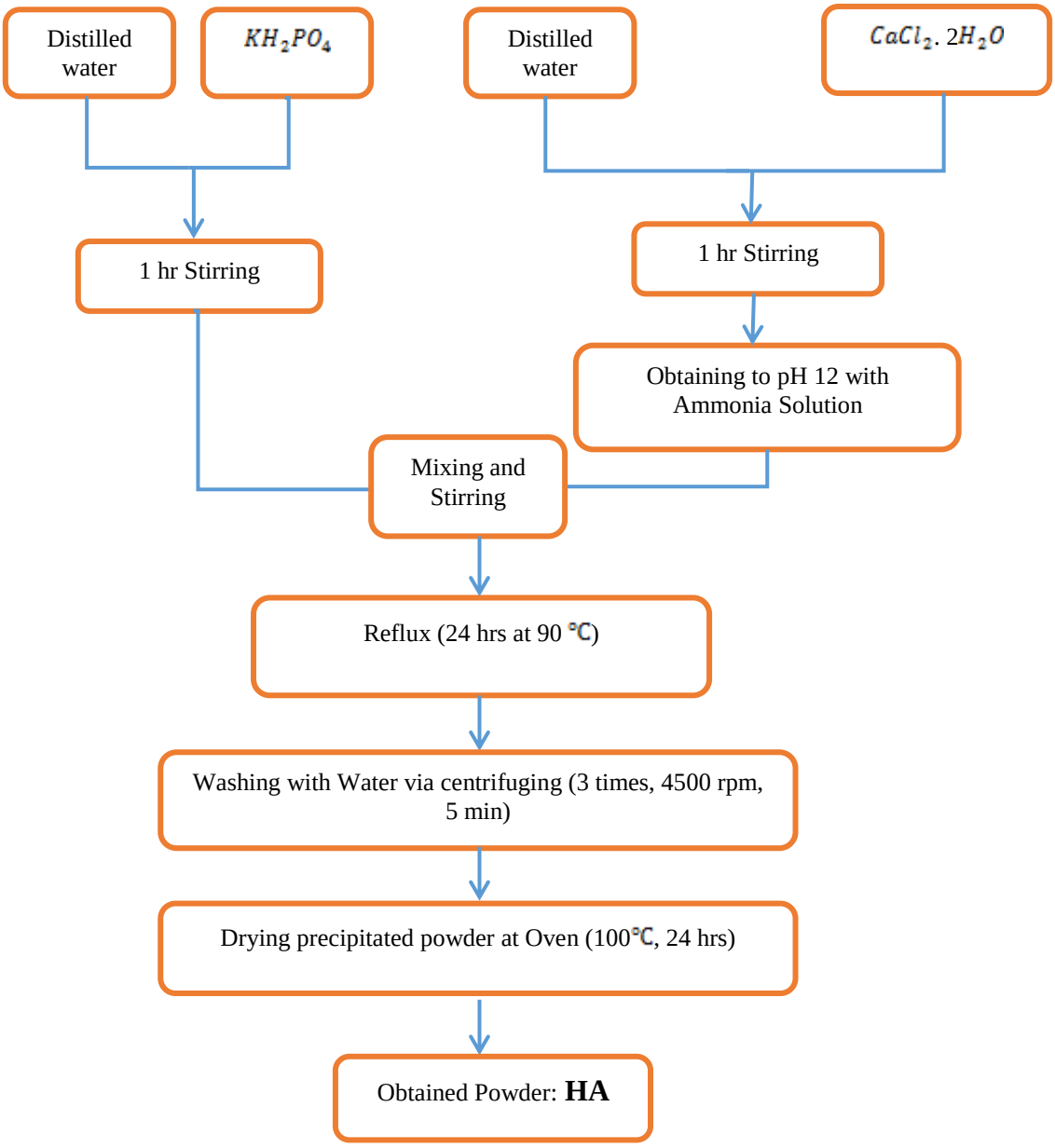


Figure (1). Schematic of synthesis procedure of HA Sample.

3. Results and Disscutions:

3.1. BET-BJH

Absorption-Desorption curve of HA indicates that Nitrogen desorption of sample is according to 5th classification of IUPAC[1] (mesoporous materials). Hysteresis of sample HA is according to IUPAC H1 hysteresis that indicates the presence of cylindrical Open pores (Fig. (2)) (A.Afshar, 2003).

