Characterization of Some Hydroxyapatite Samples Doped With Fe (III)


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Abstract:

Calcium hydroxyapatite (HAp) is considered now as the compatible inorganic component of the natural bones and it can directly bond to bone in vivo. It can be usually used as bone substitution or bone filling material. By doping a certain ions into HAp structure, new applications will appeared, and therefore it can be used as drug delivery materials and magnetic material for cancer treatment. However, some Fe (III) doped hydroxyapatite (FeHAp) samples were prepared by the wet chemical method, and these materials were characterized by XRD, IR and ME spectroscopic analysis. The results showed that the colour of the prepared samples changed from white for pure HAp to brown for iron doped HAp, and as the iron content was gradually increased, the colour becomes dark brown. XRD patterns showed that all samples were HAp single phased while the IR spectra revealed that all samples possessed the characteristic phosphate and hydroxyl absorption bands of HAp. Mossbauer Effect (ME) spectroscopy showed the paramagnetic characteristic of FeHAp samples and indicated that iron ions occupy two different sites, octa- and tetra-hedral coordination states.

ملخص الماجستير

Abstract

Calcium hydroxyapatite (HAP) appeared now of high interest, since it represents the compatible inorganic component of the natural bones and it can directly bond to bone in vivo. HAP is usually used as bone substitution or bone filling material, but by introducing new ions into HAP structure, new applications will be introduced. One of them is the use as drug delivery materials due to its biocompatibility, degradation, dissolution and non toxic properties. In recent years HAP was investigated as magnetic material for cancer treatment.
Iron is a vital element in the circulatory system and kidneys and is essential for the function of numerous proteins in cells. The concentration of iron within hard tissue is low, indicating that iron can be present within the body without disturbing the apatite structure and hence the function of bone.

This work aimed to study the effect of ferric iron on the structure and the biocompatibility of HAp as follows.

1- Sample preparation

- A system of five samples of Fe (III) doped hydroxyapatite (FeHAP) were prepared with different iron concentration (HAp 0% Fe), (FeHAp\textsubscript{1} 0.05% Fe), (FeHAp\textsubscript{2} 0.1% Fe), (FeHAp\textsubscript{3} 0.2% Fe), (FeHAp\textsubscript{4} 0.3% Fe).
- The preparation was done by wet chemical method using calcium nitrate titrahydrate [Ca (No\textsubscript{3})\textsubscript{2}.4H\textsubscript{2}O] as a source of calcium, di-ammonium hydrogen orthophosphate [(NH\textsubscript{4})\textsubscript{2} HPO\textsubscript{4}] as a source of phosphorous and ferric nitrate [Fe (No\textsubscript{3})\textsubscript{3}.9H\textsubscript{2}O] as a source of iron at constant pH (10 ± 1) and temperature (60 ± 2 °C).
- The samples were dried at 100 °C for 12 hr, and then crushed in mortar to get the fine powder.

2- Characterization of the prepared samples

- The prepared samples were characterized by X-ray diffraction (XRD), Fourier transforms infrared (FTIR) analysis and Mossbauer Effect (ME) spectroscopy, thermogravimetric analysis technique (TGA), scanning electron microscope (SEM).
- The biocompatibility of the prepared samples was measured by immersion of samples in an inorganic simulated body fluid (SBF) with ion concentrations that were almost equal to those of human blood plasma (stimulated body fluid) to study the solubility and bioactivity of these samples.

3- The obtained results

- XRD patterns showed that all samples were single phased HAp and there is an observed slight shift in the peak position, which indicates the possibility of
incorporation of iron in to the crystal structure of HAp. The calculated lattice parameters and unit cell volume of iron doped samples are smaller than that of pure HAp sample, which suggests that the substitution of iron cause a shrink to the HAp crystals combined with a decrease in the crystal size and crystallinity as the iron content increased.

- The FTIR spectra revealed that all samples possessed the characteristic phosphate and hydroxyl adsorption bands of HAp and the intensity of these peaks decreased with the increase of iron content, which indicate that iron decrease the formation of HAp. Bands belong to the two types of carbonate were assigned in the spectra of all samples, which decreased with the increase of iron content. These carbonate, formed during synthesis and are unwanted and can be eliminated by sintering.