[1] International Union of Pure and Applied Chemistry

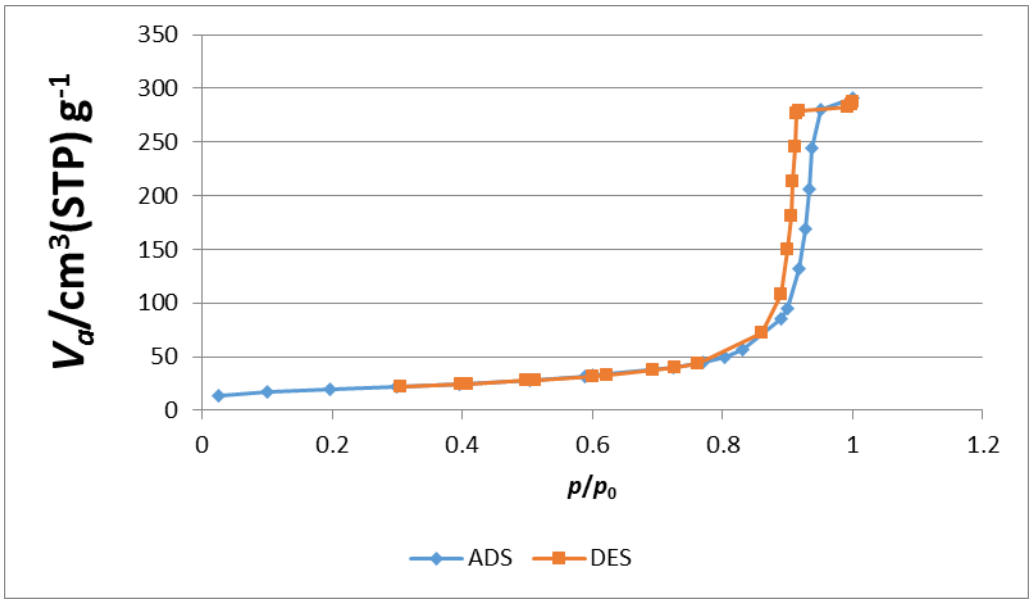


Figure (2). Nitrogen Absorption-Desorption Curve of HA Sample.

BET analysis showed that the average pore diameter and Specific Surface area in sample HA were 26 nm and 67 m^2/g, respectively. Using the BJH equation, the maximum pore diameter was 28 nm. According to Fig. (3), HA has a relatively narrow pore size distribution.

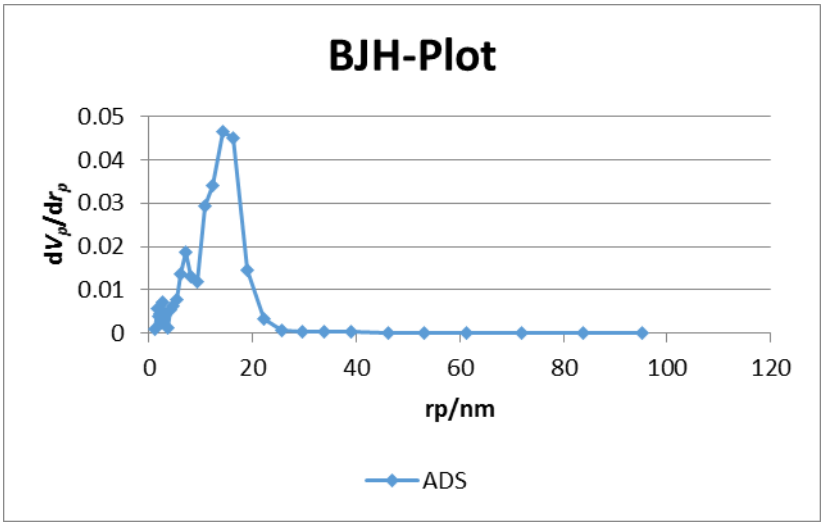


Figure (3). Pore size distribution of HA sample.

3.2. XRD

Peaks obtained in Fig.(4) indicate the presence of hexagonal hydroxyapatite phase according to standard card ICDD 00-009-432. As can be seen Crystallinity of HA Sample is lower than the standard sample and therefore expected to be slightly amorphous phase present in HA sample (Fig.(5)).