- The pure HAp and FeAHp$_1$ could not be measured by Mossbauer Effect (ME) spectroscopy due to the absence of iron in the first sample and the very low level of iron content in the second sample. ME spectra of FeHAp$_2$, FeHAp$_3$ and FeHAp$_4$ samples exhibit broad doublet indicating that all the prepared samples are paramagnetic materials. The values of Mossbauer parameters indicated that the iron ions in state (I) occupy the tetrahedral coordination while the iron ions in state (II) occupy the octahedral coordination. It can be stated also that the IS and QS values for both tetra – and octahedral states may reflect certain degree of amorphsitiy.

- The experimental densities were measured by Archimedian method and were found to be less than their corresponding theoretical densities but their value closes to that of natural bone. Also it decreases with the increase of iron content due to the decrease of the crystallinity. The evaluation of water absorption, apparent porosity and volume fraction of porosity were measured also by Archimedian method. The results showed that all the parameters increased with the increase of iron content, which attributed to the smaller ionic radius of iron compared with that of calcium.

- There were two regions only found in all thermogravimetric analysis (TGA) curves of prepared samples heated to 1000°C. The results showed that the thermal stability of all samples were found up to 1000°C and the weight loss increase with the increase of iron content.
• Spherical crystals agglomerated together were seen in SEM images and the size of the crystal decrease with the increase of iron content.

• The bioactivity of the prepared samples was examined using stimulated body fluid (SBF) as immersion media. After immersion for 28 days the immersed samples washed and dried at 100 °C for 12 hr and then examined by XRD, FTIR and SEM techniques. XRD patterns of samples after soaking in SBF results showed that the pure HAp sample doesn’t reflect any phases except HAp while all iron doped HAp samples showed a hematite as a secondary phase beside HAp and the hematite phase decrease with the increase of iron content, while the apatite phase increase with the increase of iron content. as the nucleation of HAp induced by the electrostatic attraction force between the sample surface and the cations dissolved in the solution. Accordingly Fe$^{3+}$ ions which have three positive charges may be more effective in inducing an electric field than Ca$^{2+}$ ions, which have two positive charges. Thus after dissolution most of iron ions accumulated on the sample surface due to the electrostatic force between the samples negatively charged surface and the positively charged iron ions and hence the more the iron ions the more the nucleation sites for HAp. Also an expansion in the unit cell length along the c axis and a contraction along the a axis as the iron content increase. Also the crystallinity of all iron doped samples decreased with the increase of iron content and the crystal size of pure HAp, FeHAp$_1$ and FeHAp$_2$ samples deceased gradually then it increased in samples FeHAp$_3$ and FeHAp$_4$.

• FTIR results of the immersed samples showed that the formed HAp layer on the surface of the samples is carbonate substituted HAp, which is β-type and the carbonate content increased with the increase of iron content. The intensities of all peaks of pure HAp sample are small than that of all iron doped samples, which may be attributed to the increase in the crystallinity of iron doped samples compared with that of pure HAp sample as confirmed by XRD results. Also the intensity of carbonate and hydroxyl groups increased and the peaks is sharper as the iron content increased.

• SEM images of the immersed samples showed the formation of carbonate HAp layer (bone like) on the surface of the soaked samples and these layer increased with the increase of iron content, which indicate that iron enhance the crystal growth and nucleation of HAp in-vitro.
• The solubility test reveals that the increase of the solubility with the increase of iron content which due to the substitution of carbonate. As solubility is highly sensitive to structural and chemical compositions of the apatite and depends on the buffering condition, these factors should also be considered as essential key factors for in vitro resorption. The pH value is dependent on the solubility of apatite, where in the pH decreases as the solubility increases.

• The measurement of released ions concentration showed an increase in the concentration of calcium ions with the increase of immersion time, which attributed to the release of calcium from the sample to the solution and a decrease with the increase of iron content, which may be due to the increased CHAp layer formed in the surface of the samples. Also there is a decrease in the concentration of both phosphorous and iron ions with the increase of immersion time. The decrease in the phosphorous concentration may be attributed to their uptake from the solution to the surface of the samples to form the apatite layer while the decrease of iron may be attributed to the uses of iron ions as a nucleation sites for the formed apatite layer so the number of remnant ions in the solution decrease. Also there is an increase of the amount of released iron with the increase of iron content in samples. That decrease attributed to the formation of hematite, which decreased with the increase of iron contents. The decrease of both calcium and phosphorus ions in the solution of iron doped samples with the increase of iron content may be reveals that the increase of apatite formation capability on the surface of iron doped samples.