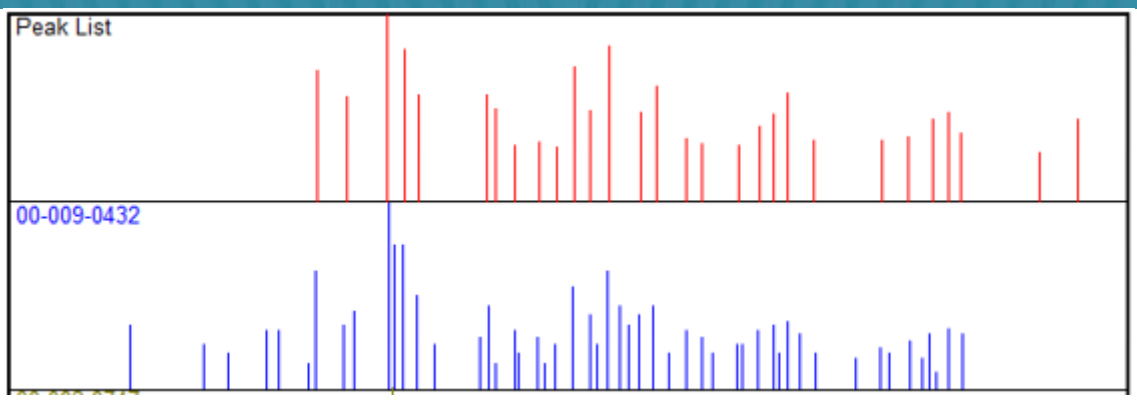


Figure (4). Comparing peaks of HA sample and Standard Card.

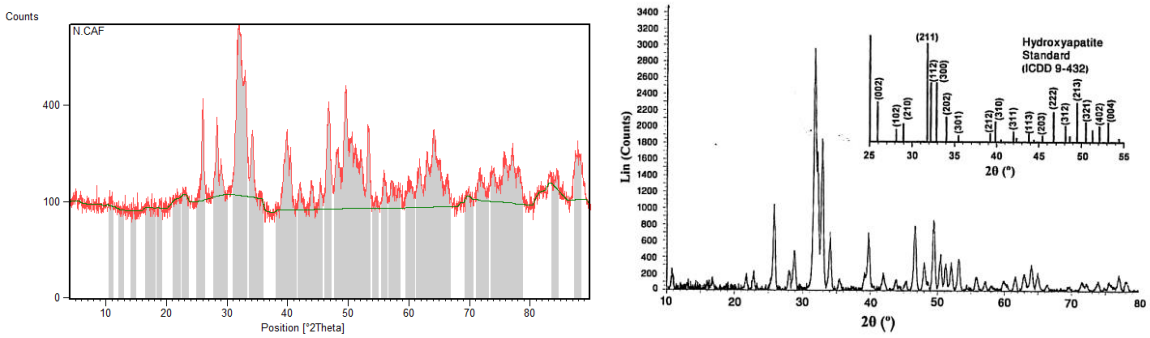


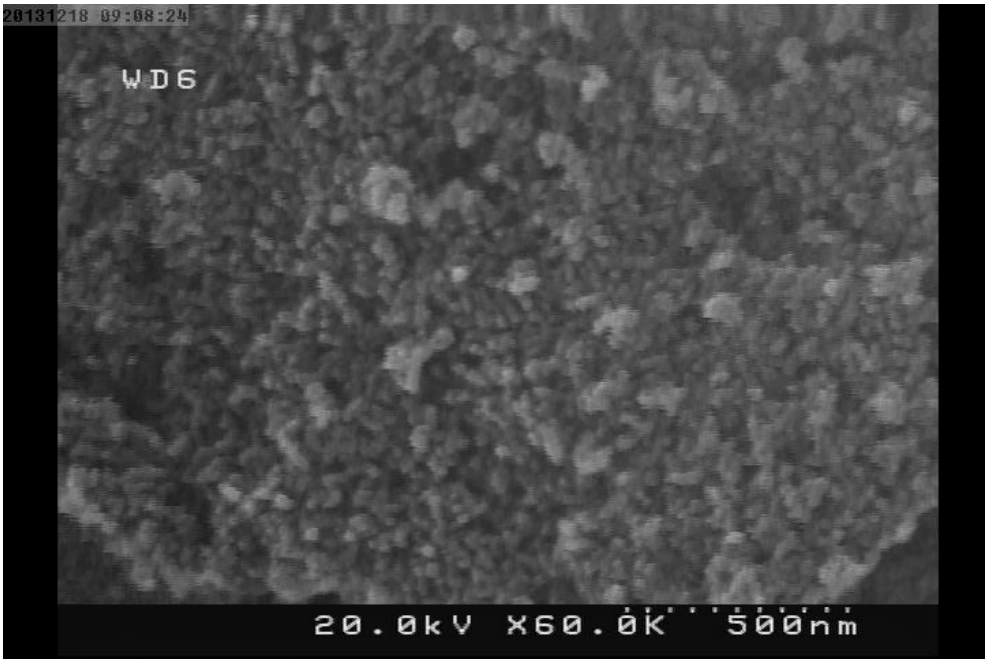
Figure (5). XRD Patterns of HA Sample and Standard Sample (left to right (M.sadat-Shojai, 2010)).

Grain size was obtained according to equation (1) that is known as the Scherrer formula. In this regard, the average size of the crystals is D, λ is the wavelength of the reflected beam, B is the Bragg's Full width at half maximum and ɵ is angle. For HA, the average crystallite size was 42 nm.

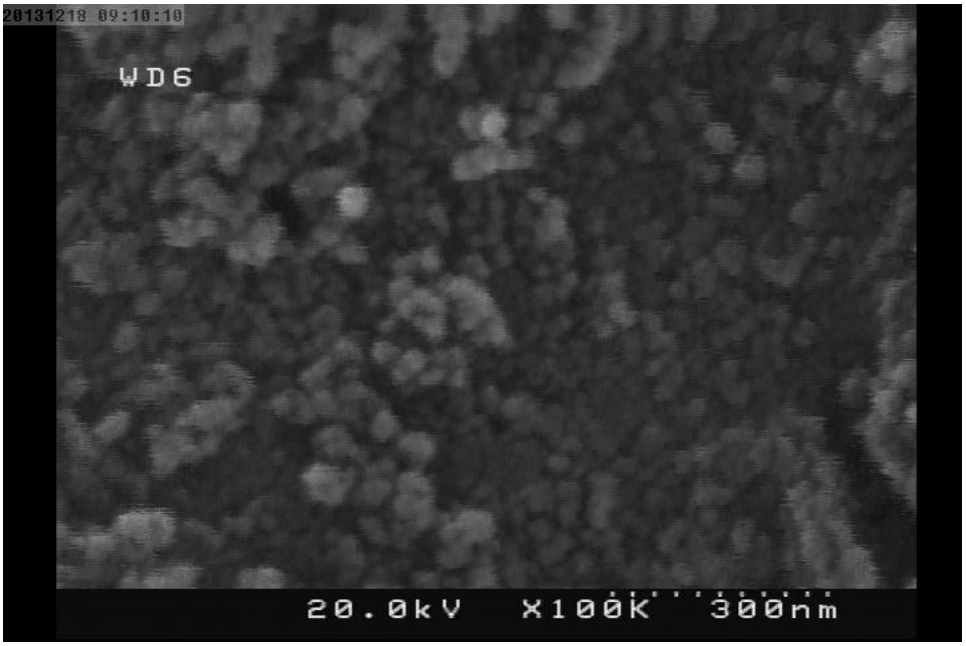
$$D = \frac{0.9\,\lambda}{B\cos\theta} \qquad (1)$$

3.3. FE-SEM

FE-SEM images were taken to obtaining HA particles morphology. Images show that the particles are spherical with diameter about 40 nm (Figures (6) and (7)).



Figures (6). FE-SEM of HA Sample with magnification 60X.



Figures (7). FE-SEM of HA Sample with magnification 100X.

Conclusion:

Hydroxyapatite Nanoparticles were succesfully synthesized via aqueous chemical precipitation at temperature 90°C and its XRD pattern was correspond to Hexagonal Hydroxyapatite. Spherical morphology was approved with FE-SEM images and Nitrogen absorption-desorption was an evidence for mesoporous structure of these nanoparticles.

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